Abstract.—Kaolin clay of known cation exchange capacity (CEC) was treated with cationic surfactant, hexadecyltrimethylammonium bromide (HDTMA-Br) and used for batch adsorption studies of nitrate ion contaminant removal at pH 7.6 and 298K. The adsorbent dosage best for adsorption was found to be 200gL⁻¹. It has a maximum removal efficiency of 81.27%. The maximum sorption capacity from the Langmuir isotherm was found to be 0.7815 mg/g. The results indicated that the Frumkin and Langmuir isotherms with highest R² values of 0.9929 and 0.9965 respectively provide the best correlation for the experimental data. The separation factor (Rₛ) was within the range 0<Rₛ<1 (0.0685-0.4131) and showed a highly favourable and acceptable adsorption. The Elovich model parameter a with a maximum value of 190.2997 mg.g⁻¹.min⁻¹ showed that adsorption was by chemisorption. The best fit kinetics was found to be the pseudo-second order model with a correlation coefficient (R²) ranging from 0.9551-0.9999. The energy of sorption was best described by the Temkin isotherm and values of heat of sorption ranging from -0.3743 to -5.1716 kJ/mol predicted exothermic process. The values of energy E (kJ/mol) from Dubinin-Radushkevich isotherm model showed that the mechanism of sorption was both physisorption and chemisorption since the values of E ranged from 4.1381-50.00 kJ/mol.

Keywords— HDTMA-Br, Isotherms, Kinetics, Nitrate ion, Organo-kaolinite clay, Sorption.

I. INTRODUCTION

The contamination of groundwater, urban and industrial wastewater by toxic inorganic and organic chemicals has increased to an alarming rate in recent years and is a worrying environmental problem that has been recognized as in issue of growing importance[1]. Nitrate occurs naturally in soil containing nitrogen-fixing bacteria, decaying plants, septic system effluent and animal manure[5].

In the United States, nitrate in drinking water poses human health risks, and nitrate contamination of groundwater has become widespread. In a study of more than 40 states, nitrate was the most frequently reported groundwater contaminant of concern[15][4]. It was reported that 60% population of developing countries have no access to safe drinking water[5].

The nitrate ion is a stable and highly soluble anion which belongs to the class of inorganic chemicals termed oxyanions and it gets into the human body through drinking water, food, drugs, etc.[6].

Organoclay refers to natural clay minerals which have their surface modified to improve their adsorption ability, capacity and affinity for oxyanion contaminants by the replacement of the natural inorganic cations with surfactant cations such as quaternary ammonium compounds (QACs)[7].

This work focus on parametric studies of the batch adsorption of nitrate ion contaminant from simulated wastewater onto kaolinite clay from Alkaleri-Bauchi state, North-eastern Nigeria with HDTMA-Br cationic surfactant.

II. SOURCES AND EFFECTS OF NITRATE CONTAMINATION

The industrialization and modification of manufacturing processes have resulted in an increase in the volume of wastewater discharge into the environment which causes water pollution[8][9] stated that wastewater from industrial operations transport many chemicals that have adverse effects on the environment.

Ammonia and amine compounds from carcass-processing, and sewage-treatment plants[10], phosphates and nitrates from paper mills, fertilizer plants, and detergent industries[9], cyanide and its compounds from electroplating and mining (extraction of gold, silver, etc.) industries[11] end up in lakes, creeks and rivers. These chemicals may be toxic to humans, environment and animals[12]. Drinking water free of toxic chemicals or having below the maximum acceptable limit of concentration is crucial for health life[13].

Nitrates are commonly considered to be one of the important contaminants in groundwater[13][14]. This is due to the stable and highly soluble nature of the ion making it difficult to remove by traditional water treatment methods[15][4]. The major sources of nitrate contamination of groundwater are agricultural activities, wastewater and organic residuals as well as surface run-off from agricultural and landscaped areas[1][14]. Excessive nitrate in drinking water may cause methemoglobinemia called blue baby disease in new-born infants[1][6][37].
Nitrate-contaminated water supplies have been linked with infectious outbreaks\textsuperscript{[18]}. Understanding of nitrate movement in soils is very important for the conservation of environmental and groundwater qualities\textsuperscript{[19,20]}. The prevailing environmental conditions such as temperature, humidity, type of natural soil and common irrigation practices are all contributing to the migration of nitrate in soil. Improperly maintained septic systems can result in nitrate contamination of groundwater supplies\textsuperscript{[21]}.

