Original Article

Simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution unto a Nigerian kaolinite clay

Folasegun Anthony Dawodu a, Kovo Godfrey Akpomie a,b,*

a Department of Chemistry (Industrial), University of Ibadan, Ibadan, Nigeria
b Materials and Energy Technology Department, Projects Research and Development Institute (PRODA), Enugu, Nigeria

ARTICLE INFO

Article history:
Received 21 October 2013
Accepted 12 March 2014
Available online 16 April 2014

Keywords:
Adsorption
Ni(II)
Mn(II)
Kaolinite
Kinetics
Isotherms

ABSTRACT

An unmodified Nigerian kaolinite clay (UAK) was utilized as a low-cost adsorbent for the removal of Ni(II) and Mn(II) ions from a binary solution of both metal ions. Batch adsorption methodology was used to evaluate the effect of solution pH, initial metal ion concentration, sorbent dose, particle size, contact time, temperature and ligand on adsorption. FTIR, XRD and SEM analysis were used to characterize the adsorbent. The equilibrium isotherm data were analyzed using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherm model. The Freundlich isotherm model provided the best fit to the experimental data for both metal ions as indicated by the values of the regression coefficient. The Langmuir monolayer maximum adsorption capacities for Ni(II) and Mn(II) ions are 166.67 mg/g and 111.11 mg/g, respectively. The kinetic data were analyzed using the pseudo-first order, pseudo-second order equations, the Elovich equation and intraparticle diffusion rate equation. The Elovich equation gave the best fit to the experimental data for both metal ions. The presence of intraparticle diffusion mechanism was indicated, although it was not the sole rate determining step. Thermodynamic studies indicated an endothermic, spontaneous and a physisorption process between both metal ions and UAK. The results showed that the kaolinite can be utilized as a low-cost adsorbent for the removal of Ni(II) and Mn(II) ions from solution.

© 2014 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. Este é um artigo Open Access sob a licença de CC BY-NC-ND

1. Introduction

The increasing discharge of industrial wastewaters containing heavy metals to the environment has been on the increase as a result of rapid growth of industries. This is a serious problem because heavy metals at high concentrations are toxic to aquatic eco-systems causing harmful effects to living organisms, plants and humans [1]. Manganese is present in ground water as a divalent ion (Mn²⁺) and is considered a pollutant mainly because of its organoleptic properties [2]. High concentrations of nickel in humans can cause health problems...
such as heart and liver damages, skin irritation, headache, dermatitis and nasal cancer [3,4]. Therefore the removal of these metals from industrial wastewaters is required before discharge into receiving waters in order to avoid these complications [5].

Numerous techniques have been utilized for the removal of heavy metals from solution, which include reverse osmosis, ion exchange, precipitation, phyto-extraction, ultra-filtration and adsorption. However, most of these processes are expensive, complicated, ineffective at low metal concentrations and applicable to a wide range of pollutants [6]. The adsorption technique has been found to be one of the most effective for the removal of metal ions from solution [7]. As a result many researchers have reported the use of different materials for adsorption, such as biomass materials [8–19], fertilizer waste [20], tea waste [21], microorganism [22], charcoal [23], yeast [24], sludge ash [25], date pits [26], lateritic minerals [27], red mud [28] and clay [29,30].

Kaolinite clay which is a layered silicate mineral has seldom been used for adsorption of metals because of its low cation exchange capacity and small surface area usually less than 20 m²/g [31]. The use of unmodified and modified kaolinite clay for the removal of heavy metal ions have been reported by some workers [32–35].

Kaolinite clay is abundantly found in Aloji, Ofu local government area, Kogi state Nigeria. As a result of its abundance and easy accessibility, this material can be used as a cheap adsorbent for the removal of heavy metals from solution.

The main objective of this study is the use of kaolinite clay as a low-cost adsorbent for Ni(II) and Mn(II) ions from aqueous solution. This is to minimize the problem of high cost involved in the treatment of industrial wastewaters in Nigeria and most developing nations. The clay was used without chemical modification in order to keep the process cost low. The effect of initial metal ion concentration, solution pH, adsorbent dose, particle size, contact time, temperature and ligands were investigated. Equilibrium, kinetic and thermodynamic parameters were also determined to help provide a better understanding of the sorption process.

2. Materials and methods

2.1. Preparation of metal solution

All the reagents used in this study were of analytical grade, obtained from Sigma–Aldrich and used without further purification. A binary stock solution of concentration 1000 mg/L of Ni(II) and Mn(II) ions was prepared by dissolving appropriate amounts of NiSO₄·6H₂O and MnSO₄·H₂O in double distilled water. The working solutions were prepared by dilution of the stock solution with double distilled water to obtain solutions of concentration 100–500 mg/L. The pH of each of the solution was adjusted to the required value by the addition of 0.1 M NaOH or 0.1 M HCl before the adsorbent was added.

