

Equilibrium, kinetic and sorber design studies on the adsorption of Aniline blue dye by sodium tetraborate-modified Kaolinite clay adsorbent

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Abstract

Raw Kaolinite clay obtained Ubulu-Ukwu, Delta State of Nigeria and its sodium tetraborate (NTB)-modified analogue was used to adsorb Aniline blue dye. Fourier transformed infrared spectra of NTB-modified Kaolinite suggests that modification was effective on the surface of the Kaolinite clay with the strong presence of inner –OH functional group. The modification of Kaolinite clay raised its adsorption capacity from 1666 to 2000 mg/kg. Modeling adsorption data obtained from both unmodified and NTB-modified Kaolinite clay reveals that the adsorption of Aniline blue dye on unmodified Kaolinite clay is on heterogeneous adsorption sites because it followed strongly the Freundlich isotherm equation model while adsorption data from NTB-modified Kaolinite clay followed strongly the Langmuir isotherm equation model which suggest that Aniline blue dye was adsorb homogeneous adsorption sites on the NTB-modified adsorbent surface. There was an observed increase in the amount of Aniline blue adsorbed as initial dye concentration was increased from 10 to 30 mg/L.

It was observed that kinetic data obtained generally gave better robust fit to the second-order kinetic model (SOM). The initial sorption rate was found to increased with increasing initial dye concentration (from 10 to 20 mg/L) for data obtained from 909 to 1111 mg kg⁻¹ min⁻¹ for unmodified and 3325–5000 mg kg⁻¹ min⁻¹ for NTB-modified adsorbents. Thereafter there was a decrease in initial sorption rate with further increase in dye concentration. The linearity of the plots of the pseudo-second-order model with very high-correlation coefficients indicates that chemisorption is involved in the adsorption process.

From the design of a single-batch adsorber it is predicted that the NTB-modified Kaolinite clay adsorbent will require 50% less of the adsorbent to treat certain volumes of wastewater containing 30 mg/L of Aniline blue dye when it is compared with the unmodified adsorbent. This will be cost effective in the use of NTB-modified adsorbent for the adsorption of Aniline blue dye from water and wastewater.

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1. Introduction

Synthetic dyes have been used extensively in the textile, paper, cosmetics, pharmaceuticals and food industries and more so in medical/research laboratories were they were used for staining substances for analysis. Strong color is an important factor in considering the safety of wastewater before its dis-

charge into water bodies [1]. Neglecting the aesthetic problem, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water body which interferes with the growth of bacteria to levels insufficient to biologically degrade impurities in the water resulting in ecological imbalance.

Color in effluents can cause problems in several ways: dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration; dyes are inherently highly visible meaning that concentrations as low as 0.005 ppm capture the attention of both the public and the

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authorities; dyes absorb and reflect sunlight entering water and so can interfere with the growth of microorganisms and hinder photosynthesis in aquatic plants [2,3]. Beyond these, dyes have been found to be stable to light, and oxidizing agents.

There is difficulty in removing these dyes/colorant from aqueous using the conventional methods such as precipitation, solvent extraction, membrane filtration and biological oxidation because these methods are only economical and efficient at high concentrations of these colorants/dye-stuffs. These and the high-capital/operational cost in addition to secondary sludge disposal cost have made these methods less attractive in the removal of dyes from wastewater. However, adsorption has been proven to be an excellent method of removing dyes from aqueous solutions because of its significant advantages like cheap, easy availability, most profitable, ease of operation, most efficient and no sludge formation, over the conventional methods from economic and environmental point of view [4,5].

Different low-cost adsorbents have been employed by scientist in an attempt to remove dyes and dye-stuffs from aqueous solutions. Such adsorbents include, Sepiolite [6], waste coir pith [7], ZnCl₂ activated agricultural waste bagasse [8], fly ash [9], spent brewery grains [10], treated sawdust [11], orange peels [12], and spent activated clay [13].

However, there appears to be dearth of information on the adsorption of acidic dyes such as Aniline blue water soluble (WS) on Kaolinite and its modified analogues. Aniline blue (WS) is used in the rapid identification of *Candida albicans* [14] in medical laboratories, in the Mallory's connective tissue stain and Gomoric's one-step trichrome stain, in differential staining for fluorescence microscopy study, as intermediates for dyestuffs in the textile industry, and anchoring dye on fibers and leathers in the tanning industry [15]. The release of Aniline blue from these processes into water body has been largely neglected and much attention has been focused on reactive dyes used in the textile industries. The presence of Aniline blue dye in water body would certainly reduce the quality of the water body and therefore renders the water undesirable for any good use. Beyond these, Aniline blue has been established as a hazardous substance [16] with the ability of causing irritation of the gastrointestinal tract, shortness of breath and coughing. Lengthy exposures may affect the ability of blood to carry oxygen (Methemoglobinemia), resulting in bluish discoloration of lips and tongue (cyanosis) [16]. Its environmental toxicity and fate are not yet known.

In this study the efficiency of sodium tetraborate (NTB)-modified Kaolinite clay adsorbent in adsorbing Aniline blue (WS) is measured against that of the unmodified Kaolinite clay adsorbent. The main objective of this work is to study the equilibrium and kinetics of the adsorption of Aniline blue (WS) onto both NTB-modified and unmodified Kaolinite clay adsorbents. The effects of some operating variables such as pH, agitation speed, adsorbent weight and initial dye concentration on the kinetics of the adsorption of Aniline blue (WS) are also considered. The design of a single-batch adsorber is studied in this work in order to consider the industrial (large scale) applicability of the

adsorbents in the removal of Aniline blue dye from wastewater.

2. Materials and methods

2.1. Purification of Kaolinite clay

Kaolinite clay was obtained from Ubulu-Ukwu, Delta State, Nigeria. On collection, it was purified by method described by Adebowale et al. [17].

Once dried, the very hard Kaolinite-resin was broken into particles and sieved into +220 μm using the appropriate mesh sieve. The specific surface area of the unmodified adsorbent was determined using the Sear's method [18]. The infrared spectra of the adsorbents were obtained by method described by Unuabonah et al. [19]. The point of zero charge of both adsorbents was determined using the method described by Ofomaja [20].

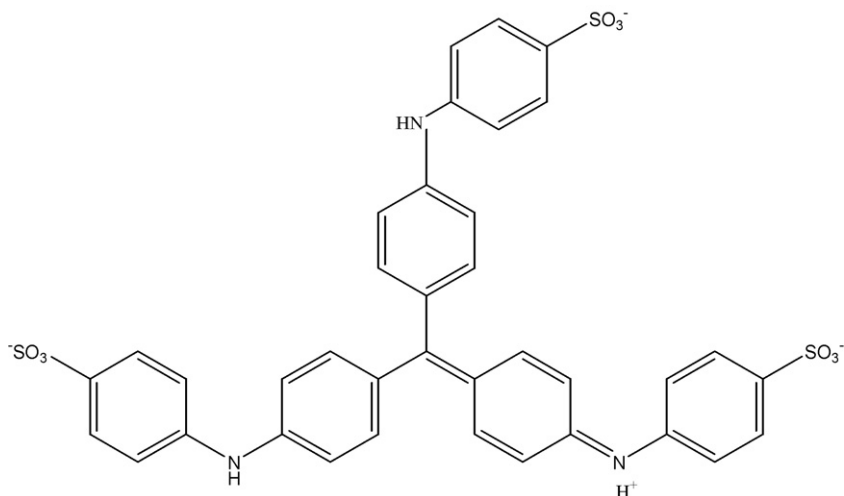
2.2. Preparation of sodium tetraborate (NTB)-modified Kaolinite

The Kaolinite clay was first treated with 2 M HNO₃ for 3 h and was then washed several times with distilled-deionized water until filtrate attained pH 7 and dried in the oven at 333 K. To 50 g of Kaolinite sample, 500 mL of a certain concentration of sodium tetraborate was added. This suspension was stirred on a power stirrer for 6 h. The suspension which had a pH of 9.6 was washed several times with distilled-deionized water until pH 8.98. The sample was then centrifuged at 1500 rpm for 15 min and dried in an oven at 333 K. It was then sieved with a +220 μm mesh size sieve. The cation exchange capacity (CEC) of both unmodified and NTB-modified Kaolinite clay adsorbents were determined by modified Ammonium acetate method [21]. In this method, 50 mL of 1 M sodium acetate (CH₃COONa) was added to two gram of the adsorbent. The suspension was then agitated for 1 h at 200 rpm. This was then filtered and the residue washed with distilled-deionized water several times to remove excess sodium acetate from the adsorbents. They were filtered and air-dried. The samples were then added to 50 mL of 1 M Ammonium acetate (pH 7.0) and agitated. This step was repeated three times and each time the supernatant were collected and kept for Na⁺ analysis using Flame Photometry. A Philip XL30 Scanning Electron Microscope/EDAX was used to obtain microgram scans of both the unmodified and NTB-modified Kaolinite clay minerals. Fourier transform infrared spectrometer (Nexus 870 FT-IR) was used for the infrared spectroscopic analysis of the samples.

