Mechanism on the sorption of heavy metals from binary-solution by a low cost montmorillonite and its desorption potential

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Abstract The potential of a low-cost Nigerian montmorillonite for the adsorption of Ni(II) and Mn(II) ions from aqueous solution was investigated by batch mode. XRD, SEM and BET analysis were used to characterize the adsorbent. The experiments were performed as a function of pH, particle size, adsorbent dose, initial metal ion concentration, contact time, ligands and temperature. The process was found to be dependent on all the parameters investigated, with a pH of 6.0 obtained for optimum removal of both metal ions. The Langmuir monolayer adsorption capacity of 166.67 and 142.86 mg/g was obtained for Ni(II) and Mn(II) ions respectively. The Freundlich isotherm gave the best fit to the experimental data than the Langmuir, Temkin and Dubinin–Radushkevich isotherms. The scatchard plot analysis indicated the existence of more than one type of active site on the montmorillonite which corroborates the good fit of the Freundlich model. The pseudo-first order, pseudo-second order and intraparticle diffusion models were applied to the kinetic data. The best fit was achieved with the pseudo-first order model and the existence of intraparticle diffusion mechanism was indicated. Thermodynamic studies showed an endothermic, dissociative, spontaneous and a physical adsorption process between the metal ions and the montmorillonite. Desorption studies revealed over 90% desorption of both metal ions from the metal loaded adsorbent.

1. Introduction

Metals and their compounds are indispensible to the industrial, technological and agricultural development of any nation. As a result, the number of applications of metals for commercial use continues to grow with the development in modern science and technology. Heavy metals discharge from industrial effluent of different industries has become a serious
environmental problem. This is because these heavy metals pose a serious threat to public health due to their toxicity, bioaccumulation in the food chain and persistence in nature [1]. Although many heavy metals are necessary in small amounts for the normal development of the biological cycles, most of them become toxic at high concentrations [2]. It has been estimated that the toxicity due to metallic discharge annually into the environment far exceeds the combined total toxicity of all radioactive and organic wastes as measured by the quantity of waste required to dilute such waste to the drinking water standard [3]. Many countries have established strict regulations for controlling the release of heavy metals into the environment. Nickel that causes gastrointestinal irritation and lung cancer is often obtained from Ni/Fe storage batteries and is also used to produce ferrous steel cutlery [4]. Manganese is usually present in groundwater as a divalent ion and is considered a pollutant mainly because of its organoleptic properties [5]. It is present in effluents from many industries such as glass, ceramics, paint and varnish, ink and dyes, match and firework and in metal galvanization plant effluents [6]. Due to the magnitude of the problem of heavy metal pollution, several techniques have been developed for their removal from aqueous solution such as chemical precipitation, electrochemical treatment, evaporation, ion-exchange, filtration, oxidation/reduction, solvent extraction, membrane technologies and adsorption [7]. However, most of these techniques have the disadvantages of high cost, low efficiency, second contamination and inapplicability to a wide range of pollutants [7]. Adsorption has been found to be superior to other techniques for water treatment in terms of initial cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants and does not result in the formation of harmful substances like most processes [8]. However, many heavy metals adsorption studies have focused on the use of activated carbon due to its very good adsorption properties [9]. However, it is quite expensive with relatively high operating cost. Hence, there is a growing demand to utilize alternative low-cost adsorbents for the removal of heavy metals. Several researchers have utilized various low-cost adsorbents for the removal of heavy metals from solution such as biomass materials [10–12], sawdust [13], slag [14], zeolite [15], fly ash [16], soil [17] and clay [18]. Montmorillonite clay has also been found to be effective for the removal of heavy metals from solution by many researchers [19–22] due to their high specific surface areas, low cost and ubiquitous presence in most soils [23]. Montmorillonite is capable of adsorbing heavy metals via two different mechanisms that include cation exchange in the interlayer resulting from the interactions between ions and negative permanent charge and secondly, the formation of inner-sphere complexes through Si–O\(^{-}\) and Al–O\(^{-}\) groups at the clay particle edges [19,22,24].