2.2. Adsorbent preparation

Kaolinite clay was collected from Aloji, in Ofu local government area, Kogi state, Nigeria. The kaolinite was dissolved in excess distilled water in a pretreated plastic container with proper stirring to ensure an effective dissolution. Thereafter it was filtered through a 500 μm sieve and the filtrate was allowed to settle for 24 h, after which excess water was decanted and the clay residue was sundried for several days, then dried in an oven at 105 °C for 4 h. The dried clay was pulverized and then passed through different mesh sieves of sizes 100–500 μm to obtain the unmodified Aloji Kaolinite clay (UAK).

2.3. Physicochemical analysis

The chemical analysis of UAK was determined using the Atomic absorption Spectrophotometer (AAS) (Buck scientific model 210VGP) after digestion of the sample with nitric acid. The cation exchange capacity (CEC) was determined by the ammonium acetate method [36], while the specific surface area was determined by the methylene blue absorption test method [37]. The slurry pH was determined by soaking 1 g of UAK in 50 ml distilled water, stirred for 24 h and filtered and the final pH was measured. The pH point of zero charge or pHpzcc was determined based on the method described [38]. The Fourier transform infrared (FT-IR) spectra of kaolinite were recorded with the Fourier transform infrared spectrophotometer (Shimadzu FT-IR 8400s). X-ray diffraction (XRD) analysis was determined using a model MD 10 Randicnon dixamtymeter operating at 25 kV and 20 mA. The scanning regions of the diffraction were 16–72° on the 2θ angle. The morphology of the adsorbent was also analyzed by the scanning electron microscope (SEM) (Hitachi S4800 model), while the pore properties and BET surface area of UAK were assessed via nitrogen adsorption–desorption isotherms using a micromeritics ASAP 2010 model analyzer.

2.4. Adsorption procedure

The adsorption was carried out in 100 ml pretreated plastic bottles at an adsorbent dose of 0.1 g, metal concentration of 100 mg/L, contact time 3 h, adsorbent particle size 100 μm, temperature of 300 K and contact time of 180 min. This was done by contacting 0.1 g of the UAK with 50 ml of the adsorbate. The effect of pH was carried out at pH values of 2–8. The influence of initial metal ion concentration was carried by varying the adsorbate concentration from 100 to 500 mg/L at a pH value of 6.0. Adsorbent dose was varied in the range 0.1–0.5 g to determine its effect. Particle size of UAK was varied from 100 to 500 μm to investigate its influence. The effect of contact time was conducted by varying the contact time from 20 to 300 min. Temperature effect was investigated by varying the adsorption temperature from 300 to 323 K using a thermostat water bath for temperature regulation. The effect of two ligands, citric acid (CA) and ethylenediaminetetracetic acid (EDTA), on the adsorption of Ni(II) and Mn(II) from solution was also determined. The ligands were made to different concentrations of 100 mg/L of CA (0.1–CA), 500 mg/L of CA (0.5–CA), 1000 mg/L of CA (1.0–CA), 100 mg/L of EDTA (0.1–EDTA), 500 mg/L of EDTA (0.5–EDTA) and 1000 mg/L of EDTA (1.0–EDTA), in solutions containing 100 mg/L of the metal ions at a pH 6.0, and the adsorption procedure was then performed. At the end of the given contact time for each experiment, the
solution was filtered and the residual Ni(II) and Mn(II) ions concentrations were determined using the AAS. The amount of metal ions adsorbed in milligram per gram was determined using the mass balance equation:

\[ q_e = \frac{(C_0 - C_e) V}{m} \]  

(1)

where \( q_e \) is the amount of Ni(II) and Mn(II) ions adsorbed onto per unit weight of UAK in mg/g, \( C_0 \) is the initial metal ion concentration in solution in mg/L, \( C_e \) is the equilibrium metal ion concentration in mg/L, \( V \) is the volume of adsorbate in liters and \( m \) is the mass of the adsorbent in g. Also, the percentage removal of metal ions from solution was calculated from the equation:

\[ \% \text{ Removal} = 100 \left( \frac{(C_0 - C_e)}{C_0} \right) \]  

(2)