Other possible impacts of nitrate ion contamination is when nitrates interact with organic compounds (secondary amines) to form N-nitrosamines including some pesticides, which are known to cause cancer\textsuperscript{[21]}.

The maximum acceptable contaminant level for nitrate set by the World Health Organization (WHO) and the US Environmental Protection Agency (EPA) for drinking water are 50mg/L and 45mg/L of nitrate respectively\textsuperscript{[22,23,24]}.

III. ADSORPTION MODELS

An adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium\textsuperscript{[25,26]}. Several two- or three-parameter models have been discussed in the literature to describe experimental data of adsorption isotherms\textsuperscript{[27,28,29,30,31]}.

A. Langmuir isotherm

Langmuir isotherm model which is probably the best known and most widely used adsorption isotherm was generally developed to describe the gas-solid phase adsorption\textsuperscript{[26]}. The linear form of the Langmuir isotherm is given as:

$$\frac{C_e}{q_e} = \frac{1}{k_LQ_0} + \frac{C_e}{Q_0}$$

(1)

Where $Q_0$ is the maximum pollutant uptake (mg/g), $k_L$ is the Langmuir constant (L/mg) related to the energy of adsorption, $C_e$ is the concentration of solute in solution at equilibrium (mg/L). The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant called the separation factor $R_L$, which is defined as follows\textsuperscript{[26]}:

$$R_L = \frac{1}{1 + k_LC_0}$$

(2)

Where $C_0$ is the amount of adsorbate initial concentration (mg/L) and $k_L$ represents the affinity between adsorbent and adsorbate.

The value of $R_L$ indicates the isotherm’s shape\textsuperscript{[13]} and the nature of the adsorption process, whether unfavourable ($R_L>1$), linear ($R_L=1$), favourable ($0<R_L<1$) and irreversible ($R_L=0$).

The Langmuir isotherm defines the equilibrium parameters of homogenous surfaces, monolayer adsorption and distribution of adsorption sites\textsuperscript{[32]}.

B. Freundlich isotherm

Freundlich isotherm is the earliest known empirical relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer\textsuperscript{[25,26]} but can be applied to heterogeneous surfaces as well as multilayer sorption. The linear form of the Freundlich isotherm is given as\textsuperscript{[25]}:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

(3)

Where, $C_e$ is the equilibrium liquid phase concentration (mg/L), $q_e$ the equilibrium solid phase concentration (mg/g) while $k_F$ and $n$ are isotherm parameters of adsorption capacity (mg/g) and adsorption intensity respectively\textsuperscript{[26,33]}.

C. Dubinin-Radushkevich isotherm

Dubinin-Radushkevich equation is another popular equation for the analysis of isotherms of a high degree of regularity. The linearized form of the Dubinin-Radushkevich isotherm model is given as\textsuperscript{[25]}:

$$\ln q_e = \ln q_s - k_{ad} \varepsilon^2$$

(4)

Where $q_s$ is the Dubinin-Radushkevich model constant or theoretical isotherm saturation capacity (mg/g); $k_{ad}$ is the Dubinin-Radushkevich isotherm constant (mol$^2$/kJ$^2$); and $\varepsilon$ is the Polanyi potential. This energy, $E$ can be computed by the relationship\textsuperscript{[26,33]}:

$$E = -\frac{1}{\sqrt{2k_{ad}}}$$

(5)

Where E (kJ/mol) gives information about the physical and chemical features of adsorption\textsuperscript{[14]}. The value of E ranges from 1.0 to 8.0 kJ/mol for physical adsorption and 9.0 to 16.0 kJ/mol for chemical ion-exchange adsorption\textsuperscript{[35,36,37]}.

