Adsorption isotherm and kinetics for the removal of nitrate from wastewater using chicken feather fiber

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O O Elemile¹, B O Akpor², E M Ibitogbe³, Y T Afolabi³ and D. O Ajani⁴

Abstract: Nitrate has been identified as a major source of water pollution and eutrophication. The use of modified chicken feathers (MCFs) as an adsorbent has not been fully explored. The study therefore assessed the use of MCFs for the adsorption of nitrate. Fresh chicken feathers, obtained from a commercial poultry farm, were first hydrolyzed with sodium hydroxide and activated with HCl (aq) to give modified chicken feathers, MCFs. Experimental constraints were varied in a series of batch tests including concentration, pH, adsorbent dosage and contact time. FTIR was used to monitor the adsorption processes (before and after) of the polluted water. The outcome showed increase in specific surface area and the favorable formation of adsorption sites of MCFs. For the understanding of adsorption mechanism, experimental data were assessed by Langmuir, Freundlich, Temkin and Sips isotherm equations. Pseudo-first and pseudo-second order models were used to evaluate time characteristics of adsorption. The optimum parameters for adsorption are found to be initial ion concentration, initial pH, adsorbent dosage and contact time 300 mg/L, 8, 10 and 480 min, respectively. This study also reveals adsorption fit the chosen isotherm models in the following order: (Sips >Langmuir > Freundlich > Temkin). Sips isotherm having the best fit infers adsorption took place on heterogeneous surface. Pseudo-second-order is suited for explaining nitrate removal based on statistical R² coefficient. The use of MCFs as an eco-friendly,
cost-effective and renewable bio-sorbent for wastewater treatment is very possible due to its adsorption ability in the removal of nitrate.

Subjects: Thermodynamics; Adsorption Science; Biotechnology; Environmental; Water Engineering; Environmental Health; Pollution

Keywords: Modified chicken feathers; adsorption; nitrate; renewable; biosorbent

1. Introduction
Access to safe drinking water is not taken for granted in developing countries, where economic growth is often sacrificed at the expense of environmental protection and water quality (Masindi et al., 2018; Pandey et al., 2020, 2021). The price of urbanization and rapid industrialization is a cost laid on the environment and this burden is a global priority. Agricultural practices also play a major role in the release of organic and inorganic chemicals to water bodies (Blowes et al., 1994). High concentration levels of nitrate in existing water tables have been associated with leaching and run-off from agricultural inputs into groundwater reserves. Land use and hydrogeology are factors that affect the levels of nitrate in water. Nitrate pollution of drinking water sources (which has been linked with certain health outcomes) is known to be increasing (Fewtrell, 2004). This increase can be associated with excessive usage of nitrogen based fertilizers, leaching of wastewater and other organic wastes into surface water and groundwater sources (Hajjamad & Almasri, 2009). Excess intake of nitrate can affect the blood by reducing hemoglobin content responsible for carrying oxygen in the blood. This phenomenon is known as blue-baby syndrome, also called infant methemoglobinemia, which is exclusively harmful to infants. Growing demands in the developing world for better water quality and stronger legislation for water safety have necessitated the need for nitrate remediation systems. Developing world has experience intensification level of nitrate contamination of groundwater with high emergent populations, putting strains on drinking water resources (Gu et al., 2013). The maximum concentration level (MCL) for nitrate as stated by the World Health Organization (WHO) is given as 50 mg/L NO₃ and 11 mg/L NO₂-N, while Environmental Protection Agency, EPA is given as 45 mg/L NO₃ and 10 mg/L NO₂-N (U.S. Environmental Protection Agency, 2012) respectively.