3. Results and discussions

3.1. Adsorbent characterization

The physicochemical analysis of UAK is presented in Table 1. The mineral analysis of UAK showed that silica and alumina form the major composition while other mineral elements are present in minute amount as impurities [39]. The pH point of zero charge (pHpzc) is necessary to be determined for an adsorbent as it helps provide better understanding of adsorption mechanism. At pH values lower than the pHpzcs, the surface of the adsorbent is positively charged favoring the adsorption of anionic species, while at pH values higher than the pHpzcs, the surface is negatively charged thereby favoring the adsorption of cations. The pHpzcs of UAK was found to be 5.5 and the slurry pH is 4.8 which is slightly close to the pHpzcs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (%)</td>
<td>53.9</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>27.9</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>0.6</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>0.4</td>
</tr>
<tr>
<td>Na₂O (%)</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>0.9</td>
</tr>
<tr>
<td>K₂O (%)</td>
<td>1.2</td>
</tr>
<tr>
<td>TiO₂ (%)</td>
<td>0.2</td>
</tr>
<tr>
<td>MnO (%)</td>
<td>0.1</td>
</tr>
<tr>
<td>LOI (%)</td>
<td>15.0</td>
</tr>
<tr>
<td>SSA (m²/g)</td>
<td>19.8</td>
</tr>
<tr>
<td>S BET (m²/g)</td>
<td>13.41</td>
</tr>
<tr>
<td>TPV (cm³/g)</td>
<td>0.0037</td>
</tr>
<tr>
<td>APD (Å)</td>
<td>11.04</td>
</tr>
<tr>
<td>pHpzc</td>
<td>5.5</td>
</tr>
<tr>
<td>Slurry pH</td>
<td>4.8</td>
</tr>
<tr>
<td>ECEC (Meq/100 g)</td>
<td>11.26</td>
</tr>
</tbody>
</table>

Table 1 – Physicochemical characterization of UAK.

is composed of various functional groups which are responsible for binding of the cations. The bands at 3695.73 cm⁻¹ and 3620.51 cm⁻¹ correspond to the inner –OH stretching vibration, while that at 3423.76 cm⁻¹ represents the outer surface –OH stretching vibration. Absorption bands at 1629.9 cm⁻¹, 1543.1 cm⁻¹, 1508.38 cm⁻¹ and 1458.23 cm⁻¹ represent the OH bending vibration of water and can also be assigned to the symmetric –COO⁻ stretching vibration [40]. The presence of the outer surface –OH and the symmetric –COO⁻ vibration might suggest the presence of smectite in the kaolinite [41]. Si–O bending vibration was observed at 1114.89 cm⁻¹, 1101.39 cm⁻¹, 1031.95 cm⁻¹ and 1008.8 cm⁻¹, while the stretching vibration was observed at 694.4 cm⁻¹ and 796.63 cm⁻¹. Absorption bands at 914.29 cm⁻¹ and 937.44 cm⁻¹ correspond to the Al–O bending vibration and peak intensities recorded at 540.09 cm⁻¹, 466.79 cm⁻¹ and 432.07 cm⁻¹ are due to Al–O–Si skeletal vibrations [42,43].

After the adsorption of metal ions from the laboratory prepared solution, there was a shift in the –OH stretching from 3423.76 cm⁻¹ to 3446.91 cm⁻¹ and the disappearance of the band at 2000.25 cm⁻¹ assigned to the –OH stretching vibration. Similarly, a shift in the –OH bending from (1629.9–1624.12 cm⁻¹, 1543.1–1541.18 cm⁻¹ and 1458.23–1384.94 cm⁻¹) clearly indicated the involvement of the –OH group as an active site for binding of positively charged cations. A shift in Si–O bending vibration from 1031.95 cm⁻¹ to 1033.88 cm⁻¹ and the disappearance of the band at 1101.39 cm⁻¹ were observed. Also, the Al–O–Si skeletal vibration at 432.07 cm⁻¹, 466.79 cm⁻¹ and 540.09 cm⁻¹ encountered a shift in absorptions to 430.14 cm⁻¹, 470.65 cm⁻¹ and 538.16 cm⁻¹, respectively. These shifts in absorptions showed the use of the Si–O and Al–O–Si groups in the adsorption of metal ions from solution.

The XRD spectrum of UAK in Fig. 3 gives information about the changes in the crystal line and amorphous or crystalline nature of the adsorbent. The sharp and intense peak at 2θ (24.86) and the presence of other weak peaks in the spectra indicates the amorphous nature of UAK [44]. The amorphous nature of the adsorbent suggests that Ni(II) and Mn(II) ions can easily penetrate the surface which is desirable for an effective removal [45].