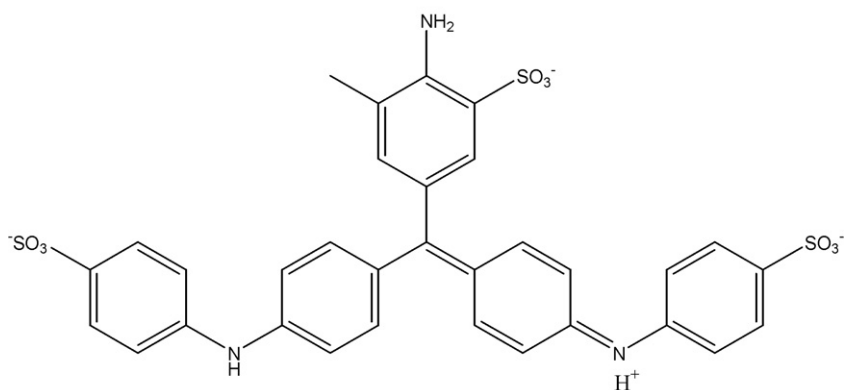
2.3. Adsorption reaction

The acid dye used in this adsorption study is Aniline blue (WS). Aniline blue is a water-soluble acid dye which is sometimes referred to as China blue.

Aniline blue is a mixture of methyl blue and water and it may also be either of them (a and b).



a. Methyl blue



b. Water Blue

Constituents of Aniline blue (Acid blue 22 CI 42755) are:

Molecular weight of aniline blue: 737.74 g/mol.

UV range: 594–610 nm.

Molecular formula: $C_{32}H_{25}N_3Na_2O_9S_3$.

Appearance: purple brown powder.

The Aniline blue dye used in this study was BDH product. The stock solution of Aniline blue (WS) (1000 mg/dm^3) was prepared in distilled-deionized water. All working solutions in the range of 10–40 mg/L were prepared by diluting the stock solution with distilled-deionized water. Some sample bottles were washed and air-dried for collection of samples. A 15, 20, and 25 g/L of the adsorbent-adsorbate was prepared using 10 mg/L of the dye solution at $\text{pH } 9.0 \pm 0.1$. Variation of pH was in the range of 4.0 ± 0.1 to 9.0 ± 0.1 and 20 g/L solution of 20 mg/L of adsorbent-adsorbate solution was used. The effect of initial dye concentration was studied with a range of 10–30 mg/L dye concentrations. These samples were agitated at 240 rpm using a power stirrer with a three-flat-blade impeller driven by an electric motor. 500 μL was taken with a micropipette into sample

bottles at time intervals in a range of time of 10 s to 30 min. Each of these samples was made up to 5.0 mL with deionized water. Each of the diluted samples was properly filtered and the absorbance values at 594 nm were used to monitor the adsorption process and the color measured according to the Lambert–Beer's law. The filtered dye-free effluent was used as blank.

For the effect of agitation speed, the stirrer speed was varied between 240 and 350 rpm. The power stirrer was mounted and positioned along side with Cary-1E-UV Visible Spectrophotometer (Varian).

Samples were also collected and dye concentrations read like in previous experiments.

Data collected were treated at statistical significance of $p \leq 0.05$.

2.4. Theory of adsorption kinetics

2.4.1. Modified pseudo-first-order kinetic model

Lumped kinetic models such as the pseudo-first-order and pseudo-second-order kinetics models have without doubts pro-

vided simple but satisfactory explanation to an adsorption process in many systems. Nevertheless, for many adsorption systems, the plot of either $\ln(q_e - q_t)$ against t , t/q_t against t , or q_t against $t^{0.5}$ may be multilinear as with the case of the adsorption of *Basic Magenta* and *Basic Brilliant Green* dyes [22]. To solve this problem it is common to segment the plot into two or more straight lines and to therefore suggest that different adsorption mechanisms control each step represented by each straight line. This practice may be quite “artificial” as it is up to the researcher to decide where to segment the multilinear plot. Although, this might help to understand the adsorption mechanism to some extent, yet the practical significance of such an approach is quite limited. To resolve this problem, Yang and Al-Duri [23] postulated the idea of incorporating a q_t -dependent rate constant into the lumped kinetic models since the rate constants of multilinear plots may vary with parameters such as time or more specifically with the solid-phase concentration q_t .

To set up the new model for the pseudo-first-order kinetic model:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

Yang and Al-Duri [23] modified Eq. (1) through the modification of its rate constant. The rate constant in the modified pseudo-first-order kinetic model was denoted by K_1 and the following equation was proposed:

$$k_1 = \frac{K_1 q_e}{q_t} \quad (2)$$

As $q_t < q_e$, the above equation implies that the rate constant k_1 is minimum when equilibrium is reached.

The modified pseudo-first-order rate equation can be derived as follows:

$$\frac{dq_t}{dt} = \frac{K_1 q_e}{q_t} (q_e - q_t) \quad (3)$$

Eq. (3) can be rearranged into

$$-dq_t + \frac{q_e dq_t}{(q_e - q_t)} = K_1 q_e dt \quad (4)$$

Integrating Eq. (4) over time t during which the solid-phase concentration increases from zero to q_t , the following algebraic equation can be obtained:

$$\frac{q_t}{q_e} + \ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (5)$$

If the adsorption process follows the modified pseudo-first-order kinetic model represented by Eq. (5), a plot of $q_t/q_e + \ln(q_e - q_t)$ against t should be a straight line.

2.4.2. Second-order kinetic model

The second-order Lagergren equation was given by Banquella and Benaissa [24] and is represented as

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (\text{linear form}) \quad (6)$$

$$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1} \quad (\text{non-linear form}) \quad (7)$$

where q_t is the amount of dye adsorbed (mg/kg) by the adsorbents at time t (min), q_e the amount adsorbed at equilibrium, and k_2 is the second-order rate constant of the adsorption ($\text{kg mg}^{-1} \text{min}^{-1}$).

2.4.3. Pseudo-second-order kinetic model

For the rate constant of the pseudo-second-order chemical sorption process the kinetic expression can be written as follows:

$$q_t = k q_e^2 t \quad (8)$$

The differential equation is as follows:

$$\frac{dq_t}{dt} = \frac{k(q_e - q_t)^2}{1 + k t} \quad (9)$$

Integrating Eq. (9) for the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, gives

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k t \quad (10)$$

When this is linearized it gives

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{t}{q_e} \quad (\text{linear form}) \quad (11)$$

and

$$q_t = \frac{t}{(1/h) + (t/q_e)} \quad (\text{non-linear form}) \quad (12)$$

where q_e is the amount of dye adsorbed at equilibrium (mg/L), q_t amount of dye adsorbed at time t (mg/g) and k is the rate constant of the pseudo-second-order sorption ($\text{g}/(\text{mg min})$).

The initial sorption rate can be obtained as q_t/t approaches zero:

$$h = k q_e^2 \quad (13)$$

where h is the initial sorption rate ($\text{mg}/(\text{g min})$).

The pseudo-second-order model constants can be obtained by plotting t/q_t against t [25].

2.5. Isotherm models

2.5.1. Langmuir isotherm

The Langmuir isotherm has been used extensively by many authors for the sorption of heavy metal ions in clay, metal oxides, soils, etc. The Langmuir isotherm is a valid monolayer sorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface. The Langmuir equation may be written as

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (\text{non-linear form}) \quad (14)$$

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (\text{linear form}) \quad (15)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), Q^0 the monolayer adsorption capacity (mg/g) and b is the constant related to the energy of adsorption ($L g^{-1}$). It is the value reciprocal of the concentration at which half the saturation of the adsorbent is attained.

2.5.2. Freundlich isotherm

The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. The Freundlich equation may be written as

$$q_e = K_F C_e^{1/n} \quad (\text{non-linear form}) \quad (16)$$

$$\ln q_e = \ln q + \frac{1}{n} \ln C_e \quad (\text{linear form}) \quad (17)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), q the constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and $1/n$ is the constant indicative of the intensity of the adsorption.