Therefore, focus and effort have been channeled in recent times towards efficient removal of nitrate contamination in water/waste water to its minimal and acceptable level for domestic usage. Physico-chemical methods of nitrate removal from water includes ion exchange, reverse osmosis and electro-dialysis and adsorption are amongst several uses (Aghapour et al., 2016). However, extractive methods like reverse osmosis and ion exchange resins are found to be cost prohibitive, the processes almost always result in subsequent pollution, which must be treated later, increasing the overall cost of the removal/treatment process (Albayati, 2019; Dioli et al., 2011). Biological processes, such as denitrification, needs continuous monitoring of pH and temperature as well as addition of a carbon source. Zero-valent iron (ZVI) has the ability to reduce different contaminants which includes nitrate in groundwater and this is why it has been studied extensively. Although, it should be noted this technology does not come without its limitation of ammonium production and a pH-controlled condition. Other physicochemical and biological methods which have been employed to remove excessive nitrate from water includes electro dialysis (Abou-Shady et al., 2012), denitrification (Fernández-Nava et al., 2008), microalgae-bacteria consortia (Abdel-Raouf et al., 2012; Jia & Yuan, 2016) and combination of bio-denitrification and sand filter systems (Aslan, 2005). Of these processes, adsorption is more preferable as it is considered to be the most attractive due to its convenience, ease of operation, simplicity of design and economic considerations specially if low-cost adsorbents having easy regenerative properties are used (Liyun et al., 2017).

Adsorption is a surface phenomenon that functions in pollutant removal of both organic and inorganic substances (Nageeb, 2013) for both domestic and industrial wastewater. It is an important removal method as it has several advantages as compared to other alternatives. This advantage is seen in their convenience, simplicity of design, ease of operation and high efficiency. It has been used in drug delivery, for example, Alkafajy & Albayati (2020). Activated carbon adsorbent prepared from
sewage sludge has been identified as a potentially attractive material for wastewater (Nageeb, 2013). Although, various materials have been identified including activated carbon as a suitable material for the adsorption of pollutants from water, it becomes uneconomical in the scenario of large-scale waste water treatment. However, utilization of cheap sorbents such as biomass in a bid to get an inexpensive means of treatment of waste water has been studied in recent years (Keränen et al., 2015). Accordingly, there is a need to develop a practical and cost effective adsorbent that can be used widely to remove nitrate from water (Yang et al., 2017).

Feathers are by-products of poultry processing produced in large quantities and is reported to be the most abundant source of keratinous biomass, making it an invaluable protein source (Onifade et al., 1998). Chicken feathers, which act as a protective covering for birds and poultry, represent 5% to 7% of the total weight and will generally end up becoming an environmental problem since they tend to degrade slowly (Coward-Kelly et al., 2006). They are seen as a natural bio-sorbent that can be used for water treatment in removal of contaminants. Chemically treated chicken feather have been discovered to be effective in the removal of Cr (VI) ions in an aqueous solution (Nurmiyanto et al., 2014). Natural and chemically treated chicken feathers (CF) were tested for their ability, as adsorbents, to remove copper and zinc from wastewater (Al-Asheh et al., 2003). Banat and Al-Asheh (1999) checked the viability of using chicken feathers as a bio-sorbent for the removal of phenol from aqueous solutions. From previous literature studies, no research has been carried out on the removal of nitrate from wastewater using chicken feather as an adsorbent. Hence, this study aims to investigate the removal of nitrate from wastewater using modified chicken feather (MCFs) fiber with aid of batch adsorption methods. In addition, FTIR analysis was carried out to better characterize the different behavior of such chicken feather samples.

2. Methods and materials
The chicken feathers were obtained from the poultry section in Landmark University Commercial Farms; NaOH was used in treating the CFs while HCl was used for their modification. The initial pH range was adjusted to the desired value using 0.1 M HCl or NaOH. The chemicals used were of analytical grade.

2.1. Preparation of chicken feathers
Raw chicken feathers (CFs) were obtained from the Landmark University Commercial Farms. These feathers were washed thoroughly using detergent, rinsed severally with deionized water for the removal of dirt and dust and then left to dry. Homogenized fiber could be obtained by detaching them from the quill after which they were stored for use. The characterization of the chicken feather in terms of proximate and ultimate analyses was reported by Chokrabarty et al. (2020b). The process was achieved by heating a known weight of the sample and considering the weight loss up to 600°C as shown in Table 1.