In this study, a montmorillonite clay of Nigerian origin was utilized to investigate its potential as a low cost adsorbent for the simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution. The montmorillonite was utilized as a cheap alternative adsorbent because it is present in an abundant amount in Ugwuoba, Oji river local government area, Enugu, Nigeria; the clay is very cheap and easily accessible. This study further considers, the equilibrium isotherm, kinetic, thermodynamic and desorption mechanism of the adsorption process.

2. Experimental

2.1. Adsorbate and adsorbent preparation

Analytical grade of NiSO\(_4\)·6H\(_2\)O and MnSO\(_4\)·H\(_2\)O was obtained from Sigma Aldrich and used in this study without further purification. A binary stock solution of 1000 mg/L containing Ni(II) and Mn(II) ions was prepared by dissolving appropriate amount of their respective salts in 11 of double distilled water. From the stock solution, several working concentrations of 100–500 mg/L were prepared by appropriate dilution. By the use of a pH meter, the pH of each of the solution was adjusted to values of 2.0–8.0 by the dropwise addition of 0.1 M NaOH or 0.1 M HCl when required. The montmorillonite was obtained from Ugwuoba, Oji river local government area of Enugu state, Nigeria. After collection, it was dissolved in excess distilled water in a pretreated plastic container and stirred properly to ensure uniform dissolution. The suspension was then passed through a 500 µm mesh sieve in order to get rid of large unwanted materials. The filtrate was left for 24 h to settle and then excess water was decanted. The residue was sun dried for several days and then dried in an oven at 105 °C for 4 h. The completely dried clay was then pulverized and passed through mesh sieves of sizes 100–500 µm to obtain the unmodified Ugwuoba montmorillonite clay (UUC).

2.2. Physicochemical characterization

The chemical composition of UUC was determined by the use of the Atomic Absorption Spectrophotometer (AAS) (Buck Scientific Model 210VGP) after digestion of the samples with nitric acid. The ammonium acetate method was used to determine the Cation Exchange Capacity (CEC) [25]. The pH point of zero charge was determined by the method described by Onyango et al. [26]. The slurry pH of UUC was obtained by soaking 1 g of the adsorbent in 50 ml of distilled water and stirred for 24 h, after which it was filtered and the pH of the filtrate was determined by the use of a pH meter. The Fourier transform infrared (FTIR) spectrum of UUC was taken by the use of the Fourier Transform Infrared Spectrophotometer (Shimadzu FTIR 8400s). XRD analysis of the adsorbent was carried out by the use of the X-ray diffractometer (Randicon MD 10 model). By the application of the BET adsorption–desorption isotherm, the pore properties and BET surface area were accessed using the micrometric ASAP 2010 model analyzer. The morphology of the adsorbent was taken by the use of the scanning electron microscope (SEM) (Hitachi S4800 model).

2.3. Adsorbent experiment

Batch adsorption procedure was used to determine the effect of various operating conditions on the adsorption process. This was performed by the addition of 0.1 g of UUC to 50 ml of the binary metal solution in a pretreated 100 ml plastic container at a room temperature of 300 K. The containers were placed in a thermostat water bath for temperature regulation when the effect of temperature on adsorption was determined. The effect of pH (2.0–8.0), adsorbent
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**3. Results and discussion**

### 3.1. Characterization of UUC

The result for the physicochemical characterization of UUC showed the following: SiO$_2$ (47.32%), Al$_2$O$_3$ (25.91%), Fe$_2$O$_3$ (2.14%), CaO (3.39%), K$_2$O (1.07%), Na$_2$O (2.86%), MgO (3.14%), TiO$_2$ (0.05–1.0 M), MnO (0.0688 cm$^2$/g), an average pore diameter (APD) of 49.35 Å and total pore volume (TPV) of 0.0688 cm$^3$/g. The $S_{BET}$ of UUC is close to that (61 m$^2$/g) obtained by Macht et al. [28] for montmorillonites.