3. Results and discussions

3.1. Physicochemical characteristics

Some of the physicochemical characteristics of the unmodified Kaolinite adsorbent used in this study have been described in Adebowale et al. [17]. However, for NTB-modified Kaolinite clay, its point of zero charge (PZC) was determined to be 3.70 as against 4.40 for the unmodified Kaolinite clay adsorbent. This suggests that modification of Kaolinite clay with sodium tetraborate reduces the PZC of Kaolinite clay and this enhances the use of Kaolinite clay in adsorbing metal ions from aqueous solutions even at low pH. The PZC plots for both adsorbents are shown in Fig. 1a and b.

The specific surface area for NTB-modified Kaolinite was observed to be $15.84 \text{ m}^2 \text{ g}^{-1}$ while that of the unmodified was $10.56 \text{ m}^2 \text{ g}^{-1}$. The unmodified Kaolinite clay adsorbent gave CEC of 7.81 mequiv/100 g of Kaolinite clay [17]. However, the cation exchange capacity of NTB-modified adsorbent was determined to be 32.18 mequiv/100 g of NTB-modified Kaolinite clay. This is four times that of the unmodified adsorbent.

From the infrared spectroscopy NTB-modified adsorbent showed broader inner –OH peaks that were not as prominent as those of the unmodified adsorbent (Fig. 2). These peaks had values shifted from those of the unmodified adsorbent (Table 1) which suggests that the –OH on the NTB-modified is quite different from that on the unmodified adsorbent via the atom they are attached to. This further confirms the surface modification of the unmodified adsorbent. However, there was the absence of the outer –OH peak which rules out the possibility for the adsorption of Pb^{2+} and Cd^{2+} onto this site on these adsorbents.

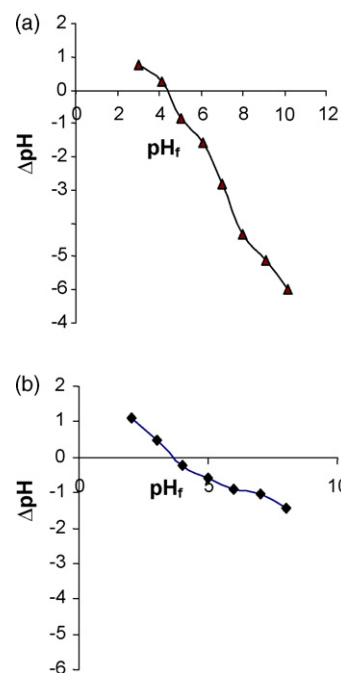


Fig. 1. (a) PZC plot for unmodified adsorbent. (b) PZC plot for NTB-modified adsorbent.

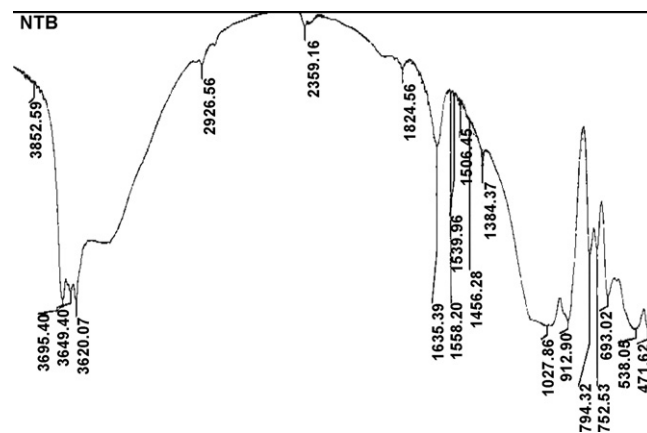


Fig. 2. Infrared spectrum of NTB-modified Kaolinite clay.

Table 1

IR spectra band assignments for unmodified and NTB-modified Kaolinite clay

IR frequencies (cm^{-1})		Band assignments
Unmodified ^a	NTB-modified	
3668.3	3695.40, 3649.40	Inner surface –OH stretching vibration
2919	–	CH_3 -Nujol mull
1733.6	1635.39	–OH bending vibration
1034.4	1027.86	Si–O, Si–O–MR bending vibration
918.7	912.90	Al–O, Al–O–MR bending vibration
792	794.32, 752.53	Si–O stretching vibration
693.8	–	Si–O stretching vibration
–	538.05	Al–O–Si deformation

MR, modifying reagent.

^a Values reproduced from Adebowale et al. [30].

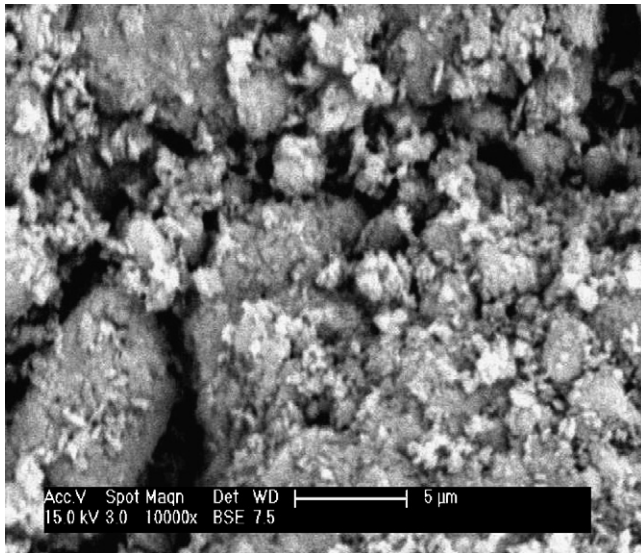


Fig. 3. SEM of unmodified Kaolinite clay.

The Si–O and Al–O peaks were found to shift from 1034.4 and 918.7 cm^{-1} in the unmodified Kaolinite clay adsorbent to 1006 and 912.62 cm^{-1} , respectively in the NTB-modified Kaolinite clay adsorbent. However, because of the structure of sodium tetraborate, it is possible to say that the –OH site may not be the only site available for the adsorption of Aniline blue dye molecule but there could also be the presence of lone pairs of electrons present on the boron atom.

The scanning electron microgram (SEM) of both adsorbents (Figs. 3 and 4) presents the NTB-modified adsorbent having particles bearing more whitish substance than the unmodified adsorbent. These substances have been described to be non-clay materials [26] which in this case will include sodium tetraborate reagent.

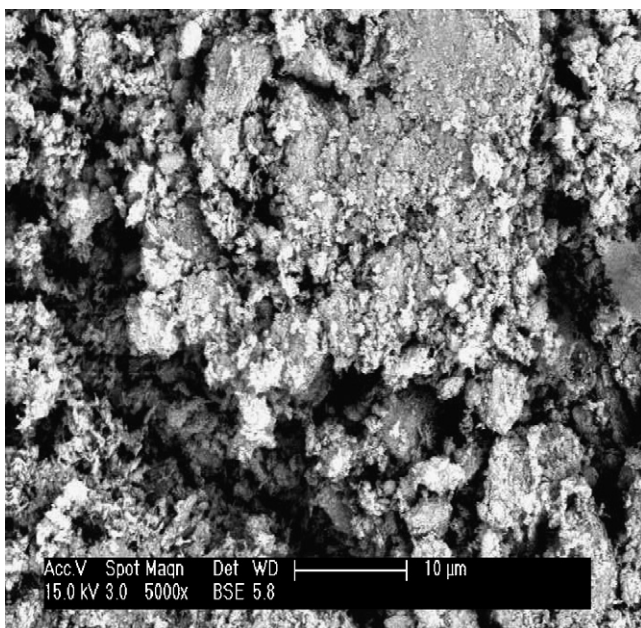


Fig. 4. SEM of sodium tetraborate-modified Kaolinite clay.

Table 2
Equilibrium constants for Langmuir and Freundlich isotherms

	Unmodified	NTB-modified
Langmuir		
Q^0 (mg/kg)	1666.67	2000
b (L kg^{-1})	6.316×10^{-2}	2.17×10^{-1}
R^2	0.9821	0.9927
χ^2	112.05	7.01
Freundlich		
k_f (mg/kg)	222.34	904.78
n	2.29	7.59
R^2	0.9940	0.8322
χ^2	7.27	68.47

3.2. Adsorption equilibrium

To effectively analyze and design an adsorption process there need to understand the relevant adsorption equilibria which is an important piece of information in any adsorption process. Adsorption equilibrium provides the basic physicochemical data for evaluating the applicability of the adsorption process as a unit operation. Two isotherm models are commonly employed in this regard: Langmuir and Freundlich isotherm models. The linear and non-linear forms of these isotherms are shown in Eqs. (14)–(17).