2.2. Chicken feather treatment using NaOH
Sodium hydroxide solution was prepared by dissolving 1 g of NaOH pellets in 250 mL of distilled water. The CFs were hydrolyzed with the solution to get rid of the lipid layer that surrounded the surface of the feather fiber and left for about 2–3 days. Finally, the treated CF was separated from the solution by filtration, washed severally using distilled water after which it was activated using hydrochloric acid (HCl).

2.3. Activation using aqueous hydrochloric acid (HCl)
Thirty seven percent (37% v/v) HCl was added to the treated CFs and gently stirred to allow for homogeneous mixing. The slurry was then left for 30 min for activation to take place and washed multiple times to remove the excess hydrochloric acid. The washed adsorbent was placed in the oven (105°C) to remove moisture. The modified (HCl-treated CFs) were removed and placed in a desiccator until use.
2.4. Preparation of nitrate
Solution of nitrate was prepared following the method described by Yang et al., 2017). Using analytic grade potassium nitrate salt (KNO3) for the batch experiment, the required concentration was prepared by means of serial dilution in a series of 250 mL conical flask. Nitrate solution here refers to dissolving 0.7218 g of potassium nitrate (KNO₃) in 1 L of distilled water to yield a 100 mg L⁻¹ nitrate standard stock solution.

2.5. Nitrate analysis
The spectrometric method was employed in this study by using the UV-visible spectrophotometer (Photolab 6600 model). The underlying principle is such that paranitrosalicylate is produced in the presence of nitrates and sodium salicylate.

2.6. Adsorbent characterization

2.6.1. Fourier Transform-Infrared Spectroscopy (FTIR)
The surface functional group was investigated by a Fourier transform infrared (FTIR) spectroscopy with the spectra wavelength considered from 4000 to 500 cm⁻¹ (Table 2). The samples were examined in a similar fashion as done by Battas et al., 2019 in powder form (ATR method).

2.7. Batch equilibrium studies
Batch equilibrium method was carried out to achieve the maximum amount of NO₃⁻ removal, while the effect on the adsorption intake of nitrate onto the MCFs for different parameters such as contact time, pH, the amount of adsorbent, and initial concentration of nitrate was investigated. The adsorption test was conducted in a conical flask with desired adsorbent to adsorbate ratio.
placing 200 mL from the previously prepared stock solutions into beakers and on a thermo-regulated magnetic mixer. The resulting sorbate was filtered and final concentration determined by the method described earlier.

The amount of nitrate adsorbed at equilibrium, \( q_e \) (mg/g) was calculated as

\[
q_e = \frac{C_o - C_e}{M} \times V
\]

where \( C_o \) and \( C_e \) (mg/L) are the liquid-phase concentrations for initial sorbate and equilibrium respectively. \( V \) is the volume of the solution (dm\(^3\)) and \( M \) is the mass of MCFs used.

The efficiency of \( \text{NO}_3^- \) % removal was calculated as follows:

\[
\% \text{ Removal} = \frac{C_o - C_f}{C_o} \times 100
\]

where \( C_o \) is the initial concentration (mg/L) and \( C_f \) is the final concentration (mg/L) of the sorbate.

### 2.8. Effect of initial concentration

Nitrate solution of 200 ml, with known initial concentration (300, 600, 900, 1200 and 1500) mg/L was put in a series of 250 ml Erlenmeyer flasks. 10 g of the MCFs was then added to each flask and placed on the magnetic stirrer with a set rotation speed of 120 rpm. The procedure as described was carried out under a constant temperature of 25°C and pH 8.0.

### 2.9. Effect of pH

pH is important in sorption processes and could influence the properties of the adsorbent as well as the solution's constituent (Alfaro-Cuevas-Villanueva et al., 2014; Battas et al., 2019). This effect was studied by varying the initial pH of solution from 4 to 10. By adding a few drops of 0.1 M NaOH or 0.1 M HCL, the pH was adjusted and recorded using a pH meter. The adsorbent dosage, rotation speed, initial concentration and solution temperature were fixed at 10 g, 120 rpm, 300 mg/l and 22 °C respectively.