The parameter $\varepsilon$ can be obtained as:

$$\varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right]$$

(6)

$R$, $T$ and $C_e$ represent the gas constant (8.314 J/mol K), absolute temperature in Kelvin (K) and adsorbate equilibrium concentration (mg/L) respectively\textsuperscript{[25]}.
D. Temkin isotherm

The Temkin isotherm assumes that the fall in heat of adsorption of all the molecules in the layer would decrease linearly rather than logarithmically with coverage due to sorbate/sorbent interactions\textsuperscript{[26,27,28,30]}. The linearized form of the Temkin isotherm is given as\textsuperscript{[25]}

\[
q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e
\]

(7)

Where \( B \) is the Temkin constant related to heat of sorption (J/mol); \( A_T \) is the Temkin isotherm equilibrium binding constant (L/g); \( R \) is the gas constant (8.314 J/mol.K); and \( T \) is the absolute temperature (K)\textsuperscript{[25,38,39]}

E. Frumkin isotherm

The Frumkin isotherm is given by the relation\textsuperscript{[11]}

\[
q_e = n_T \ln K_T + n_T \ln C_e
\]

(9)

Where \( q_e \) is the sorbed amount (mg/g); \( C_e \) is the equilibrium concentration of the sorbate (mg/L) while \( K_T \) (L/g) and \( n_T \) are the Frumkin constants. The constant \( K_T \) is analogous to the Temkin isotherm equilibrium binding constant \( A_T \). This factor explicitly takes into account the adsorbent-adsorbate interactions\textsuperscript{[25]}, while the values of \( n_T \) are analogous to the Temkin constant \( B \), related to the heat of sorption\textsuperscript{[39]}.

F. Sips isotherm

The Sips isotherm is a combined form of the Langmuir-Freundlich isotherm equations. It was deduced for predicting the heterogeneous adsorption systems\textsuperscript{[37]} and circumventing the limitations of the rising adsorbate concentration associated with Freundlich isotherm model\textsuperscript{[25]}

The sips isotherm has a linear form given as\textsuperscript{[25]}

\[
\beta_s \ln C_e = - \ln \frac{K_s}{q_s} + \ln a_s
\]

(10)

Where \( q_e \) (mg/g) is the adsorptive capacity \( C_e \) (mg/L) is the sorbate concentration at equilibrium, \( K_s \) is the Sips model isotherm constant (L/g), \( a_s \) is the Sips model constant (L/mg) and \( \beta_s \) is the Sips model exponent\textsuperscript{[26]}.

IV. ADSORPTION KINETIC MODELS

It is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants. To develop sorption kinetics, knowledge of the rate law describing the sorption system is required\textsuperscript{[30]}.

A. Pseudo-first order kinetic model

A kinetic model for sorption analysis in the liquid-solid phase is the pseudo-first order rate expression of Lagergen based on the adsorption rate. The linearized form can be presented as follows:

\[
\log(q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303} t
\]

(11)

Where \( q_e \) and \( q_t \) (mg/g) are the adsorption capacities at equilibrium and at time \( t \) (hr) respectively, \( k_{p1} \) is the rate constant (min\(^{-1}\)). It has been used to describe adsorption of pollutants from wastewater in different fields, such as the adsorption of methylene blue from aqueous solution by broad bean peels\textsuperscript{[41]} and the removal of malachite green from aqueous solutions using oil palm trunk fibre\textsuperscript{[42,43]}.

B. Pseudo-second order kinetic model

A pseudo-second order rate expression based on sorption equilibrium capacity can be presented in linearized form as:

\[
\frac{t}{q_t} = \frac{1}{k_{p2} q_s^2} + \frac{1}{q_s} t
\]

(12)

Where \( k_{p2} \) is the rate constant for pseudo second-order adsorption (g/(mg.hr)) and \( k_{p2} q_s^2 \) or \( h \) (mg/hr) is the initial adsorption rate.