The BET nitrogen adsorption–desorption analysis of UAK showed a BET surface area (SBET) of 13.41 m²/g, with a total pore volume (TPV) and average pore diameter (APD) of 0.0037 cm³/g and 11.04 Å, respectively. SBET assumes to measure the surface area in micropores within pore sizes of the adsorbent [46]. Also, the specific surface area (SSA) which is the accessible area of adsorbent surface per unit mass of material was calculated as 19.8 m²/g, from the methylene blue absorption test method. Both surface areas obtained were less than 20 m²/g, which is the range recorded by most kaolinite minerals [31]. SEM analysis is another important tool used in the determination of the surface morphology of an adsorbent. The SEM image of UAK is shown in Fig. 4. The irregular and porous surface structure, which is a requirement for a potential adsorbent, is clearly seen in the image. The porous structure indicates that physical adsorption plays a major role in the removal of metal ions from solution [47].
3.2. Influence of initial solution pH

The initial pH of solution is one of the most important factors in the adsorption of metal ions unto adsorbents as it affects the surface charge of the adsorbent and the degree of ionization and specification of the adsorbate [48]. The effect of pH on the simultaneous removal of Ni(II) and Mn(II) unto UAK is shown in Fig. 5. It was observed that low adsorption was obtained for both metal ions at pH values 2–4 after which a sharp increase in adsorption at pH 5 was recorded; this is a pH value close to the pHpzc at which the surface of the adsorbent becomes negative favoring the adsorption of the
positively charged cations. From pH 6 to 8 a negligible increase in adsorption was recorded. The pH value of 6.0 was chosen in this study for all subsequent experiments because optimum adsorption was recorded and metal precipitation associated with higher pH values was avoided [49]. As expected, the adsorption decreased at lower pH values because the aluminol and silanol groups (active sites) are more protonated and are less available to retain the studied metal ions [50,51]. At higher pH values, fewer protons are available to compete with the metal ions in solution for the active sites on UAK leading to the increase in adsorption recorded. Also, comparing the adsorption of the two metal ions, it was observed that at lower pH values 2–4, Mn(II) ions were adsorbed more than Ni(II).
but a reverse trend was noted at higher pH values of 5–8. This implies that at pH values lower than the pHzc, UAK has a higher affinity for Mn(II) ions compared to Ni(II) ions. However, as the surface of the adsorbent becomes negatively charged, the active sites showed a greater affinity for Ni(II) ions.

3.3. Effect of initial metal ion concentration

The adsorption rate of metal ions onto adsorbents is a function of the initial concentration of the metal ions which makes it an important factor to be determined for an effective sorption. The effect of initial metal ion concentration on the adsorption of Ni(II) and Mn(II) ions unto UAK is shown in Fig. 6. It was observed that the percentage removal for both metal ions decreased with increase in the initial concentration of metal ions from 100 to 300 mg/L after which it became fairly stable. The decrease in adsorption is due to the fact that all adsorbents have a fixed number of active sites and at higher concentrations the active sites become saturated [52]. On the other hand, an increase in the adsorption capacity for both metal ions with increase in initial metal ion concentration was observed as presented in Fig. 7. This is a result of the increasing concentration gradient which acts like a driving force to overcome the resistance to mass transfer of the metal ions between the adsorbate and adsorbent species [53].

3.4. Adsorption isotherm

Adsorption isotherm expresses the relationship between the amount of adsorbate removed from the liquid phase by unit mass of adsorbent at a constant temperature. Adsorption isotherms are basic requirements for the design of adsorption systems. A precise mathematical description of equilibrium adsorption capacity is very important for reliable prediction of adsorption parameters and quantitative comparison of adsorption behavior for different adsorbent systems. The parameters of equilibrium isotherms often give useful information on sorption mechanism, surface properties and affinity of the adsorbent. It is therefore important to determine the most suitable correlation of equilibrium curves in order to optimize the conditions for designing adsorption systems [54]. In this study, the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms were tested to analyze the equilibrium data, and the results are shown in Table 2.

The Langmuir isotherm is used to describe adsorption phenomena and is based on the assumption that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. The linear form of the Langmuir isotherm equation can be expressed as [55]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$  

(3)

where $q_e$ is the monolayer adsorption capacity of the adsorbent (mg/g), $K_L$ is the Langmuir adsorption constant (L/mg) related to the energy of adsorption, which quantitatively

![Fig. 6 - The effect of initial metal ion concentration on the percentage removal of Ni(II) and Mn(II) ions from solution unto UAK. pH 6.0, adsorbent dose 0.1 g, temperature 300 K, particle size 100 μm, and contact time 180 min.](image)