### 2.10. Effect of adsorbent dose

The effect of the adsorbent on retaining nitrate ions was studied for varying adsorbent values (5 g, 10 g, 15 g, 20 g and 25 g). The concentration of residual nitrate was measured thereafter.

### 2.11. Adsorption isotherms

This was achieved by fitting the equilibrium data into the adsorption isotherm models namely; Freundlich, Langmuir, Temkin and Sips isotherm models. The appropriateness of the models was compared using the coefficient of determination values \( R^2 \) and normalized standard deviation, \( q_e \). The method used by Ahmad et al. (2014) was adopted in determining isotherm parameters using linear regression.

#### 2.11.1. Freundlich isotherm model

The empirical Freundlich isotherm model, based on sorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites (Mustapha et al., 2019) as shown in Eq. (3)

\[
\ln(q_e) = \ln(K_f) + \frac{1}{n} \ln(C_e)
\]

where \( q_e \) (mg/g) is the uptake at the equilibrium concentration, \( C_e \) (mg/L), \( K_f \) and \( (1/n) \) are the equilibrium concentration, adsorption capacity and adsorption intensity, respectively. The
The experimental value of n is based on the slope while \( K_f \) is given by the intercept from the graph of linear plot of \( \ln q_e \) versus \( \ln C_e \). Figure 4 show equilibrium data were fitted for Freundlich isotherm model.

### 2.11.2. Langmuir isotherm model

The Langmuir adsorption isotherm assumes that a homogeneous monolayer exists at all sorbent surface sites, with the ability of no interaction of adsorbed molecules with the neighboring adsorption sites. The linearized form is given in Eq. (4).

\[
\frac{1}{q_e} = \frac{1}{K_lC_e} + \frac{1}{q_l}
\]  

(4)

where \( q_e \) (mg/g) is the uptake at the equilibrium concentration, \( C_e \) (mg/L), and \( q_l \) (mg/g) is the maximum number of ions required to form a monolayer. The equilibrium data were analyzed using the linearized Langmuir adsorption isotherm as shown in Figure 5. The Langmuir constants, \( K_l \) and monolayer sorption capacity, \( q_m \), were calculated from the slope and intercept of the plot between \( 1/q_e \) and \( 1/C_e \) and are presented in Table 3.

### 2.11.3. Temkin isotherm model

The rate of nitrate ion transport from bulk solution to the surface of adsorbent determines the kinetics of adsorption, which provides an insight into the possible mechanism of adsorption and the reaction pathways (Khan et al., 2015). Temkin suggested that the heat of adsorption of all the molecules in the

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**Table 3. Contrast of adsorption isotherm of nitrate onto MCFs**

| Isotherms | Freundlich | | Langmuir | | Temkin | | Sips |
|-----------|------------|---|-----------|---|---------|---|-------|
|           | \( K_f \)  | \( 1/n \) | \( R^2 \) | \( q_{max} \) | \( R^2 \) | \( K_L \) | \( B \) | \( R^2 \) | \( q_{max} \) | \( R^2 \) |
| HCl treated MCF | 0.25 | 0.51 | 0.8575 | 0 | 10.99 | 0.8616 | 1.48 | 3 | 0.7881 | 1.2 | 22.76 | 0.9638 |

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**Table 4. Kinetic parameters of pseudo-first-order and pseudo-second-order expressions**

| Kinetic model | Pseudo-first order | Pseudo-second order |
|---------------|--------------------|---------------------|
|               | \( K_1 \) | \( q_e \) | \( R^2 \) | \( K_2 \) | \( q_e \) | \( R^2 \) |
| HCL-treated MCFs | 0.004 | 2.224 | 0.6322 | 0.184 | 5.405 | 0.992 |