This equation has been successfully applied to the desorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions\textsuperscript{[44,45,46,47,48,49,50]}.

C. Elovich kinetic model

In reactions involving chemisorption of the adsorbate on a solid surface without desorption of products, adsorption rate decreases with time due to an increased surface coverage\textsuperscript{[26]}. The linearized form of the Elovich kinetic model is given as\textsuperscript{[51]}:

\[
q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t
\]

(13)

Where \( \alpha \) is the initial adsorption rate (mg/g min), \( q_i \) (mg/g) represents the amount of gas adsorbed at time \( t \) (hrs.) and \( \beta \) is related to the extent of surface coverage and activation energy for chemisorption\textsuperscript{[52,53]}.

Elovich model has been widely used to describe the adsorption of gas onto solid systems\textsuperscript{[54,55,56]}.
V. EXPERIMENTAL SECTION

A. Kaolin clay and cationic surfactant HDTMA-Br

A well characterized kaolin clay from Alkaleri Bauchi state, Northeastern Nigeria was used. The cationic surfactant (HDTMA-Br) was imported from Xiamen Xm-innovation Chemical Co. LTD, China. It has a purity of 99% and molecular weight of 364.45g/mol and was used without any further treatment.

HDTMA-Br solution equivalent to twice kaolin clay CEC was prepared and mixed with known mass of kaolin clay and then stirred continuously for 24 hours (time required to achieve equilibrium) at about 740rpm and 298K. The aqueous bilayer modified clay (BMC) was centrifuged at 3000rpm for 30 minutes with a Gallenkamp Angle Head Centrifuge. The supernatant was decanted and the solid part (organo-kaolinite clay) was washed with distilled water four times and dried in oven at 60°C for 20 hours and stored in a desiccator for further use.

B. Contaminant preparation and batch adsorption

Deionised water was obtained from Gubi Water Treatment Plant, Bauchi state. A stock solution containing 50mM (310.05mg/L) concentration of nitrate ion (\(\text{NO}_3^-\)) from sodium nitrate (NaNO\(_3\)) salt was prepared and confirmed by DR 2000 spectrophotometer. The BMC in the range of 50-250mg was precisely weighed at 50mg interval and shaken laterally at 1200rpm in 10mL of oxyanion contaminant solution for 0-8 hours at 298K. A centrifuge was used to separate the two phases. The DR Spectrophotometer was used to analyse the supernatant. The amount of nitrate ion contaminant left in the supernatant was determined. The equilibrium relationship curve was used to know the trend of sorption at different adsorbent dosage. The optimum adsorbent dosage was established. Equilibrium isotherm parameters and kinetic parameters were determined.

VI. RESULTS AND DISCUSSION

A. Equilibrium studies

The initial concentration of the sorbate is very important because a given mass of sorbent can adsorb only a fixed amount of sorbate. The plot of amount of nitrate ion contaminant adsorbed onto the surface of the adsorbent versus time is shown in Fig. 1.

![Fig. 1: Nitrate ion adsorbed by different mass of adsorbent](image1)

The curve of each dosage of the modified clay is facing concave downwards. This indicates a strongly favourable adsorption because more adsorption occurs at lower concentrations. From equation 14, the maximum adsorptive capacity of 1.6065 mg/g after 8 hours was obtained for BMC dosage of 1.0g.

\[
q_e = (C_0 - C_e)V/m
\]  

(14)

The maximum percentage removal occurred at BMC dosage of 2.0 g after 8 hours with a value of 81.27% and least for dosage 0.5g with a value of 23.08%.

Langmuir Isotherm

From equation 1, the linear plots of Langmuir isotherm was obtained (only 2g in 10mL shown as Fig. 2) and the evaluated parameters are presented in Table I. The correlation coefficients for Langmuir isotherm were in a range from 0.9486 – 0.9965.