From Table 2 it can be seen that the modification of Kaolinite clay with sodium tetraborate enhanced its adsorption capacity for Aniline blue dye as there was an observed increase of adsorption capacity of the Kaolinite clay from 1666.67 to 2000 mg/kg. The binding energy constant, b , also showed an increase from 0.06316 to 0.217 L kg^{-1} . This implies that the adsorption complex formed between the NTB-modified Kaolinite clay and Aniline blue dye could be more stable than that formed between the dye and the unmodified Kaolinite clay.

To predict the adsorption capacity of both adsorbents at equilibrium using both the Langmuir and Freundlich isotherms, the following equations were produced.

For unmodified Kaolinite clay:

- Langmuir isotherm

$$q_e = \frac{105.3C_e}{1 + 0.063C_e} \quad (18)$$

- Freundlich isotherm

$$q_e = 222.3C_e^{0.437} \quad (19)$$

For NTB-modified Kaolinite clay:

- Langmuir isotherm

$$q_e = \frac{434.0C_e}{1 + 0.217C_e} \quad (20)$$

- Freundlich isotherm

$$q_e = 904.1C_e^{0.132} \quad (21)$$

These predicted Langmuir and Freundlich isotherm equations for the adsorption of Aniline blue onto both Kaolinite clay and NTB-modified Kaolinite could be useful for design calculations in the adsorption of Aniline blue dye onto both natural Kaolinite and NTB-modified Kaolinite clay adsorbents.

In modeling the experimental equilibrium adsorption capacity data obtained against those obtained from predicted Langmuir and Freundlich isotherm equations, the Chi-square method of model analysis was used. In Chi-square method of model analysis, an error is required to evaluate the fit of an equation to the experimental data obtained from the optimization process employed. In this study, a non-linear Chi-square test was used [27]. The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from the models, with each squared difference divided by the corresponding data obtained by calculating from the models. The equivalent mathematical statement is

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{22}$$

where $q_{e,m}$ is the equilibrium capacity obtained by calculating from the model (mg/g) and q_e is experimental data of the equilibrium capacity (mg/g). If data from model are similar to the experimental data, χ^2 will be small in number, while if they differ, χ^2 will be a bigger number. Therefore, it is necessary to also analyze the data set using the non-linear Chi-square test to confirm the best-fit isotherm for the sorption system.

From Table 2 it was observed that experimental data obtained for the unmodified adsorbent showed better fit to the Freundlich isotherm model. This is seen from the lower χ^2 of 7.27 and higher correlation coefficient R^2 of 0.9940 as against those obtained for NTB-modified Kaolinite clay. However, equilibrium data obtained for the NTB-modified adsorbent showed better fit to the Langmuir isotherm model. This may suggest that the unmodified Kaolinite clay has heterogeneous adsorption sites as suggested by the Freundlich isotherm model but on modification with sodium tetraborate, the sites became homogeneous as suggested by the Langmuir isotherm model. Although, we have both -OH and perhaps some lone pairs of electrons as possible adsorption sites on NTB-modified adsorbent, it is therefore plausible to perhaps assume that only one of either adsorption site was involved in the adsorption of Aniline blue onto the NTB-modified adsorbent. Model plots with experimental data are shown in Figs. 5 and 6.

The dimensionless constant separation factor or equilibrium parameter was used to determine the favorability of the adsorption of Aniline blue onto both adsorbents. The equation is given by

$$K_R = \frac{1}{1 + bC_0} \tag{23}$$

where K_R is a dimensionless separation factor, C_0 the initial metal ion concentration (mg/L) and b is Langmuir constant

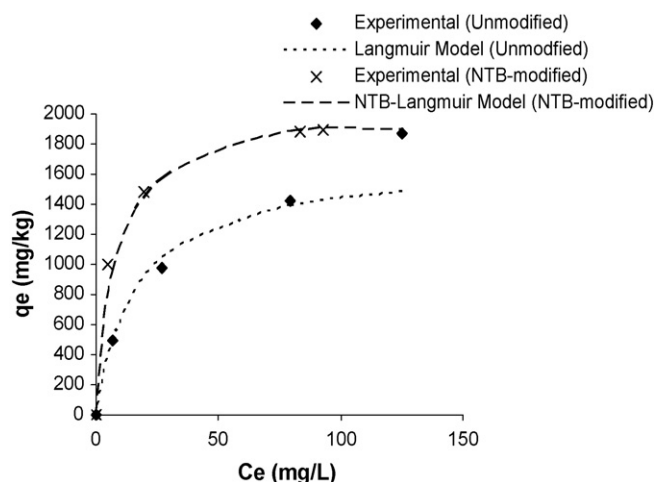


Fig. 5. Langmuir isotherm model curves for the adsorption of Aniline blue onto both unmodified and NTB-modified Kaolinite clay adsorbents at 298 K.

(L/mg). The parameter K_R indicates the shape of the isotherm accordingly.

Values of K_R	Type of Isotherm
$K_R > 1$	Unfavorable
$K_R = 1$	Linear
$0 < K_R < 1$	Favorable
$K_R = 0$	Irreversible

The calculated K_R values at various initial concentrations of the dye for both adsorbent are shown in Fig. 7. Values of K_R obtained for both adsorbents were found to be in the range of 0–1 which confirms the favorable uptake of Aniline blue onto both adsorbents. The adsorption of the dye was found to be more favorable with increasing initial concentration of the dye. However, the adsorption of the dye was found to be more favorable with NTB-modified adsorbent.

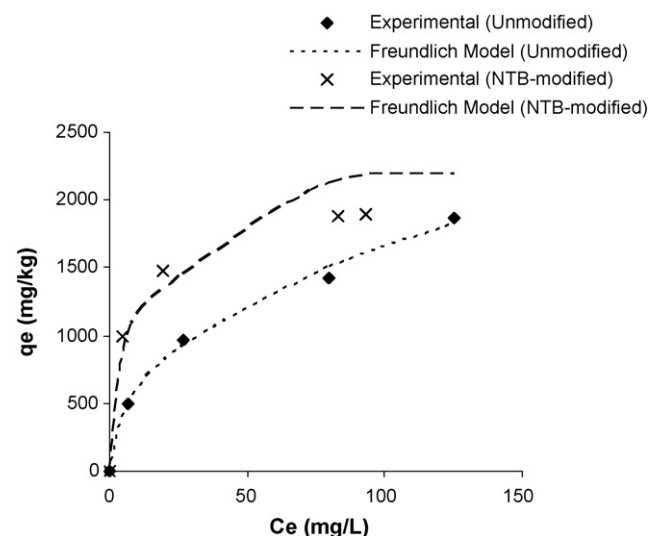


Fig. 6. Freundlich isotherm model curves for the adsorption of Aniline blue onto both unmodified and NTB-modified Kaolinite clay adsorbents at 298 K.

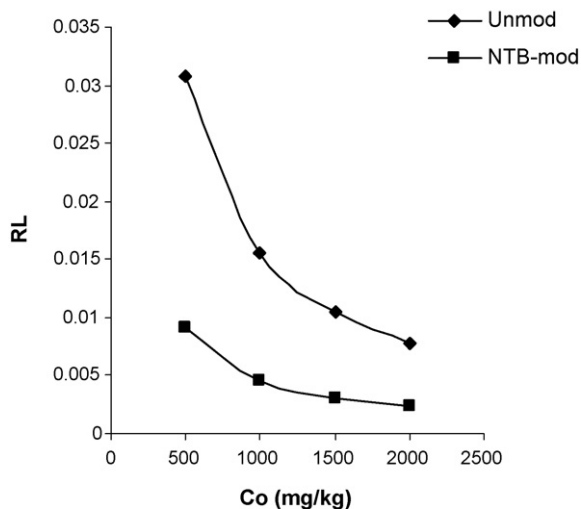


Fig. 7. Separation factor for the adsorption of Aniline blue on both unmodified and NTB-modified Kaolinite clay.