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**Table 5. Comparative evaluation of removal efficiency and other experimental conditions of different adsorbents for nitrate removal**

| Adsorbent          | Experimental conditions | Isotherm model         | References          |
|--------------------|-------------------------|------------------------|---------------------|
| Activated carbon   | pH 7.0, 480 min, 83%    | Langmuir (\( r = 0.99 \)) | Mazarj et al., 2017 |
| Modified steel slag| pH 4.0, 180 min, 36%    | Freundlich (\( r = 0.98 \)) | Yang et al., 2017   |
| Modified rice husk | pH 7.0, 90 min, 93.40%  | Freundlich (\( r = 0.99 \)) | Katal et al., 2012  |
| Modified cocoa shell| pH 5.6, 180 min, 58%    | Langmuir (\( r = 0.99 \)) | Nkuique et al., 2021|
| Modified Chicken feather | pH 8.0, 480 min, 89.3% | Sips (\( r = 0.96 \)) | This study |
adsorbent layer would decrease linearly with coverage and this governs the adsorbate/adsorbent interactions. The Linear form of Temkin isotherm is given in Eq. (5) as

\[ q_e = B\ln K_T + B\ln C_e \]  \hspace{1cm} (5)

where \( q_e \) (mg/g) is the adsorbent capacity, \( C_e \) (mg/L) is equilibrium concentration of the solution, \( K_T \) is the equilibrium binding constant (L/mol), which corresponds to the maximum binding energy, \( B = \frac{a R}{b} \) is related to the adsorption heat, \( R \) is universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)) and \( T \) is the temperature (K). Plotting \( q_e \) versus \( \ln(C_e) \) permits the determination of constants \( B \) and \( K_T \).

2.11.4. Sips isotherm model

The Sips model is a hybrid of the Langmuir and Freundlich models. Its behavior is similar to that of the Freundlich model at low adsorbate concentrations, and at higher adsorbate concentrations, it predicts monolayer adsorption like the Langmuir isotherm (Foo & Hameed, 2010). The model is useful for predicting the heterogeneous adsorption system and overcomes the drawback associated with Freundlich isotherm model of continuing increase in the adsorbed amount with increase in concentration. Sips equation (Eq. (6)) is similar to the Freundlich equation, but it has a finite limit when the concentration is sufficiently high.

\[ q_e = \frac{K_s C_e \frac{1}{n_s}}{1 + \alpha_s C_e \frac{1}{n_s}} \]  \hspace{1cm} (6)

where \( C_e \) is the equilibrium concentration of the adsorbate, \( q_e \) and \( K_s \) are the Sips equilibrium adsorption capacity and adsorption affinity constant, respectively, while \( n_s \) describes surface heterogeneity index. In its linearized form, it can be expressed as given in Eq. (7):

\[ \frac{1}{n_s} \ln(C_e) = -\ln\left(\frac{K_s}{q_e}\right) + \ln(\alpha_s) \]  \hspace{1cm} (7)

2.12. Adsorption kinetic studies

Adsorption kinetics is a linear relationship describing the rate of retention or release of adsorbate from an aqueous environment to a solid-phase interface under various conditions (Kadhum et al., 2020). The amount of nitrate adsorbed onto the adsorbent (depicts the quantity of fixed nitrate ions per gram of adsorbent) at time \( t \), \( q_t \) (mg/g) is calculated as follows (Eq. (8)):

\[ q_t = \frac{C_0 - C_t}{M} \times V \]  \hspace{1cm} (8)

where \( C_0 \) and \( C_t \) (mg/L) represent the liquid-phase adsorbate concentration at initial and any time, \( t \), \( V \) is the volume of aqueous solution (L) and \( M \) (g), the mass of MCFs used. The pseudo-first-order and second-order models were used to describe adsorption mechanism as suggested by Lagergren (1898).

2.12.1. Pseudo-first-order model

The linearized form of pseudo-first-order model is given by the following Eq. (9)

\[ \log(q_e - q_t) = \log q_e + \frac{K_t}{2.303} t \]  \hspace{1cm} (9)
2.12.2. Pseudo-second-order model

The pseudo-second-order rate model depends on the number of adsorption sites and the number of sorbate ions in the liquid phase. Linearized form of pseudo-second-order kinetic model is given by the following expression (Eq. (10)):

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]  

(10)

where \( q_e \) and \( q_t \) are the amounts of nitrate ions adsorbed onto treated MCFS (mg/g) at equilibrium and at a time, \( t \), respectively. The rate constant, \( K_1 \) and \( K_2 \), are the first and second order rate constant, respectively. The plot of \( \log (q_e - q_t) \) against \( t \), gives a straight line with the slope of \( K_1 \) and \( \log q_e \) as the intercept. The linear plot of \( t/q_t \) versus \( t \) gives \( 1/h \) and \( 1/q_e \) as the intercept and slope, respectively.