The FTIR analysis was utilized to determine the functional groups on the surface of UUC responsible for adsorption and is shown in Fig. 1. The spectrum revealed the presence of certain functional groups responsible for the adsorption of the metal ions from solution and has been discussed extensively [29]. Fig. 2 reflects the X-ray diffraction spectrum of the adsorbent, the d-spacing values of the XRD spectra of UUC indicated montmorillonite as the major constituent and also the presence of quartz, kaolinite and gibbsite [29]. The SEM morphology of the adsorbent revealed a porous structure as shown in Fig. 3. The porous nature of UUC is desirable as the metal ions can easily penetrate the pores of UUC for efficient adsorption [30].
3.2. Effect of solution pH

The pH of a solution is one of the most important parameters controlling the adsorption process and so it is necessary to be determined [30]. The solution pH affects the surface charge of the adsorbent and the degree of ionization and specification of the adsorbate. Fig. 4 shows the effect of pH on the percentage of Ni(II) and Mn(II) ions adsorbed by UUC. The result indicates that the removal of both metal ions from solution is strongly affected by the pH of the medium. The adsorption was low in acidic medium but increases with increases in the pH of the solution. The percentage adsorbed increased from 17.9% to 64.8% and from 14.8% to 54.8% when the pH was increased from 2.0 to 6.0 for Ni(II) and Mn(II) respectively. At higher pH values greater than 6.0 there is a possibility of the precipitation of the hydroxide species of the metal ions. Therefore, pH 6.0 was chosen in this study for all subsequent experiment, since optimum removal was achieved and metal precipitation was avoided at this pH. At low pH values, the adsorption of both metal ions was low because large quantities of protons compete with the metal cations for the active sites on UUC. As the pH of the solution increases, the number of positively charged available sites decreased and the number of negatively charged active sites increased. The surface of UUC becomes negatively charged at pH greater than the pHpzc of 3.7 and this increases the adsorption of the positively charged metal ions through electrostatic forces of attraction and ion exchange [31]. In general, metal sorption involves a complex mechanism of ion exchange, chelating of metals with various anionic functional groups, adsorption of physical forces and ion entrapment in the inner spaces of the structural network of the adsorbent [32].

3.3. Effect of adsorbent particle size

The effect of adsorbent particle size on the percentage removal of Ni(II) and Mn(II) ions from solution by UUC is shown in Fig. 5. A slight decrease in the percentage removal of both metal ions with increase in particle size from 100 to 500 μm was obtained. The percentage removal at equilibrium decreased from 64.8% to 49.8% and from 54.8% to 39.5%, respectively for Ni(II) and Mn(II), when the particle size was increased from 100 to 500 μm. The higher percentage removal with smaller particle sizes could be attributed to the fact that smaller particles provided a larger specific surface area for adsorption, but as the particle size increased the surface area also decreased [33]. The breaking of larger particles tends to open tiny cracks and channels on the particle surface of UUC, resulting in more accessibility to better diffusion, owing to the smaller particle size [34]. Similar results have also been reported by other researchers [33,35]. The particle size of 100 μm was used for further experiments because of its high removal compared to other particle sizes.

3.4. Effect of adsorbent dosage

The experimental data relating the effect of adsorbent dosage on the percentage removal of Ni(II) and Mn(II) ions from solution unto UUC are shown in Fig. 6a. The result showed that increasing the dosage of UUC from 0.1 to 0.5 g resulted in an increase in the percentage removal of both metal ions. The amount adsorbed increased from 64.8% to 79.7% and from 54.8% to 70.0% respectively for Ni(II) and Mn(II). The increase in the percentage removal could be due to an increase in the surface area and the availability of more active sites on the surface of UUC [36]. However, the equilibrium
adsorption capacity showed an opposite trend as illustrated in Fig. 6b. The adsorption capacity decreased from 32.4 to 7.97 mg/g and from 27.4 to 7.0 mg/g for Ni(II) and Mn(II) ions respectively. This may be due to a decrease in the effective specific surface area available for metal ions resulting from the overlapping or aggregation of adsorption sites, which increase the diffusion path length for metal ions [37]. This aggregation becomes increasingly significant as the weight of adsorbent is increased. Another explanation may be due to the higher UUC dose providing more active adsorption sites which resulted in the adsorption sites remaining unsaturated after adsorption [38]. Thus with increasing the adsorbent weight the amount of metal ions adsorbed unto unit mass of UUC becomes reduced, leading to a decrease in the $q_e$ value.