![Fig. 2: Langmuir isotherm plot for BMC](image2)
Table I
Langmuir isotherm parameters for BMC

<table>
<thead>
<tr>
<th>BMC (g)</th>
<th>( R^2 )</th>
<th>( K_L ) (L/mg)</th>
<th>( Q_0 ) (mg/g)</th>
<th>( R_L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.9486</td>
<td>-0.004583</td>
<td>0.1366</td>
<td>0.4131</td>
</tr>
<tr>
<td>1.0</td>
<td>0.9271</td>
<td>-0.007984</td>
<td>0.3177</td>
<td>0.2877</td>
</tr>
<tr>
<td>1.5</td>
<td>0.9876</td>
<td>-0.016206</td>
<td>0.5835</td>
<td>0.1659</td>
</tr>
<tr>
<td>2.0</td>
<td>0.9965</td>
<td>-0.043829</td>
<td>0.7815</td>
<td>0.0685</td>
</tr>
<tr>
<td>2.5</td>
<td>0.9947</td>
<td>-0.034320</td>
<td>0.5763</td>
<td>0.0859</td>
</tr>
</tbody>
</table>

The maximum sorption capacity \( Q_0 \) is 0.7815 mg/g at adsorbent dosage of 2g in 10mL. The values of \( K_L \) are negative showing that the energy of sorption may be exothermic. The value of the separation factor \( R_L \) is favourable (0.0685-0.4131)\(^{[13]}\). This implies that the adsorption mechanism can be described by Langmuir isotherm.

**Freundlich Isotherm**

From equation 3, the linear plots of Freundlich isotherm was obtained (only 2g in 10mL shown as Fig. 3). The evaluated parameters are shown in Table II. The correlation coefficient \( R^2 \) for all masses were reasonably high ranging from 0.9793 - 0.9870.

![Fig. 3: Freundlich isotherm plot for BMC](image)

Figure 3: Freundlich isotherm plot for BMC

Table II
Freundlich isotherm parameters for BMC

<table>
<thead>
<tr>
<th>BMC (g)</th>
<th>( R^2 )</th>
<th>( K_F ) (mg/g)</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.9793</td>
<td>1.1066×(10^{13})</td>
<td>-0.1847</td>
</tr>
<tr>
<td>1.0</td>
<td>0.9604</td>
<td>1.7346×(10^4)</td>
<td>-0.5413</td>
</tr>
<tr>
<td>1.5</td>
<td>0.9845</td>
<td>63.3286</td>
<td>-1.2164</td>
</tr>
<tr>
<td>2.0</td>
<td>0.9870</td>
<td>5.9034</td>
<td>-2.6406</td>
</tr>
<tr>
<td>2.5</td>
<td>0.9833</td>
<td>6.2791</td>
<td>-2.2727</td>
</tr>
</tbody>
</table>

The value of \( K_F \) is an indicator of adsorption capacity, the highest occurred at mass 0.5g with a value of \( 1.1×10^{13} \) mg/g implying that the best performing sorbent dosage was at mass 0.5g. This value decreased with increasing adsorbent dosage because a given mass of sorbent can adsorb only a fixed amount of sorbate. Values of the slope correspond to the values of 1/n for the adsorption systems and they are less than one. The values of n below unity imply chemisorption process\(^{[59]}\). This shows that the adsorption can be modelled by the Freundlich isotherm.

**Dubinin-Radushkevich Isotherm**

From equation 4, the linearized plots of the Dubinin-Radushkevich Isotherm model was obtained (only 2g in 10mL shown as Fig. 4) and summary of the parameters obtained from the plots are shown in Table III.

![Fig. 4: Dubinin-Radushkevich isotherm plot for BMC](image)