![Fig. 7 - The effect of initial metal ion concentration on the adsorption uptake capacity of UAK for Ni(II) and Mn(II) ions from solution. pH 6.0, adsorbent dose 0.1 g, temperature 300 K, particle size 100 μm, and contact time 180 min.](image)

| Table 2 – A comparison of the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm constants for the adsorption of Ni(II) and Mn(II) ions unto UAK. |
|-----------------|-------|-------|
| Isotherm models  | Ni(II) | Mn(II) |
| Langmuir model  | $q_m$ (mg/g) | 166.67 | 111.11 |
|                 | $K_L$ (L/mg) | 0.004 | 0.004 |
|                 | $R^2$ | 0.515 | 0.621 |
| Freundlich model| $K_f$ (mg/g) (mg/L)$^n$ | 22.13 | 3.61 |
|                 | $n$ | 7.75 | 2.07 |
|                 | $R^2$ | 0.993 | 0.836 |
| Temkin model    | $B$ (mg/g) | 28.44 | 21.17 |
|                 | $A$ (L/g) | 0.054 | 0.053 |
|                 | $R^2$ | 0.684 | 0.700 |
| Dubinin–Radushkevich model | $q_m$ (mg/g) | 65.63 | 51.73 |
|                 | $\beta$ (mol$^2$/kJ$^2$) | 0.0001 | 0.0001 |
|                 | $R^2$ | 0.541 | 0.549 |
reflects the affinity between the adsorbent and adsorbate, and \( q_e \) is the maximum monolayer adsorption capacity of adsorbent (mg/g). The constants \( q_L \) and \( K_L \) can be determined from the slope and the intercept of the linear plot of \( Ce/qe \) against \( Ce \).

From Table 2, the correlation coefficient (\( R^2 \)) of both metal ions are very low, 0.515 and 0.621, indicating a poor fit of the monolayer Langmuir isotherm to the adsorption of Ni(II) and Mn(II) by UAK. The monolayer adsorption capacity for Ni(II) and Mn(II) removal by UAK are 166.67 mg/g and 111.11 mg/g, respectively.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (\( R_L \)) defined by the relationship [56]:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

where \( C_0 \) is the initial metal ion concentration in (mg/L) and \( K_L \) is the Langmuir equilibrium constant (L/mg). The value of the separation factor provides important information about the nature of the adsorption process. The adsorption is said to be irreversible (\( R_L = 0 \)), favorable (\( 0 < R_L < 1 \)), linear (\( R_L = 1 \)) or unfavorable (\( R_L > 1 \)). For the initial metal concentration from 100 to 500 mg/L for both metal ions used in this study, the values of \( R_L \) ranged from 0.71 to 0.33; this indicates a favorable adsorption of Ni(II) and Mn(II) ions unto UAK.

The Freundlich isotherm model is applied to non-ideal sorption on heterogeneous surfaces and the linear form of the equation is given as [57]:

\[
\log qe = \log K_f + \frac{1}{n} \log Ce
\]

where \( K_f \) (mg/g) (mg/L)^{1/n} and \( n \) are Freundlich adsorption constants related to the adsorption capacity and intensity of the adsorbents respectively. The constants were determined by the linear plot of \( \log qe \) versus \( \log Ce \).

As can be seen from Table 2, the values of the correlation coefficient (\( R^2 \)) is 0.993 for Ni(II) and 0.836 for Mn(II). Thus the Freundlich isotherm gave a better fit to the data than the Langmuir isotherm model for both metal ions. Furthermore, if the value of \( n \) lies between 1 and 10, it indicates a favorable adsorption [58]. The value of \( n \) obtained is 7.75 and 2.07 for Ni(II) and Mn(II) ions respectively, indicating a favorable adsorption process.

The Temkin isotherm model unlike the Langmuir and Freundlich isotherms takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [59]. The linear form of the Temkin isotherm model is expressed [60]:

\[
qe = B \ln A + B \ln Ce
\]

where \( B = RT/b_f \), \( T \) is the temperature (K), \( R \) is the ideal gas constant (8.314 J/mol K) and \( A \) and \( b_f \) are constants. The constant \( B \) is related to the heat of adsorption and \( A \) is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. The plot of \( qe \) versus \( \ln Ce \) enables the determination of \( A \) and \( B \). The values of the regression coefficient (\( R^2 \)) of 0.684 for Ni(II) and 0.70 for Mn(II) are lower than that of the Freundlich isotherm model, although better than the Langmuir isotherm. Therefore the adsorption of both metal ions unto UAK does not fit the Temkin isotherm as well as the Freundlich isotherm does.

The Dubinin–Radushkevich (D–R) isotherm model which does not assume a homogenous surface or a constant adsorption potential as the Langmuir model was also applied in the analysis of the experimental data. The linear form of the D–R isotherm model is written as [61]:

\[
\ln qe = \ln qm - \beta \varepsilon^2
\]

where \( \beta \) is the coefficient related to the mean free energy of adsorption per mol of the adsorbate (mol^2/2), \( qm \) is the theoretical saturation capacity (mg/g) and \( \varepsilon \) is the Polanyi potential expressed as:

\[
\varepsilon = RT \ln \left( 1 + \frac{1}{Ce} \right)
\]

where \( R \) (J/mol K) is the gas constant and \( T \) (K) is the absolute temperature. The D–R constants \( qm \) and \( \beta \) were calculated from the linear plot of \( \ln qe \) versus \( \varepsilon^2 \) and are shown in Table 2. From linear regression, the \( R^2 \) values of 0.541 and 0.549 for Ni(II) and Mn(II) ions, respectively, are also lower than the Freundlich values. Therefore among the four isotherms tested the Freundlich isotherm gave the best fit to the experimental data.