3.5. Influence of initial metal ion concentration

The initial metal ion concentration is a very important factor to be investigated in adsorption studies as most contaminated wastewaters usually present different concentrations of metal ion, so determination of its effect is necessary for an elaborate adsorption study. The effect of initial metal ion concentration on the percentage removal of Ni(II) and Mn(II) ions by UUC is shown in Fig. 7a. The percentage removal of both metal ions decreased with increase in the initial metal concentration from 100 to 300 mg/L. A decrease from 64.8% to 37.63% and from 54.8% to 30.57% for Ni(II) and Mn(II) respectively was obtained. This decrease is due to the fact that all adsorbents have a fixed number of active sites and at higher concentrations, the active sites become saturated [39]. However, as the concentration was increased further from 300 to 500 mg/L a slight increase in the percentage removal from 37.63% to 44.18% for Ni(II) and 30.57% to 35.76% for Mn(II) ions was obtained. Fig. 7b also showed an increase in the adsorption capacity of both metal ions with increase in metal concentration from 100 to 500 mg/L. This increase is simply due to higher concentration gradient which acts as a driving force to overcome resistances to mass transfer of metal ions between the aqueous phase and the solid phase [33].

3.6. Adsorption isotherms

The equilibrium data, commonly known as adsorption isotherm are basic parameters for the design of adsorption systems and those data provide information on the adsorbent capacity or the amount required to remove a pollutant mass under the system conditions [40]. The Langmuir, Freundlich, Dubinin–Radushkevich, Temkin and scatchard isotherm models were applied to the analysis of the equilibrium sorption data. The Langmuir isotherm is used to describe a monolayer
adsorption onto the surface of an adsorbent with finite number of identical sorption sites. The linear form of the Langmuir isotherm model can be expressed as \[ Ce/qe = 1/q_L K_L + Ce/q_L \] (4)

where \(K_L\) (L/mg) is the Langmuir adsorption constant and \(q_L\) (mg/g) is the monolayer adsorption capacity of the adsorbent. Therefore a plot of \(Ce/qe\) versus \(Ce\) gives a straight line of slope \(1/q_L K_L\) and intercepts \(1/q_L\). From the low values of the correlation coefficient (\(r^2\)) shown in Table 1 for both metal ions, the Langmuir isotherm did not provide a good fit to the experimental data. The monolayer adsorption capacities of UUC for Ni(II) and Mn(II) are 166.67 and 142.86 mg/g respectively. The adsorption process can be evaluated to see whether it is favorable by the use of a Langmuir dimensionless separation factor \(R_L\) defined as

\[ R_L = 1/[1 + K_L C_0] \] (5)

where \(C_0\) (mg/L) is the initial metal ion concentration in solution. If the value of \(R_L\) is less than 1.0, the adsorption is considered to be favorable but it is unfavorable if \(R_L\) is greater than 1.0. The calculated \(R_L\) values at different concentrations fall within the range of 0.29–0.67 and 0.4–0.77 for Ni(II) and Mn(II), respectively, indicating a favorable adsorption process.

The Freundlich model is applied to non-ideal sorption on heterogeneous surfaces and the linear form of the isotherm can be represented as \[ \log qe = \log K_F + 1/n \log Ce \] (6)

where \(K_F\) and \(n\) are the Freundlich adsorption constants, which can be determined by the linear plot of \(\log qe\) versus \(\log Ce\). The high value of \(r^2\) obtained (Table 1) shows that this model provided a good fit to the experimental data. Also, the value of \(n\) for both metal ions lies between 1 and 10 indicating a favorable adsorption [43].

The Temkin isotherm 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. The linear form of the isotherm is expressed as \[ qe = BM + CNc \] (7)

where \(A\) (L/g) is the equilibrium binding constant and \(B = RT/b_T\) is related to the heat of adsorption, \(R\) is the gas constant (8.314 J/mol K), \(T\) (K) is the absolute temperature and \(b_T\) is the Temkin constant. The constants \(A\) and \(B\) were obtained from the linear plot of \(qe\) versus \(lnCe\). From Table 1, the \(r^2\) values obtained for both metal ions are low which shows a poor fit to the experimental data.