3. Results and discussions

3.1. Fourier transform infrared analysis

The Fourier transform infrared (FTIR) spectra aided analysis of the active/functional groups and bands involved in adsorption of nitrate onto the adsorbent. The FTIR spectra of HCl (aq) (treated) MCFS before and after adsorption is presented in Figures 1 and 2, respectively, showed several adsorption bands. As seen in the spectrum band of HCl (aq) (treated) MCFS before adsorption, a broad and intense peak around 3417 cm\(^{-1}\) matches the -OH group. The peak at 2924 cm\(^{-1}\) represents the -CH stretching vibrations. The peaks between 1250 and 1050 cm\(^{-1}\) are assigned to -C-OC Bending and another peak at 1234 cm\(^{-1}\) corresponds to amide N-H stretching (Mondal et al., 2019). A substantial shift from 3417 cm\(^{-1}\) to 3387 cm\(^{-1}\) for the -OH group was noticed. These shifts are attributed to the changes in counter ions associated with carbonyl and hydroxylate anions, suggesting that acidic groups, carboxyl and hydroxyl, are predominant contributor’s in the ion exchange processes (Wahab et al., 2010).

3.2. Effect of initial concentration

A typical experiment to show the initial concentration of nitrate solution was varied from 300 to 1500 mg/L to investigate the effect of initial concentration on adsorption of nitrate as shown in Figure 3. The adsorbent dosage used was 10 g with a contact time of 480 min. The % removal efficiency shows a decreasing trend with an increasing concentration of nitrate from 300 to 1500 mg/L which is in contrast with the adsorption capacity of the sorbent which increased with

![Figure 1. FTIR spectrum of HCl-treated MCFS before adsorption.](image-url)
the increasing concentration. It is perhaps a result of increase in the mass transfer driving force and hence, the rate at which nitrate molecules pass from the bulk solution to the particle surface (Mondal et al., 2015). The maximum adsorption efficiency occurred at 300 mg/L for the MCFs. The experimental data were analyzed by the isotherm models of Freundlich, Langmuir Temkin and Sips isotherm models as shown in Figures 4–7 respectively. The parameters of the Langmuir, Freundlich, Temkin and Sips R-P isotherm models were obtained by the linear plots, summarized in Table 3. The value of the R² of all the isotherm parameters was compared and found that the Sips model has the highest value of R².

The Langmuir adsorption model was employed to describe mono-layer adsorption onto homogeneous adsorption surfaces, where the adsorbent can only take one layer of molecules. Simply put, the adsorbent consists of homogeneous adsorption sites on its surface. At the point of qmax (mg/g) which depicts the maximum adsorption capacity, one layer of adsorbent is saturated by ions. The separation factor (RL) in equation 11 without the dimension is known as adsorption desirability (Dehghani et al., 2019).
Figure 4. Freundlich isotherm plot for nitrate sorption onto HCL-treated MCFs (adsorbent dose: 10.0 g; contact time: 480 min; temperature: 22°C, pH 8).

Figure 5. Langmuir isotherm plot for nitrate sorption onto HCL-treated MCFs (adsorbent dose: 10.0 g; contact time: 480 min; temperature: 22°C, pH 8).

Figure 6. Temkin isotherm plot for nitrate sorption onto HCL-treated MCFs (adsorbent dose: 10.0 g; contact time: 480 min; temperature: 22°C, pH 8).
where $C_0$ is the initial concentration of pollutant (mg/L). If $R_L$ is between 0 and 1, the adsorption is desirable. If $R_L > 1$, the adsorption is undesirable (Dehghani et al., 2019).