Figure 4: Dubinin-Radushkevich isotherm plot for BMC

Table III
Dubinin-Radushkevich isotherm parameters for BMC

<table>
<thead>
<tr>
<th>BMC (g)</th>
<th>( R^2 )</th>
<th>( q_e ) (mg/g)</th>
<th>( k_{ad} ) (mol(^2)/kJ(^2))</th>
<th>( E ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.9636</td>
<td>0.0647</td>
<td>-0.0292</td>
<td>4.1380</td>
</tr>
<tr>
<td>1.0</td>
<td>0.9016</td>
<td>0.4175</td>
<td>-0.0051</td>
<td>9.9015</td>
</tr>
<tr>
<td>1.5</td>
<td>0.9362</td>
<td>0.7374</td>
<td>-0.0011</td>
<td>21.3201</td>
</tr>
<tr>
<td>2.0</td>
<td>0.9243</td>
<td>0.9137</td>
<td>-0.0002</td>
<td>50.0000</td>
</tr>
<tr>
<td>2.5</td>
<td>0.9015</td>
<td>0.6932</td>
<td>-0.0003</td>
<td>40.8248</td>
</tr>
</tbody>
</table>

Regression coefficient \( R^2 \) for Dubinin-Radushkevich isotherm model falls within the range 0.9015-0.9636. The constant \( K_{ad} \) is related to the adsorption energy per mole of the sorbate as it is transferred to the surface of the solid\(^{[33]}\). The values range from -0.0003 to -0.0292 mol\(^2\)/kJ\(^2\).
According to [33], results of their study gave a value for $E$ as 5.78 kJ/mol and concluded that the adsorption was by physisorption. Similarly, the work of [27] stated that the typical range of bonding energy for ion-exchange mechanisms is 8-16 kJ/mol. From the results obtained in this study, the values of $E$ ranges between 4.138-50.0 kJ/mol. Since these values are not within 8 and 16 kJ/mol, the adsorption may not be by ion-exchange. This shows that chemisorption may play an important role in the adsorption process [27] and the maximum adsorbent dosage is shown to be mass 2.0 g. Since chemisorption explained the adsorption mechanism, it revealed that the organoclay synthesized was rather stable, desorption did not occur to a considerable amount and the sorption of oxyanion was found to be almost irreversible [60].

**Temkin and Frumkin Isotherm**

From equations 7 and 9, the linear plots of the Temkin and Frumkin isotherms model were obtained (only 2g in 10mL shown as Fig. 5) and the parameters obtained from the model are shown in Tables IV and V respectively. The Temkin isotherm with higher correlation coefficient values is a better choice in explaining sorption energies [39].

The regression coefficients for Frumkin isotherm ranges between 0.9915-0.9994 which are closer to unity. The value of $B$ and $n_T$ from the Temkin and Frumkin isotherms respectively vary within a range -0.3743 to -5.1716 J/mol and relates to heat of sorption, predicting exothermic process as sorbate interacts with the sorbent. The Temkin isotherm with higher correlation coefficient values is a better choice in explaining sorption energies [39].

The equilibrium binding constant $A_T$ and $K_T$ obtained from the Temkin and Frumkin isotherms were found to vary within the range 0.001084-0.003176 L/g respectively.

**Sips Isotherm**

From equation 10, the linearized Sips isotherm plot was obtained (only 2g in 10mL shown as Fig. 6) with the summarized parameters shown in Table VI.
The correlation coefficients $R^2$ vary within a range, 0.9604-0.9870. When compared to other adsorption isotherm models, the Sips isotherm has correlation coefficients identical to the Freundlich isotherm. This is an indication that the Sips model reduced to the Freundlich isotherm due to low adsorbate concentrations arising from increase in adsorbent dosage\(^{26}\). Also, the Sips model exponent $\beta_s$ decreases from a maximum value of 5.4149 at modified clay dosage of 0.5g to the least value of 0.3787 at clay dosage of 2.0g as the adsorbent dose increases showing that the adsorption data for bilayer modified clay is more of Freundlich form than Langmuir form\(^{25}\). This is an indication that the sorption mechanism was to some extent heterogeneous.

### B. Adsorption kinetics

For evaluating the adsorption kinetics of sorption of nitrate ion contaminant onto BMC, pseudo-first order, pseudo-second order and Elovich models were employed to analyse the experimental data obtained.