The Dubinin–Radushkevich (D–R) isotherm, which does not assume a homogenous surface or a constant adsorption potential as the Langmuir isotherm was applied and is given as \[ lnqe = lnqm - \beta e^2 \] (8)

where \(\beta\) (mol²/J²) is a coefficient related to the mean free energy of adsorption, \(qm\) (mg/g) is the maximum adsorption capacity and \(e\) is the Polanyi potential which is expressed as \(e = RTln(1 + 1/Ce)\) (9)

The D–R constants were calculated from the linear plot of \(lnqe\) versus \(e^2\) and the values are shown in Table 1. Again the \(r^2\) values obtained for the D–R isotherm for both metal ions indicated a poor fit to the experimental data.

Furthermore, since the Freundlich isotherm gave the best fit to the experimental data, it indicates a heterogeneous surface of UUC. To verify this, the Scatchard plot analysis also called independent site oriented model was applied and can be written as \[ qe/Ce = qsb - qeb \] (10)

where \(qs\) (mg/g) and \(b\) (L/mg) are the adsorption isotherm parameters. If a straight line is obtained from the plot of \(qe/Ce\) versus \(qe\) then the adsorbent presents only one type of binding sites, but if it shows a deviation from linearity then the adsorbent presents more than one type of binding site (heterogeneous surface) [46]. From Table 1, the \(r^2\) values obtained for both metal ions showed a great deviation from linearity which indicates a heterogeneous surface of UUC. This accounts for the good fit to the experimental data obtained by the Freundlich model.

### 3.7. Effect of CA and EDTA

It is very important to study the adsorption of metal ions in the presence of ligands because most contaminated effluents from industries usually contain organic pollutants apart from heavy metals. In this regard, the effect of two ligands, citric acid (CA) and EDTA having low and high complexation constants respectively was determined. The concentration of these ligands was made to be the same, higher and in excess i.e. (0.1-CA and 0.1-EDTA), (0.5-CA and 0.5-EDTA) and (1.0-CA and 1.0-EDTA), respectively when compared to the concentration of metal ions. This was performed so as to...
determine the effect of ligand concentration on adsorption. The experiment was also performed at pH 6.0 to enable the formation of metal–ligand complexes and minimize the formation of hydroxo-species at higher values of pH in the alkaline region [22]. Fig. 8 illustrates the effect of ligand on the adsorption of Ni(II) and Mn(II) ions unto UUC. It is observed that the presence of both ligands hindered the adsorption of metal ions compared to the situation when they were absent i.e. without ligand (WL). Furthermore, as the concentration of both ligands increased, a decrease in the adsorption of metal ions was recorded. This decrease may be due to the fact that the ligand might compete with the metal ions for some of the active sites of UUC at higher concentrations. It may also be due to the formation of metal–ligand complexes at higher concentration, which may hinder their adsorption into the interlayers of UUC [27]. The presence of EDTA also hindered the adsorption of metal ions compared to CA. This is simply as a result of the higher complexation of EDTA compared to CA, which forms larger sizes of metal–ligand complexes thereby presenting a more difficult diffusion into the clay layers [22]. A very important observation is that the adsorption of Mn(II) ions became higher than Ni(II) ions in the presence of both ligands. This is due to the larger metal–ligand complexes formed by Ni(II) with both ligands than Mn(II) due to its higher complexation constant than Mn(II). We obtained a similar result when kaolinite clay was used as the adsorbent [27].

3.8. Effect of contact time and adsorption kinetics

The effect of contact time on the percentage removal of Ni(II) and Mn(II) ions unto UUC is shown in Fig. 9. The removal rate for both metal ions was quite rapid initially and then gradually diminished to attain an equilibrium time of around 120 min for Ni(II) and 140 min for Mn(II). Further increase in contact time resulted in no significant increase in the rate of removal. A contact time of 180 min was chosen in this study as maximum removal of both metal ions was achieved. The fast adsorption at the initial stages is due to the availability of abundant active sites on the surface of the adsorbent which becomes used up with time and becomes saturated.