3.5. Influence of adsorbent dose

The effect of adsorbent dose on the percentage removal of both metal ions from solution is shown in Fig. 8. It was observed that as the weight of UAK increased from 0.1 to 0.5 g a corresponding increase in the percentage removal was obtained for both metal ions. This is mainly due to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the adsorbent with increase in
adsorbent dose [62]. However, a reverse trend was observed as presented in Fig. 9, where a decrease in the adsorption capacity with increase in adsorbent dose was recorded. This may be as a result of a decrease in the total adsorption surface area available for metal ions to bind due to overlapping or aggregation of adsorption sites [63]. Therefore, as the adsorbent dose increased, the amount of metal ions adsorbed unto a unit mass of UAK decreased, resulting in the decrease in the adsorption capacity. However, the maximum adsorption capacity of an adsorbent can be determined from column experiments by the use of excess amount of the adsorbate [64].

3.6. Effect of particle size

The effect of varying the adsorbent particle size on the adsorption of both metal ions unto UAK is shown in Fig. 10. A higher percentage removal was observed for smaller particles but as the particle size increased from 100 to 500 μm, a decrease in the percentage removal was recorded. This is probably due to the increase in the total surface area which provided more active sites for adsorption of the metal ions at smaller particle sizes [23,63,65]. The breaking of large particles helps to open up more sites and channels on the surface of the adsorbent resulting in more accessibility for metal ions due to better diffusion [66]. The particle size of 100 μm was maintained in all the experiments in this study as maximum removal of both metal ions was achieved at this particle size.

3.7. Effect of contact time

The effect of contact time on the percentage removal of Ni(II) and Mn(II) ions unto UAK is presented in Fig. 11. It is observed that the rate of removal of both metal ions from solution was initially rapid and then diminished gradually until an equilibrium time beyond which there was no significant increase in the removal rate. Equilibrium removal was achieved around 120 min and increased slightly up to 180 min for both metal ions. However, further increase in contact time (up to 300 min) recorded a slight decrease in the percentage removal. Hence, a contact time of 180 min was chosen to ensure optimum removal of metal ions. The initial fast adsorption rate is due to the availability of abundant active sites on the surface of UAK. The sorption rapidly occurs and is normally controlled by the diffusion process from the bulk of the solution to the adsorbent surface [53]. The slow uptake in the later stages is probably due to an attachment controlled process caused by less available active sites for sorption, while the slight decrease in percentage removal with further increase in contact time at 300 min may be due to the saturation of the surface of UAK with metal ions followed by the subsequent adsorption and desorption processes [67].

3.8. Kinetic studies

Adsorption kinetic models were applied to the experimental data in order to analyze the rate of adsorption and possible...
adsorption mechanism of Ni(II) and Mn(II) ions unto UAK. The kinetic models applied in this study are the Lagergren first order, pseudo-second order, Elovich equation and the intraparticle diffusion equation.

The pseudo-first order kinetic model also known as the Lagergren equation is expressed as [68]:

$$\log(qe - qt) = \log(qe) - \left( \frac{Kt}{2.303} \right)$$  \hspace{1cm} (9)

where $qt$ and $qe$ are the amounts of metal ions adsorbed at time t and at equilibrium in (mg/g), respectively. $K_t$ is the pseudo-first order adsorption rate constant (min$^{-1}$). The slope and intercept of the plots of $\log(qe - qt)$ versus t were used to determine the rate constant ($K_t$) and $qe$, and the values are recorded in Table 3. From Table 3, it is seen that the pseudo-first order equation provided a good fit to the experimental data of both metal ions. This is indicated by the high values of their linear regression ($R^2$) close to 1. However, the values of $qe_{cal}$ were higher than the experimental values obtained.

The pseudo-second order kinetic model is based on the assumption that chemisorptions is the rate determining step and is given as [69]:

$$\frac{t}{qt} = \frac{1}{K_e q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (10)

where $K_e$ is the equilibrium rate constant of pseudo-second order adsorption (g/mg min). The values of $qe$ and $K_e$ were calculated from the slope and intercept of the linear plot of $t/qt$ against t and the values are recorded in Table 3. The initial sorption rate, h (mg/g min), was also calculated from the equation:

$$h = K_e q_e^2$$  \hspace{1cm} (11)

The pseudo-second order model did not provide a good fit to the experimental data as can be seen from the low regression ($R^2$) values of 0.536 and 0.010 for Ni(II) and Mn(II) ions, respectively. Although the pseudo-second order model have been found to provide the best fit to most adsorption studies [7,53,70]. This model was not found applicable in the description of the sorption of Ni(II) and Mn(II) ions unto UAK.