#### Pseudo-First Order Kinetic Model

From equation 11, the linear plot of pseudo-first-order kinetic model for varied mass of BMC is shown in Fig. 7 and the corresponding evaluated parameters are summarized in Table VII. The value for the correlation coefficient ($R^2$) was in the range, 0.8888-0.9757, with the maximum value at BMC dosage 2.0g. The values of $q_e$ calculated was in a range from 0.6383 to 2.4395 mg/g.

#### Pseudo-second order kinetic model

From equation 12, the linear plot of pseudo-second-order kinetic model is shown in Fig. 8 below and the kinetic parameters are summarized in Table VIII. It is observed that pseudo-second order model best fits adsorption of nitrate ions using BMC because the $R^2$ values obtained ranged from 0.9551-0.9999.

The maximum value of the rate constant is 1.1457hr\(^{-1}\) at clay dosage 2.0g. According to\(^{40}\), the pseudo-first order rate equation has been widely applied to sorption systems which could not be modelled by simple sorption kinetics such as, first order and second order kinetic models.

#### Pseudo-second order kinetic model

From equation 12, the linear plot of pseudo-second order kinetic model is shown in Fig. 8 below and the kinetic parameters are summarized in Table VIII. It is observed that pseudo-second order model best fits adsorption of nitrate ions using BMC because the $R^2$ values obtained ranged from 0.9551-0.9999.
Elovich Kinetic Model

From equation 13, the Elovich kinetic model was plotted as shown in Fig. 9 below and the evaluated parameters are summarized in Table IX below. The correlation coefficient ranged from 0.8068-0.9165 for all modified clay dosages. The initial adsorption rate α represents chemisorption and is highest (190.2997 mg.g⁻¹.min⁻¹) at adsorbent dosage 2.0g and least (2.1329 mg.g⁻¹.min⁻¹) for mass 0.5g.

\[ q_t = \frac{1}{\beta} \ln \left( \frac{1}{\alpha} + \frac{1}{\beta} \right) \]

\[ q_t = \frac{1}{\beta} \ln \left( \frac{1}{\alpha} + \frac{1}{\beta} \right) \]

The extremely high value indicates that the adsorption takes place fastest at modified clay dosage 2.0g as this is the maximum adsorbent dose. The parameter β is related to the extent of surface coverage and varied from 1.805g.hr/mg to a maximum of 9.634g.hr/mg at clay dosage of 2.5g due to the exothermic nature of the present adsorption process and increased surface area of modified clay dosage. These results correlate with those of the pseudo-second order kinetics and the adsorption probably occurred through chemisorption process.

VII. Conclusions

The following conclusions could be drawn from the results of this study:

- The isotherm models which described the adsorptive mechanism include the Langmuir and Frumkin isotherms. The best-fit model is the Frumkin isotherm with correlation coefficient (R²) values ranging from 0.9915-0.9994. This isotherm predicts monolayer adsorption.
- The Sips and Freundlich isotherms predicted multilayer adsorption as well as a heterogeneous surface of the modified clay. Thus the adsorption mechanism is complex.
- The separation factor R_L from the Langmuir isotherm was found to be within the range 0<R_L<1 (0.08-0.4) indicating a highly favourable and acceptable adsorption process.
- From the analyses, the mechanism of adsorption was determined from the values of E (kJ/mol) ranging from 4.138-50.00 to be physisorption and chemisorption and the nitrate ion contaminant removal was almost irreversible.
- The maximum percentage removal was determined and occurred at mass 2.0 g after 8 hrs with a value of 81.27% and the maximum adsorption capacity of modified clay was obtained from the Langmuir isotherm Q_e at mass 2.0 g with a value of 0.7815 mg/g.
- The plot of adsorption capacity against time was found to show a strongly favourable process with the curves pointing concave downwards.
- The energy of sorption was best described by Temkin isotherm due to a higher correlation coefficient than the Dubinin-Radushkevich isotherm. The reaction is exothermic from the Langmuir and Temkin isotherm models.
- The best-fit kinetic model to describe the sorption process appears to be pseudo-second order kinetic model with highest R² values ranging from 0.9551-0.9999 for varied mass of modified clay while the parameters of the Elovich model confirmed chemisorption process.

REFERENCES

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