The Freundlich model is an experimental model introduced for the heterogeneous adsorption system. The amount of $1/n$ illustrates the adsorption desirability for the Freundlich Isotherm. In the range of $0.1 < n < 1$, the adsorption is desirable, while the $1/n > 1$ shows the lack of adsorption desirability. Third, Temkin isotherm was used for the description of adsorption process where the regression coefficient was not considerable. Comparing the correlation characteristics of the four models as shown in Table 3, the Sips model gives a more precise explanation of the adsorption in this study ($R^2 = 0.9638$) with an order; Sips > Langmuir > Freundlich > Temkin with heterogeneity factor calculated as $(n = 0.48)$, the adsorption is a heterogeneous one.

### 3.3. Effect of pH on sorption
Aqueous phase pH is a significant controlling factor governing the dissociation of active functional sites on the adsorbent. The adsorption of nitrate by MCFs was studied at varying pH values from 4.0 to 10.0 (Figure 8). It is clear that the highest removal efficiency of nitrate occurred at (89.3 %) for a PH value of 8.0. When the initial pH is less than 8, the adsorption removal efficiency of nitrate increases along with the pH increase, as shown in Figure 8 and begins to decrease when the initial pH value is greater. For pH values below 8.0, the decrease in removal efficiency could be caused by dissociation of functional groups on the sorbent (Katal et al., 2012).

#### 3.3.1. Adsorption mechanism
The adsorption mechanism serves to explain the pathway, binding nature and type of reaction taking place during adsorption. Here, we consider the role of surface charge of the bio-sorbent as well as the type of functional group. As seen earlier, the FTIR spectra show the presence of hydroxyl groups as seen in the wider peak before adsorption which becomes a lot sharper after adsorption which may be a result of association between this surface group and nitrate. Electrostatic attraction could be the main mechanism behind nitrate adsorption. In acidic
conditions, the surface of the chicken feather is positively charged which provides conditions for anionic adsorption (Chakraborty et al., 2020b). The point of zero surface charge was not carried out during this study, however, past literature reveals chicken feathers to fall within the range of 7.36 to 7.66 (Chakraborty et al., 2020b; Mondal et al., 2019).

The acidic medium creates conditions necessary for the MCFs surface to undergo protonation reaction, equation 12. This allows a positive charge to be acquired by the adsorbent surface (equation 13). Higher pH values create OH\(^-\) ions which compete with existing nitrate ions for sorption sites. Sorption of excess OH\(^-\) ions could create a negative charge on the surface of the MCFs thus resulting in repulsion of negatively charged nitrate ions, hence, the decrease in adsorption, see, equation 4. The behavior of the adsorbent in this study is similar to the description offered by (Liyun Yang et al., 2017; Zhou et al., 2020) in their study. The mechanism is illustrated in Figure 9.

\[ \text{MCFs} - \text{OH}^- + H^+ \rightarrow \text{MCFs} - \text{OH}_2^+ \] (12)
\[ \text{NO}_3^- + \text{MCFs} \rightarrow \text{OH}_2^- \rightarrow \text{MCFs} - \text{OH} \rightarrow \cdots \rightarrow \text{NO}_3^- \]  
(13)

\[ \text{MCFs} - \text{OH}^- + \text{OH}^- \rightarrow \text{MCFs} - \text{O}^- + \text{H}_2\text{O} \]  
(14)

3.4. **Effect of adsorbent dosage on sorption**

As adsorbent dosage is increased from 5 g/100 mL to 10 g/100 mL, there is also a corresponding increase from 45.8% to 60.5% of its removal efficiency as displayed in Figure 10. This increase can be attributed to a larger surface area leading to more adsorption sites for nitrate uptake. However, as the adsorbent dosage is increased from 10 g/100 mL to 25 g/100 mL, the nitrate removal efficiency decreases gradually to 15.2%. This occurrence may be due to the aggregation of adsorbent particles as dosage is increased leading to failure of adsorption sites (Teimouri et al., 2016).