The adsorption data was also analyzed using the Elovich equation. The Elovich equation was first developed to describe the kinetics of chemisorptions of gas unto solids [71]. The linear form of the Elovich equation is presented:

$$qt = \left[ \frac{1}{\beta} \right] \ln(\alpha \beta) + \left[ \frac{1}{\beta} \right] \ln t$$  \hspace{1cm} (12)

where $\alpha$ is the initial sorption rate constant (mg/g min) and the parameter $\beta$ is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg). The constants $\alpha$ and $\beta$ were obtained from the slope and intercept of the linear plot of $qt$ versus ln t and the values are presented in Table 3. From Table 3, the correlation coefficient of both Ni(II) and Mn(II) ions are also very high, close to 1, and better than that of the pseudo-first order model, indicating a good fit of the Elovich equation to the adsorption of the ions unto UAK.

The kinetic data were also analyzed by the Weber and Morris intraparticle diffusion model to elucidate the diffusion mechanism. The initial rate of the intraparticle diffusion is expressed as [72]:

$$qt = K_d t^{1/2} + l$$  \hspace{1cm} (13)

where $K_d$ is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and l is the intercept. The intercept of the plot indicated the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate controlling step. The constant $K_d$ was obtained from the slope of the plot of $qt$ versus $t^{1/2}$. Intraparticle diffusion is the sole rate-determining step if the plot is linear and passes through the origin. From Table 3, as indicated by the higher regression coefficient ($R^2$) for both metal ions and also the presence of the intercept (l), it shows that the plots did not pass through the origin but were close to it. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the adsorption process [53]. The good regression of both metal ions (close to 1) showed the existence of intraparticle diffusion mechanism on the sorption of Ni(II) and Mn(II) ions unto UAK. Moreover, the presence of the boundary layer effect (l) showed the existence of the surface sorption indicating that intraparticle diffusion was not the only rate-limiting step.

3.9. Effect of ligand

Most effluents from industries also contain organic contaminants apart from heavy metals and so it is important to examine the adsorption of heavy metals in the presence of organic ligands. The effect of the presence of two ligands, EDTA and citric acid (CA) having high and low complexation constants respectively on the adsorption of Ni(II) and Mn(II) ions unto UAK were investigated. The concentration of these ligands were chosen to be the same (0.1-EDTA and 0.1-CA), higher (0.5-EDTA and 0.5-CA) and in excess
adsorption minimizes the formation of hydroxo-species associated with higher pH values.

The result is shown in Fig. 12, where WTL signifies the absence of ligand. A decrease in the adsorption of both metal ions with increase in concentration of the two ligands was obtained. This is probably due to the formation of Me-ligand complexes at higher ligand concentration. Furthermore, the adsorption of both metal ions were lower in the presence of EDTA than CA, except at a low concentration of EDTA (0.1-EDTA), in which a slightly higher adsorption was obtained when compared to CA (1.0-CA). The reason for lower adsorption of metals in the presence of EDTA is due to the high complexation constant of the ligand which forms larger sizes of Me-ligand complexes thereby hindering their introduction into the interlayer of UAK [73]. On the other hand, CA has a smaller complexation constant and probably forms smaller complexes with the metal ions for easy adsorption into the clay layers [73]. Furthermore, it was observed that the percentage removal of Mn(II) ions became higher than that of Ni(II) ions in the presence of CA and EDTA; this is because Ni(II) forms larger complexes with both ligands due to higher complexation constants than Mn(II) ions.

### 3.10. Adsorption thermodynamics

The result on the effect of temperature on the simultaneous adsorption of Ni(II) and Mn(II) ions unto UAK is presented in Fig. 13. From the graph, a slight increase in adsorption of both metal ions with increase in solution temperature from 300 to 323 K was obtained. This shows that the process is endothermic in nature. The increase in percentage removal of metal ions at higher temperature may be due to a greater kinetic energy acquired by the metal ions with temperature increase resulting in an easier diffusion from the bulk solution unto the surface of UAK.