3.3. Kinetics of adsorption

3.3.1. Modified pseudo-first-order kinetic model (MPFOM) and second-order kinetic model (SOM)

Table 4 shows the modified pseudo-first-order and second-order rate constants for a range of various operating variables. Figs. 8 and 9 show the modified pseudo-first-order plots for the adsorption of Aniline blue dye onto both unmodified and NTB-modified Kaolinite clay adsorbents, respectively. Increasing initial concentration of the dye and increasing agitation speed were found to reduce the rate constant of the modified pseudo-first-order (MPFOM). NTB-modified adsorbent showed similar trend with increasing initial dye concentration but a reverse trend with increasing agitation speed. Although, Yang and Al-Duri [23] had similar findings when they studied the adsorption of reactive dyes on activated carbon with increasing concentra-

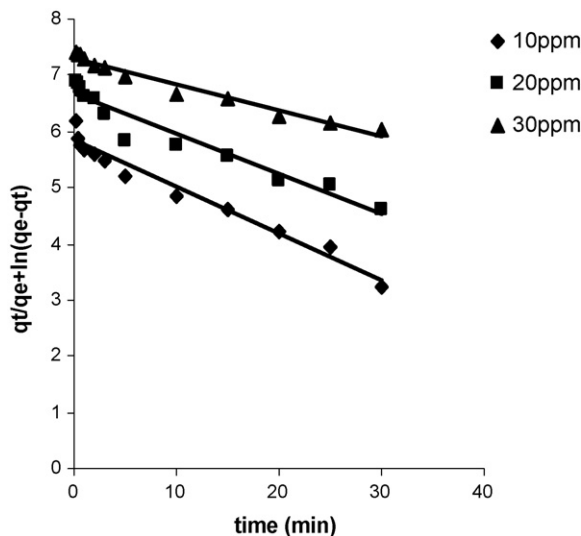


Fig. 8. Modified pseudo-first-order plot for the adsorption of Aniline blue by unmodified Kaolinite clay adsorbent.

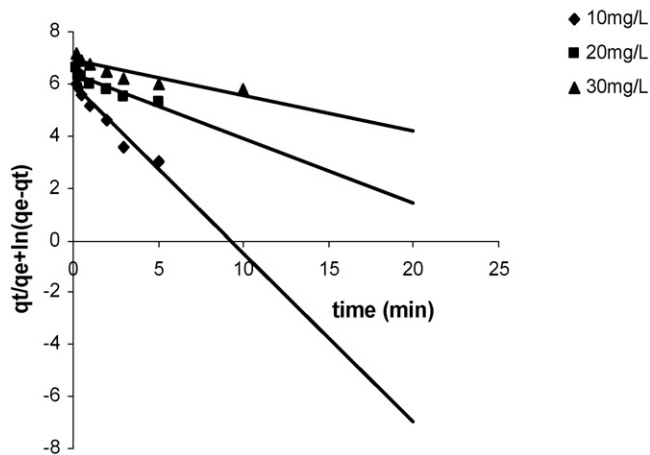


Fig. 9. Modified pseudo-first-order plot for the adsorption of Aniline blue by NTB-modified Kaolinite clay adsorbent.

tion of the dyes, yet no explanation could be proffered for this trend. It might be reasonable to assume that the trend is as a result of the fact that with increasing dye concentration there are less adsorption sites available on the surface of the unmodified Kaolinite clay to meet the increasing concentration of the dye and thus there will be competition between the dye molecules for the adsorption sites. This might have had a negative effect on the rate of adsorption of the dye onto unmodified Kaolinite clay. Increasing agitation speed may possibly have caused some desorption of the dye molecules from the unmodified adsorbent's surface thereby slowing down its rate of adsorption of the dye.

However, with increasing pH (from 4 ± 0.1 to 9 ± 0.1) and with increasing adsorbent dose the modified pseudo-first-order rate constant was found to increase for unmodified adsorbent (Table 4). This might be because increasing both variables increases the number of adsorption sites available for the adsorption of Aniline blue dye. MPFOM rate constant for NTB-modified adsorbent decreased with increasing pH but increased with increasing adsorbent dose. Increasing adsorbent dose was found to give higher MPFOM rate constants than those obtained from other operating variables for unmodified adsorbent while for NTB-modified adsorbent increasing initial dye concentration gave higher MPFOM rate constants than those obtained from other operating variables. This may signify that the adsorption of Aniline blue dye onto both adsorbents is more of an external/film diffusion controlled adsorption process especially for NTB-modified adsorbent.

Similar trends were obtained when data were fitted into the SOM except with increasing agitation speed where NTB-modified adsorbent showed a decrease in SOM rate constant.

From the correlation coefficient, R^2 , of both kinetic models, it was observed that kinetic data obtained generally gave better robust fit to SOM than to MPFOM. By implication, this could mean that the adsorption of Aniline blue dye onto both unmodified and NTB-modified Kaolinite clay adsorbent is not only time dependent as suggested by MPFOM but also concentration dependent as suggested by SOM.

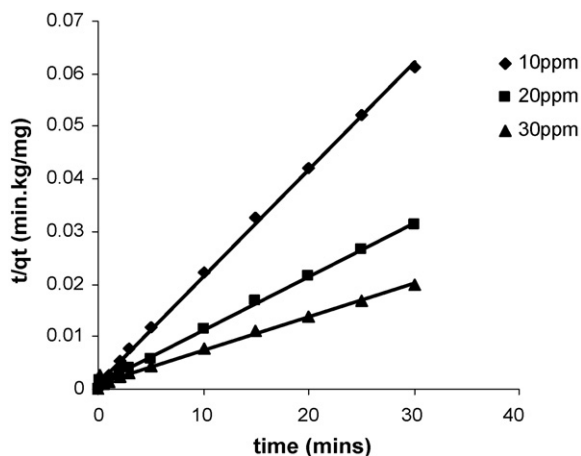


Fig. 10. Pseudo-second-order plot for the adsorption of Aniline blue by unmodified Kaolinite clay adsorbent.

3.3.2. Pseudo-second-order kinetic model (PSOM)

3.3.2.1. Adsorption capacity. Parameters obtained from the pseudo-second-order kinetic model are shown in Table 3. Figs. 10 and 11 depict the pseudo-second-order plots for the adsorption of Aniline blue dye onto both unmodified and NTB-modified Kaolinite clay adsorbents respectively. Increasing initial dye concentration and increasing agitation speed were observed to increase the adsorption capacity q_e of the unmodified adsorbent for Aniline blue dye while increasing adsorbent dosage increased adsorption capacity of unmodified adsorbent up to 20 g/L and thereafter this variable did not change its adsorption capacity. The same trend was observed with increasing pH.

NTB-modified adsorbent showed an increase in q_e with increasing initial dye concentration, increasing agitation speed and increasing adsorbent dosage. However, increasing pH did not change q_e for this adsorbent. No explanation can be yet proffered for this trend shown by increasing pH for both adsorbents.

Increasing initial dye concentration produces a higher driving force across the film that forms a boundary layer between the adsorbate and the adsorbent. This increases the amount of the dye adsorbed and hence the q_e of the adsorbent. Increasing agita-

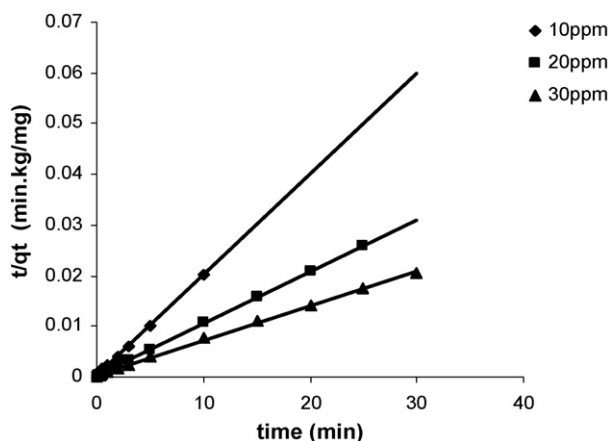


Fig. 11. Pseudo-second-order plot for the adsorption of Aniline blue by NTB-modified Kaolinite clay adsorbent.

tion increases the shear force on this boundary film layer between the adsorbate and the adsorbent and subsequently decreases the boundary layer surrounding the suspended adsorbent particle. This again increases the adsorption capacity, q_e , of the adsorbent.

3.4. Initial sorption rate

The initial sorption rate, h , was found to generally increase with increasing initial dye concentration for adsorbent as the overall pseudo-second-order rate constant rate constant decreased for both unmodified and NTB-modified Kaolinite (Table 3). Although Vadivelan and Kumar [1] observed a reversed trend when they studied the sorption of methylene Blue on rice husk, it is likely that the adsorption of Aniline blue onto both unmodified and NTB-modified adsorbent is initially rapid because increasing initial dye concentration produces higher driving force that reduces the film layer between the adsorbate and adsorbent surface but as equilibrium is achieved, the overall rate of sorption of the dye reduces. Ho et al. [28] have also suggested that to maintain the initial sorption rate of an adsorption process there is the need to have a higher adsorption capacity as initial concentration of adsorbate increases which is only possible with more adsorption sites on the adsorbent's surface or increased adsorbent weight per unit volume of adsorbate solution. Since this cannot be achieved while adsorption reaction is on, the rate of adsorption will thus drop. This accounts for reducing pseudo-second-order rate constant but increasing initial sorption rate of Aniline blue onto unmodified and NTB-modified Kaolinite clay adsorbents as initial dye concentration increases.