The kinetic mechanism of the adsorption process was determined by the use of the pseudo-first order, pseudo-second order and intraparticle diffusion model. The kinetic parameters obtained are presented in Table 2.

The Pseudo-first order or Lagergren model considers that the rate of adsorption sites occupation is proportional to the number of unoccupied sites [47]. The linear form of the pseudo-first order equation is given as

$$\log\left(\frac{q_e}{C_0} - \frac{q_t}{C_0}\right) = \frac{K_I}{2.303} t$$

where $q_t$ and $q_e$ are the amounts of metal ion adsorbed at time $t$ and equilibrium (mg/g), respectively, and $K_I$ is the rate constant of pseudo-first order adsorption (min $^{-1}$). The values of $K_I$ and $q_e$ were obtained from the slope and intercept of the linear plot of $\log(1 - q_t/q_e)$ versus $t$. From Table 2, the values of the regression coefficient, $r^2$, obtained for both metal ions showed a good fit to the adsorption process.

The pseudo-second order model that is based on the assumption that adsorption follows a second order chemisorption was applied and is expressed as [48]

$$t/q_t = 1/K_2q_e^2 + t/q_e$$

Table 2 Kinetic model parameters of the adsorption process.

<table>
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<tr>
<th>Kinetic models</th>
<th>Ni (II)</th>
<th>Mn (II)</th>
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<tr>
<td>Pseudo-first order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_e,_{cal}$ (mg/g)</td>
<td>89.54</td>
<td>41.98</td>
</tr>
<tr>
<td>$K_I$ (min $^{-1}$)</td>
<td>0.037</td>
<td>0.021</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.964</td>
<td>0.972</td>
</tr>
<tr>
<td>Pseudo-second order</td>
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<td></td>
</tr>
<tr>
<td>$b$ (mg/g min)</td>
<td>0.51</td>
<td>0.27</td>
</tr>
<tr>
<td>$K_2$ (g/mg min)</td>
<td>$1.47 \times 10^{-4}$</td>
<td>$3.89 \times 10^{-5}$</td>
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<tr>
<td>$q_e,_{cal}$ (mg/g)</td>
<td>58.82</td>
<td>83.33</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.818</td>
<td>0.483</td>
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<tr>
<td>Intraparticle diffusion</td>
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<tr>
<td>$K_d$ (mg/g min$^{1/2}$)</td>
<td>2.94</td>
<td>2.69</td>
</tr>
<tr>
<td>C</td>
<td>3.31</td>
<td>6.36</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.923</td>
<td>0.957</td>
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</table>

Figure 8 Effect of ligands on the adsorption of metal ions from solution unto UUC. (Co 100 mg/L, pH 6.0, adsorbent dose 0.1 g, temp 300 K, time 180 min, particle size 100 μm.)
where $K_2$ (g/mg min) is the pseudo-second order equilibrium rate constant. The initial sorption rate was calculated from the following equation:

$$h = K_2 qe^2$$  \hspace{1cm} (13)

The values of $K_2$ and $q_e$ were calculated from the linear plot of $t/q_t$ versus $t$ and are recorded in Table 2. Also, the low $r^2$ values presented by the pseudo-second order equation showed that this model did not provide a good fit to the experimental data for both metal ions. This suggests that chemisorptions are not the principal mechanism for the sorption of Ni(II) and Mn(II) ions unto UUC.

The intraparticle diffusion model was also applied to the kinetic data to elucidate the diffusion mechanism. The model equation is expressed as [49]:

$$q_t = K_d t^{1/2} + C$$  \hspace{1cm} (14)

where $K_d$ (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant and $C$ is the intercept. The intercept reflects the boundary layer effect. The larger the intercept the greater is the contribution of the surface sorption in the rate controlling step. Intraparticle diffusion is the sole rate determining step if the plot of $q_t$ versus $t^{1/2}$ is linear and passes through the origin ($C = 0$). From Table 2, the good value of $r^2$ obtained for both metal ions showed the existence of the intraparticle diffusion mechanism in the sorption process. However, the plot did not pass through the origin due to the occurrence of the intercept $C$, which indicates the existence of some boundary layer effect and showed that intraparticle diffusion is not the rate determining step in the overall sorption process.