The standard free energy (ΔG0), enthalpy change (ΔH0) and entropy change (ΔS0) thermodynamic parameters were determined to evaluate the feasibility of the adsorption process [74]. The standard free energy of the adsorption is related to the thermodynamic equilibrium constant (Kc) by the following equation:

\[
\Delta G = -RT \ln Kc
\]  
where T is the temperature (K), R is the ideal gas constant (8.314 J/mol K) and Kc is defined by the equation:

\[
Kc = \frac{Ca}{Ce}
\]

where Ca is the metal ion concentration adsorbed from solution at equilibrium (mg/L) and Ce is the equilibrium metal ion concentration in solution (mg/L). Also, the Gibb's free energy is related to the enthalpy change (ΔH0) and entropy change (ΔS0) at a constant temperature by the Van’t Hoff [7] equation:

\[
\ln Kc = -\left( \frac{\Delta G0}{RT} \right) = -\left( \frac{\Delta H0}{RT} \right) + \left( \frac{\Delta S0}{R} \right)
\]

The values of ΔH0 and ΔS0 were calculated from the slope and intercept of the plot (ln Kc versus 1/T) and the calculated thermodynamic parameter values are presented in Table 4.

The values of ΔH0 obtained for both metal ions are positive, indicating the endothermic nature of the adsorption process, which explains the fact that adsorption efficiency increased with increase in temperature. Positive values of ΔS0 also indicated an increase in randomness at the solid/liquid interface during the sorption process while low values of ΔS0 indicated that no remarkable change on entropy occurred. It is clear that the reaction is spontaneous in nature as negative values of ΔG0 were obtained at all temperatures studied. It was also observed that the change in ΔG0 increased with increase in
temperature which indicates an increase in the spontaneity of the process with temperature.

The magnitude of the enthalpy change ($\Delta H^\circ$) provides information about the type of sorption. The heat evolved during physisorption generally lies in the range of 2.1–20.9 kJ/mol, while the heat of chemisorptions generally falls in the range of 80–200 kJ/mol [74]. From Table 4, the values of $\Delta H^\circ$ for Ni(II) and Mn(II) ions are 15.13 and 14.17 kJ/mol, respectively. This indicates that the adsorption of Ni(II) and Mn(II) ions unto UAK may be attributed to a physical adsorption process. This may be one of the reasons why the data did not fit the pseudo-second equation, since the pseudo-second order equation depicts a chemisorptions mechanism. This low energy is desirable, as physisorption processes usually require a low energy barrier to be overcome by metals ions for binding onto the surface of UAK and also enhances easy desorption of the metal ions from the surface, when regeneration of the adsorbent is required.

### 4. Conclusions

Natural kaolinite clay of Nigerian origin was successfully utilized as a low-cost adsorbent for the simultaneous removal of Ni(II) and Mn(II) ions from aqueous solution by batch adsorption method. The adsorption process was found to be dependent on many factors such as the solution pH, initial concentration of metal ions, contact time, adsorbent dose, adsorbent particle size, the presence of ligands such as EDTA and citric acid (CA) and also temperature. The adsorption of Ni(II) ions by UAK was found to be higher than that obtained for Mn(II) ions. The percentage removal of both metal ions decreased with increase in initial metal ion concentration but showed a slight increase at a higher concentration of 500 mg/L. However, there was a steady increase in the adsorption capacity. Optimum removal of both metal ions was obtained at a pH of 6.0, contact time of 180 min and an adsorbent particle size of 100 µm. The presence of EDTA and CA ligands in the solution decreased the percentage removal of both metal ions. The presence of EDTA decreased the adsorption of the metals when compared to CA, probably due to its high complexation constant relative to that of CA. The equilibrium data were tested using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherm model and the best fit was obtained with the Freundlich model. Kinetic parameters were also analyzed using the Lagergren pseudo-first order, pseudo-second order, Elovich equation and intraparticle diffusion rate equation. The Elovich equation provided the best fit to the experimental data and the result also indicated the presence of intraparticle diffusion on the sorption of both metal ions, although it was not the sole rate determining step. Thermodynamic analysis showed that the process was spontaneous and endothermic in nature. The value of the enthalpy change $\Delta H^\circ$ indicated a physisorption mechanism for both metal ions unto the adsorbent. The Langmuir and Freundlich isotherms showed a favorable adsorption process between the adsorbent and metal ions in solution. Furthermore, the high adsorption capacity of 166.67 mg/g and 111.11 mg/g obtained from the Langmuir isotherm for Ni(II) and Mn(II) ions, respectively, suggests that unmodified Aloji Kaolinite clay can be used as a low cost adsorbent for the removal of the metal ions from solution.

### Conflicts of interest

The authors declare no conflicts of interests.

### References


andnickelfromaqueoussolutionusingrawricedust.


Lawal OS, Sanni IA, Ajayi IA, Rabiu OO. Equilibrium, thermodynamics and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of Calophyllum inophyllum. J Hazard Mater 2010;177:829–35.