Increasing pH and increasing adsorbent dosage tend to increase the initial sorption rate as well as the PSOM rate constant in the unmodified adsorbent. This likely so as dye concentration in both variables remain constant but more adsorption sites are produced by increasing pH and increasing adsorbent dosage. Increasing agitation speed decreased both initial sorption rate and PSOM rate constant for the unmodified adsorbent. This could be linked to the fact that since shear force is greater than electrostatic attraction force, desorption of the dye molecules from the adsorbent's surface with increasing speed of agitation applied to the adsorption system will result. This will thus decrease both the initial sorption rate of the dye and its overall kinetic adsorption rate constant.

For NTB-modified adsorbent, increasing pH reduced both initial sorption rate and PSOM rate constants. It very likely that increasing pH do not favor the adsorption of Aniline blue onto NTB-modified adsorbent as this trend was also observed with MPFOM and SOM kinetic models in this study (Table 4). However, increasing adsorbent dosage only increased initial sorption rate and PSOM rate constants for NTB-modified adsorbent up to 10 g/L. Above this solid-liquid ratio the PSOM rate constant decreased but the initial sorption rate increased. The might be that increasing adsorbent dose could have resulted in some particle-particle aggregation that may have affected the overall kinetic rate of adsorption of the dye onto NTB-modified adsorbent. Increasing agitation speed enhanced both initial sorption

Table 3
Data for the pseudo-second-order rate constant for the different operating variables

	Unmodified			NTB-modified		
	10 ^a	20 ^a	30 ^a	10 ^a	20 ^a	30 ^a
Effect of initial dye concentration (unmodified: pH 9.0, w/v = 20 g/L, speed = 240 rpm; NTB-modified: pH 4.0, w/v = 20 g/L, speed = 350 rpm)						
q_e (mg/kg)	500	1000	1666.67	500	1000	1728.57
h (mg kg ⁻¹ min ⁻¹)	435	1111.11	1000	3325	5000	3326.53
k (kg mg ⁻¹ min ⁻¹)	1.74×10^{-3}	1.11×10^{-3}	3.60×10^{-4}	1.33×10^{-2}	5.00×10^{-3}	1.63×10^{-3}
R^2	0.9970	0.9984	0.9917	0.9989	0.9999	0.9988
	Unmodified			NTB-modified		
	4.0 ^b	7.0 ^b	9.0 ^b	4.0 ^b	7.0 ^b	9.0 ^b
Effect of pH (concentration = 20 mg/L, w/v = 20 g/L, speed = 240 rpm)						
q_e (mg/kg)	769.23	1000	1000	1000	1000	1000
h (mg kg ⁻¹ min ⁻¹)	212.77	434.78	1111.11	5000	2500	2000
k (kg mg ⁻¹ min ⁻¹)	3.60×10^{-4}	4.35×10^{-4}	1.11×10^{-3}	5.00×10^{-3}	2.50×10^{-3}	2.00×10^{-3}
R^2	0.9697	0.9940	0.9984	0.9999	0.9997	0.9991
	Unmodified			NTB-modified		
	240 ^c	300 ^c	350 ^c	240 ^c	300 ^c	350 ^c
Effect of agitation (unmodified: concentration = 30 mg/L, pH 9.0, w/v = 20 g/L; NTB-modified: concentration = 20 mg/L, pH 9.0, w/v = 20 g/L)						
q_e (mg/kg)	1666.67	1428.37	1250	909.09	909.09	1000
h (mg kg ⁻¹ min ⁻¹)	1000	232.56	161.29	1111.11	1428.92	5000
k (kg mg ⁻¹ min ⁻¹)	3.60×10^{-4}	1.14×10^{-4}	1.032×10^{-4}	1.34×10^{-3}	1.73×10^{-3}	5.00×10^{-3}
R^2	0.9917	0.9342	0.8305	0.9986	0.9986	0.9999
	Unmodified			NTB-modified		
	15 ^d	20 ^d	25 ^d	5 ^d	10 ^d	20 ^d
Effect of adsorbent weight (Unmodified: conc. = 10 mg/L, pH = 9.0, speed = 240 rpm; NTB-modified: conc. = 20 mg/L, pH 4.0, speed = 350 rpm)						
q_e (mg/kg)	476.19	500	500	833.33	909.09	1000
h (mg kg ⁻¹ min ⁻¹)	303.04	435	555.56	909.08	1000	5000
k ($\times 10^{-3}$ kg mg ⁻¹ min ⁻¹)	1.34	1.74	2.22	1.31	9.20	5.00
R^2	0.9941	0.9970	0.9986	0.9961	0.9950	0.9999

^a Concentration (mg/L).

^b pH.

^c Speed (rpm).

^d Weight (g/L).

rate and PSOM rate constant for NTB-modified adsorbent. This is in contrast to observations made with unmodified adsorbent.

3.5. Sorption mechanism

Although, the modified pseudo-first-order, second-order and pseudo-second-order kinetic model mechanisms have been applied to kinetic data obtained in this study, however, for the adsorption of dyes, which are large molecules, it will more appropriate to study the data using a diffusion-controlled mechanism. The intraparticle diffusion model have been used but the double nature of the intraparticle plot confirms the presence of both film and pore diffusion. However, since we are dealing with a large molecule in this study, adsorption into pores of the adsorbents would be most unlikely.

Therefore, from this study, it was observed that agitation speed reduced the both adsorption capacity, modified pseudo-first-order rate constant and overall pseudo-second-order rate constant of the adsorption of Aniline blue onto the unmodified adsorbent but the reverse was the case with NTB-modified

adsorbent. Furthermore, pH enhanced the adsorption capacity, modified pseudo-first-order rate constant and the overall pseudo-second-order rate constant of the adsorption of Aniline blue onto the unmodified adsorbent and vice-versa for the NTB-modified adsorbent.

These may suggest that adsorption of Aniline blue onto NTB-modified is by *chemisorption* mechanism perhaps via the lone pair of electron on the modified surface of the adsorbent since increasing agitation speed enhances surface adsorption. For the unmodified it could be by *ion-exchange* mechanism which is further strengthened by the positive effect pH has on the adsorption of the dye onto its surface. The linearity of the plots of the pseudo-second-order model (Figs. 10 and 11) with very high-correlation coefficients (Table 3) indicates that chemical reaction is the main rate-controlling step throughout most of the adsorption process.

3.6. Design of batch adsorption from isotherm data

Adsorption process is known to proceed by various mechanisms: external mass transfer of solute onto the surface of the

Table 4
Data for the pseudo-first-order rate constant for the different operating variables

	Unmodified			NTB-modified		
	10 ^a	20 ^a	30 ^a	10 ^a	20 ^a	30 ^a
Effect of Initial dye concentration (unmodified: pH 9.0, w/v = 20 g/L, speed = 240 rpm; NTB-modified: pH 4.0, w/v = 20 g/L, speed = 350 rpm)						
k_1	8.30×10^{-2}	7.17×10^{-2}	4.70×10^{-2}	6.43×10^{-1}	2.49×10^{-1}	1.36×10^{-1}
k_2	1.70×10^{-3}	7.00×10^{-4}	2.0×10^{-4}	1.99×10^{-2}	1.20×10^{-3}	8.00×10^{-4}
R^2	0.9688 (0.9792)	0.9315 (0.9559)	0.9679 (0.9914)	0.9585 (0.9466)	0.8855 (0.9810)	0.9468 (0.9646)
	Unmodified			NTB-modified		
	4.0 ^b	7.0 ^b	9.0 ^b	4.0 ^b	7.0 ^b	9.0 ^b
Effect of pH (concentration = 20 mg/L, w/v = 20 g/L, speed = 240 rpm)						
$k_1 (\times 10^{-2})$	1.92	6.15	7.17	9.05	8.99	7.08
k_2	9.00×10^{-5}	5.00×10^{-4}	7.00×10^{-4}	1.20×10^{-3}	1.10×10^{-3}	8.00×10^{-4}
R^2	0.9812 (0.9719)	0.9898 (0.9645)	0.9315 (0.9559)	0.8028 (0.9810)	0.8553 (0.9724)	0.9442 (0.9684)
	Unmodified			NTB-modified		
	240 ^c	300 ^c	350 ^c	240 ^c	300 ^c	350 ^c
Effect of agitation (unmodified: concentration = 30 mg/L, pH 9.0, w/v = 20 g/L; NTB-modified: concentration = 20 mg/L, pH 9.0, w/v = 20 g/L)						
$k_1 (\times 10^{-2})$	4.70	1.94	1.28	5.13	5.25	7.94
k_2	2.00×10^{-4}	5.00×10^{-5}	3.00×10^{-5}	4.00×10^{-3}	4.00×10^{-3}	1.20×10^{-3}
R^2	0.9679 (0.9914)	0.9782 (0.9751)	0.9940 (0.9898)	0.9390 (0.9744)	0.9148 (0.9618)	0.8487 (0.9810)
	Unmodified			NTB-modified		
	15 ^d	20 ^d	25 ^d	5 ^d	10 ^d	20 ^d
Effect of adsorbent weight (unmodified: concentration = 10 mg/L, pH 9.0, speed = 240 rpm; NTB-modified: concentration = 20 mg/L, pH 4.0, speed = 350 rpm)						
k_1	1.14×10^{-1}	1.15×10^{-1}	1.29×10^{-1}	2.81×10^{-2}	3.46×10^{-2}	7.37×10^{-1}
k_2	7.00×10^{-4}	3.30×10^{-3}	4.60×10^{-3}	1.00×10^{-4}	2.00×10^{-4}	1.20×10^{-3}
R^2	0.8879 (0.9391)	0.9271 (0.9773)	0.9931 (0.9021)	0.8546 (0.8906)	0.8776 (0.8915)	0.8730 (0.9810)