![Figure 10. The effect of dosage on the removal efficiency of MCFs (contact time: 480 min; volume of solution: 200 mL; initial concentration: 300 mg/L; and temperature: 22°C).](image)

![Figure 11. The effect of contact time on the removal efficiency of MCFs (adsorbent dose: 10 g; volume of solution: 200 mL; initial concentration: 300 mg/L; and temperature: 22°C).](image)
3.5. Adsorption kinetics

3.5.1. Effect of contact time on sorption
The influence of contact time on nitrate removal was studied for a time period of 0 to 1500 min using 300 mg/L nitrate solution at ambient temperature. The adsorption data for the uptake of nitrate versus contact time is presented in Figure 11. The result indicates that with increasing contact time of up to 480 min, a total nitrate uptake (65.3%) occurred in the HCl (aq) (treated) MCFs. The rate of adsorption with respect to residence time showed initial rapid increase till equilibrium time was reached (480 mins) after which there was a decrease. This decline reveals a slow adsorption rate often referred to as desorption owing to the accumulated sorbate ions on the surface of the adsorbent. Considering these results, a contact time of 480 min was chosen with regards to HCl (aq) treated MCFs for further experiments.

3.6. Kinetics
Transformation of adsorption-based processes for various solid phases are usually time dependent (Katal et al., 2012). It is important to comprehend the dynamic interactions of nitrate with MCFs and to predict their fate with time which is why the knowledge of the kinetics of these
processes is important. Pseudo-first-order kinetics model (Figure 12) is based on the assumption that the amount of solid adsorption was applied to the liquid phase adsorption, while the pseudo-second-order kinetic model (Figure 13) was based on the assumption that the adsorption rate was controlled by the chemical adsorption mechanism. The residual nitrate ion was useful in providing adsorption data for the kinetic study (assumption is that there is no mass transfer resistance both internally and externally to the overall adsorption process).

The graph of log (qe - qt) vs. t and t/qt vs. t which represent pseudo-first-order and pseudo-second-order kinetics models respectively were used to obtain the rate parameters. The fit graphs were used in calculating the parameters which govern the kinetic adsorption of nitrate (Table 4). It can be seen that the pseudo-second-order kinetic model was more suitable for simulating the actual adsorption process of nitrate because the model had a high correlation coefficient ($R^2$) while the theoretical $q_e$ of the MCFs were closer to experimental $q_e$. This result bears similar findings to that obtained by (Yang et al., 2017).

3.7. Contribution to knowledge
This work bears its novelty from three reasons; First, the research based on use of chicken feathers as bio-sorbents has hardly been done and literature on this is scarce. Second, modifications to low-cost bio-sorbents have only recently gained traction and little is known about its adsorption mechanisms, although adsorption of heavy metals are been researched, little has taken place in the sphere of bio-sorption and uptake of anions such nitrate and phosphate ions using these materials. Finally, the choice of this chicken feather presents the opportunity to benefit from a cheap bio-sorbent material which is currently regarded as a waste material. Chicken feather fiber when compaed with other sorbent shows potential for the removal of nitrate at favourable conditions (Table 5).

4. Conclusion
This present work was conducted to investigate on an experimental scale, the use of modified chicken feathers, MCFs on the uptake of nitrate ions. The experimental investigations were extremely important for understanding the adsorption mechanism of nitrate ions such as the initial concentration, adsorbent dosage, pH and time. The optimal condition for maximum removal of nitrate from an initial concentration of 300 mg/L was 10 mg/L for adsorbent dosage, pH of 8.0 with a contact time of 480 min. The nitrate adsorption isotherms for HCl (aq) treated MCFs were relatively well fitted and based on the comparison of the regression coefficients, sips isotherm model seemed to be the most suitable model; (Sips > Langmuir > Freundlich > Temkin). Pseudo-second-order equation was adequate to describe adsorption mechanism for the MCFs. In addition, there was observed improved removal efficiency of nitrate with increase in pH of the solution. The result of this study has shown that MCFs could be used as a renewable biosorbent for various pollutants and aqueous solution. It is recommended that additional investigative efforts should be made towards the study of MCFs in relation to uptake of toxic substances and other unwanted pollutants.

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