k_1 , modified pseudo-first-order rate constant (min^{-1}); k_2 , second-order rate constant ($\text{kg mg}^{-1} \text{min}^{-1}$); R^2 in bracket is for k_2 .

^a Concentration (mg/L).

^b pH.

^c Speed (rpm).

^d Weight (g/L).

adsorbent followed possibly by intraparticle diffusion mechanism.

Thus, to predict the adsorber size and efficiency in the removal of Aniline blue by unmodified and NTB-modified Kaolinite clay adsorbent, an empirical procedure based on the adsorption equilibrium is designed. Adsorption equilibrium is a dynamic concept based on the equal rate of both adsorption and desorption process taking place on the adsorbent’s surface. The complex nature of adsorption has made it impossible to use a single-adsorption theory to explain all adsorption systems. However, adsorber design engineering requires equilibrium data. Vadivelan and Kumar [1] have previously predicted the efficiency of a single-batch adsorber for the adsorption of methylene blue onto rice husk using equilibrium data obtained.

A schematic diagram for a single-batch adsorber for the adsorption of Aniline blue onto both unmodified and NTB-modified Kaolinite clay adsorbent is shown in Fig. 12. The design objective is to reduce the dye solution of volume V (L) from an initial concentration of C_0 to C_1 (mg/L). The amount of the adsorbent is M and the solute loading changes from q_0

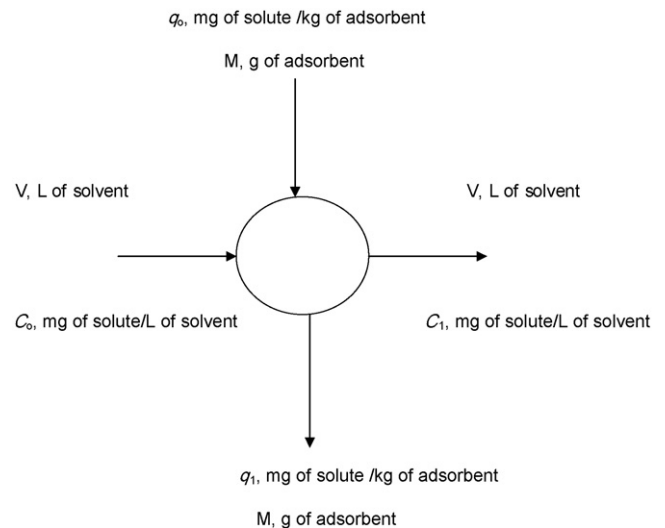


Fig. 12. Schematic diagram for a single-batch adsorber for the adsorption of Aniline blue.

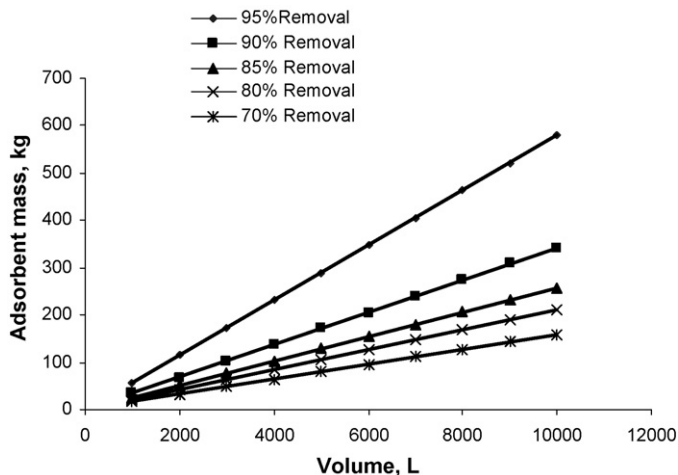


Fig. 13. Predicted unmodified Kaolinite clay adsorbent mass against volume of wastewater containing Aniline blue dye.

(mg/kg) to q_1 (mg/kg). At time $t=0$, $q_0=0$ and as time proceeds the mass balance equates the dye removed from the liquid to that adsorbed by the adsorbents. The mass balance for the adsorption system in Fig. 13 can be written as

$$V(C_0 - C_1) = M(q_0 - q_1) = Mq_1 \quad (24)$$

Under equilibrium conditions:

$$C_1 \rightarrow C_e \quad \text{and} \quad q_1 \rightarrow q_e$$

From adsorption studies and from model results it was observed the Langmuir model gave better robust fit to equilibrium data from NTB-modified adsorbent while the Freundlich model gave the better robust fit the experimental from unmodified adsorbent. On this basis, Langmuir and Freundlich isotherm equations were designed for NTB-modified and unmodified Kaolinite clay adsorbents to predict the amount of the adsorbents required to remove a certain percentage of Aniline blue dye from various volumes of wastewater.

The equations include:

- For Langmuir isotherm:

$$\frac{M}{V} = \frac{(C_0 - C_e)}{q_1} = \frac{(C_0 - C_e)}{q_e} = \frac{(C_0 - C_e)}{Q^0 b C_e / (1 + b C_e)} \quad (25)$$

- For Freundlich isotherm:

$$\frac{M}{V} = \frac{C_0 - C_e}{q_1} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{k_f C_e^{1/n}} \quad (26)$$

Figs. 13 and 14 shows the plot for the predicted amount of unmodified and NTB-modified Kaolinite clay adsorbents required to remove certain percentage of 30 mg/L of Aniline blue dye from specific volumes of wastewater solutions in a single-batch adsorber. For example to remove 95% of 30 mg/L Aniline blue dye from 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10L aqueous solution at 298 K using unmodified Kaolinite clay, requires 107.4, 214.8, 322.1, 429.5, 536.9, 644.3, 751.7, 859.1, 966.4, and 1073.8 kg of unmodified Kaolinite clay adsorbent. For NTB-

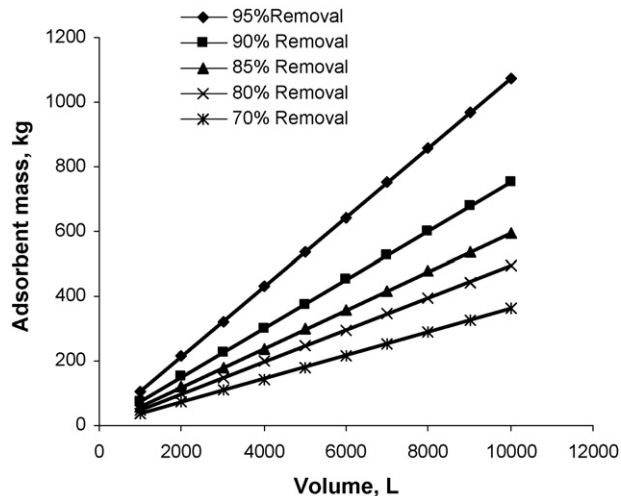


Fig. 14. Predicted NTB-modified Kaolinite clay adsorbent mass against volume of wastewater containing Aniline blue dye.

modified Kaolinite clay under same adsorption conditions it is 58.0, 116.1, 174.1, 232.1, 290.1, 348.1, 406.2, 464.2, 522.3, and 580.3 kg of NTB-modified Kaolinite clay adsorbent. To adsorb 95% of 30 mg/L of Aniline blue from a ton of wastewater solution, 107.38 kg of unmodified Kaolinite clay and 58.03 kg of NTB-modified Kaolinite clay would be required. The ratio of clay to wastewater volume for the unmodified adsorbent is approximately 1:10 which supports Coles and Yong's [29] suggestion for the ratio of Kaolinite clay to volume of adsorbate solution during an adsorption process. However, this ratio is significantly changed by the modification of Kaolinite with sodium tetraborate reagent.

The above data suggest that the use of NTB-modified Kaolinite clay adsorbent reduces by approximately 50% the amount of Kaolinite needed to adsorb Aniline blue from wastewater solutions. This could further suggest that NTB-modified is far more cost effective and efficient for use in treatment plants for the adsorption of Aniline blue dye from aqueous solutions.

4. Conclusion

This research has shown that modification of Kaolinite clay with Sodium Tetraborate reagent not only increases the adsorption capacity of the adsorbent from 1666.67 to 2000 mg/kg for Aniline blue dye but also its initial sorption rate for the dye. Increase in pH, and adsorbent weight increased the adsorption of Aniline blue dye onto the unmodified adsorbent. However, for NTB-modified adsorbent, increasing pH did not increase its adsorption capacity but increased its overall pseudo-second-order rate constant while increasing adsorbent dose increased both initial sorption rate and adsorption capacity of NTB-modified Kaolinite clay.

Increasing agitation speed increased the adsorption capacity of both adsorbents but decreased the initial sorption rate and overall pseudo-second-order rate constant for the adsorption of Aniline blue onto the unmodified adsorbent. NTB-modified showed a reversed trend.

Fitting kinetic data obtained to modified pseudo-first-order, second-order and pseudo-second-order kinetic models suggest that adsorption of Aniline blue onto unmodified Kaolinite clay adsorbent could be by ion-exchange while for NTB-modified it is possibly by chemisorption mechanism.

Modeling equilibrium data against non-linear isotherm equation of Langmuir and Freundlich, data from NTB-modified adsorbent showed better fit to Langmuir isotherm which suggest that adsorption sites on this adsorbent is homogeneous in nature while those for the unmodified adsorbent showed better fit to the Freundlich isotherm which indicates that its sites is heterogeneous in nature.

From the design of a single-batch adsorber it is predicted that the NTB-modified adsorbent will require 50% less of the adsorbent to treat certain volumes of wastewater containing 30 mg/L of Aniline blue dye when it is compared with the unmodified adsorbent. This will be cost effective in the use of Kaolinite clay for the adsorption of Aniline blue dye from water and wastewater.

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References

- [1] V. Vadivelan, V.K. Kumar, Equilibrium, kinetics, mechanism and process design for the sorption of methylene blue onto rice husk, *J. Colloid Interf. Sci.* 286 (1) (2005) 90–100.
- [2] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, Kinetic modeling of the adsorption of basic dyes by kudzu, *J. Colloid Interf. Sci.* 286 (2005) 101–109.
- [3] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study, *Dyes Pigments* 51 (2001) 25–40.
- [4] A. Ozcan, E.M. Oncu, A.F. Ozcan, Kinetics, isotherm and thermodynamic studies of the adsorption Acid blue 193 from aqueous solutions onto natural Sepiolite, *Colloids Surf. A: Physicochem. Eng. Aspects* 277 (2006) 90–97.
- [5] A. Mittal, L. Krishnan, V.K. Gupta, Removal and recovery of malachite green from wastewater using agricultural waste material, de-oiled soya, *Sep. Purif. Technol.* 43 (2005) 125–133.
- [6] M. Alkan, O. Demirbas, S. Celikcapa, M. Dogan, Sorption of Acid red 57 from aqueous solution onto Sepiolite, *J. Hazard. Mater.* B116 (2004) 135–145.
- [7] C. Namasivayam, D.M. Kumar, K. Selvi, R.A. Begum, T. Vanathi, R.T. Yamuna, “Waste” coir pith—a potential biomass for the treatment of dyeing wastewaters, *Biomass Bioenergy* 21 (2001) 477–483.
- [8] W.T. Tsai, C.Y. Chang, M.C. Lin, S.F. Chien, H.F. Sun, M.F. Hsieh, Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl₂ activation, *Chemosphere* 45 (2001) 51–58.
- [9] P. Janos, H. Buchtova, M. Ryznarova, Sorption of dyes from aqueous solutions onto fly ash, *Water Res.* 37 (2003) 4938–4944.
- [10] P.J. Silva, S. Sousa, J. Rodrigues, H. Antunes, J.J. Porter, I. Goncalves, S. Ferreira-Dias, Adsorption of Acid orange 7 dye in aqueous solutions by spent brewery grains, *Sep. Purif. Technol.* 40 (2004) 309–315.
- [11] V.K. Garg, R. Gupta, B.A. Yadav, R. Kumar, Dye removal from aqueous solution by adsorption on treated sawdust, *Bioresour. Technol.* 89 (2003) 121–124.
- [12] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solution, *Waste Manage.* 21 (2001) 105–110.
- [13] C.H. Weng, Y.F. Pan, Adsorption of a cationic dye (methylene blue) onto spent activated clay, *J. Hazard. Mater.* 144 (1–2) (2007) 355–362.
- [14] M.C. Goldschmidt, D.Y. Fung, R. Grant, J. White, T. Brown, Rapid identification and isolation of *Candida albicans*, *J. Clin. Microbiol., Am. Soc. Microbiol.* 29 (6) (1991) 1095–1099.
- [15] S. Patai, in: Z. Rappaport (Ed.), *Anchoring Dye on Fiber*, John Wiley and Sons Ltd., 2007.
- [16] Material Safety and Data Sheet, in: Environmental Health & Safety (USA) MSDS Number: A6680, Mallinckrodt Baker Inc., 2005.
- [17] K.O. Adebowale, E.I. Unuabonah, B.I. Olu-Owolabi, Adsorption of some heavy metal ions on sulphate and phosphate-modified Kaolin, *Appl. Clay Sci.* 29 (2) (2005) 145–148.
- [18] G.W. Sears, Determination of specific surface area of colloidal silica by titration with sodium hydroxide, *Anal. Chem.* 28 (1956) 1981–1983.
- [19] E.I. Unuabonah, B.I. Olu-Owolabi, K.O. Adebowale, A.E. Ofomaja, Adsorption of lead and cadmium ions from aqueous solutions by tripolyphosphate-impregnated Kaolinite clay, *Colloids Surf. A: Physicochem. Eng. Aspects* 292 (2007) 202–211.
- [20] A.E. Ofomaja, Kinetics and mechanism of methylene blue sorption onto Palm kernel fibre, *Process Biochem.* 42 (1) (2007) 16–24.
- [21] H.D. Chapman, in: C.A. Black, al. et (Eds.), *Methods of Soil Analysis. Agronomy, Part 2, 9*, Am. Soc. of Agron. Inc., Madison, WI, 1965, pp. 891–901.
- [22] Q. Sun, L.Z. Yang, The adsorption of basic dyes from aqueous solution on modified-peat resin particle, *Water Res.* 37 (2003) 1535–1544.
- [23] X. Yang, B. Al-Duri, Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon, *J. Colloid Interf. Sci.* 287 (2005) 25–34.
- [24] B. Banquella, H. Benaissa, Cadmium removal from aqueous solutions by Chitin: kinetic and equilibrium studies, *Water Research* 36 (2002) 2463–2474.
- [25] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.* 34 (2000) 735–742.
- [26] E. Galan, P. Aparicio, A. Miras, K. Michailidis, A. Tsirambides, Technical properties of compounded Kaolin sample from Griva (Macedonia, Greece), *Appl. Clay Sci.* 10 (1996) 477–490.
- [27] Y.S. Ho, A.E. Ofomaja, Kinetics and thermodynamics of lead ion sorption on palm kernel fiber from aqueous solution, *Process Biochem.* 40 (2005) 3455–3461.
- [28] Y.S. Ho, J.C.Y. Ng, G. McKay, Removal of lead(II) from effluents by sorption on peat using second-order kinetics, *Sep. Sci. Technol.* 36 (2) (2001) 241–261.
- [29] C.A. Coles, R.N. Yong, Aspects of Kaolinite characterization and retention of Pb and Cd, *Appl. Clay Sci.* 22 (2002) 39–45.
- [30] K.O. Adebowale, I.E. Unuabonah, B.I. Olu-Owolabi, The effect of some operating variables on the adsorption of lead and Cadmium ions on Kaolinite clay, *J. Hazard. Mater.* B134 (2006) 130–139.