3.9. Thermodynamic studies

The variation in the amount of Ni(II) and Mn(II) adsorbed unto UUC as a function of solution temperature is shown in Fig. 10. It was observed that the adsorption of both metal ions increased slightly as the temperature increased from 300 to 323 K. This indicates that a high temperature favors the adsorption process. The improved adsorption capability with increasing temperature suggests that the adsorption is an endothermic one. This trend may be due to the creation of more additional adsorption sites on the adsorbent surface with increase in temperature as a result of the dissociation of some of the surface components on UUC [21]. It may also be due to the tendency of Ni(II) and Mn(II) ions gaining more kinetic energy to diffuse from the bulk phase to the solid phase with an increase in solution temperature.

In order to evaluate the feasibility of the adsorption process, thermodynamic parameters such as the standard free energy ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) were estimated. The Gibb’s free energy change of adsorption was calculated from the following equation:

$$\Delta G^0 = -RT \ln K_c$$  \hspace{1cm} (15)

where $R$ is the ideal gas constant (8.314 J/mol K), $T$ (K) is the absolute temperature and $K_c$ is the thermodynamic equilibrium constant that is expressed as

$$K_c = C_a/C_e$$  \hspace{1cm} (16)

where $C_a$ (mg/L) is the amount of metal ion adsorbed at equilibrium, and $C_e$ (mg/L) is the concentration of metal ion in solution at equilibrium. The Gibb’s free energy is also related to the enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) at constant temperature by the Van’t Hoff equation as follows:

$$\ln K_c = -\Delta G^0/RT = -(\Delta H^0/RT) + (\Delta S^0/R)$$  \hspace{1cm} (17)

The values of $\Delta H^0$ and $\Delta S^0$ were calculated from the slope and intercept of the plot of $\ln K_c$ versus $1/T$ and the thermodynamic parameters are listed in Table 3. The negative values of $\Delta G^0$ obtained at all temperatures for both metal ions indicate that the adsorption process is spontaneous in nature. It was also observed that the change in free energy increases with increase in temperature suggesting that higher temperatures make the adsorption easier. The positive value of $\Delta H^0$ indicates an endothermic process which is supported by the increase adsorption of Ni(II) and Mn(II) with rise in temperature. The magnitude of $\Delta H^0$ is very useful in describing the type of adsorption. If the magnitude of $\Delta H^0$ is in the range 2.1–20.9 kJ/mol, it denotes a physical adsorption process, while chemisorptions fall within the range of 80–200 kJ/mol [50]. From Table 3, the value of $\Delta H^0$ obtained for both metal ions showed a physical adsorption process unto the surface of UUC. This physical adsorption explains the reason why the kinetic data did not fit the pseudo-second order model (chemisorptions model). Furthermore, positive values of $\Delta S^0$

<table>
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<th>Table 3 Adsorption thermodynamic parameters.</th>
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<td>Metal</td>
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<tr>
<td>Ni(II)</td>
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indicate an increase in randomness at the solid/solution interface during adsorption while low values of $\Delta S^0$ indicate that no remarkable change in entropy occurs [51]. Also, the magnitude of $\Delta S^0$ reveals whether the adsorption reaction involves an associative or dissociative mechanism. If the value of $\Delta S^0$ is larger than $-10 \text{ J/mol K}$, it means that the adsorption conforms to a dissociative mechanism [37]. The values of $\Delta S^0$ (Table 3) obtained show that the adsorption of Ni(II) and Mn(II) ions unto UUC involves a dissociative adsorption mechanism, as the values obtained were far greater than $-10 \text{ J/mol K}$.

3.10. Desorption/recycling

An effective and potential adsorbent for the removal of metal ions must not only have a good adsorption capacity but also a good desorption of metal ions. For this reason, it was necessary to investigate the desorption of Ni(II) and Mn(II) ions from UUC. The selected stripping agent for desorption processes must be low cost, highly efficient and non-damaging to the adsorbent. Several studies have shown HCl to be more effective in desorbing heavy metals from their loaded adsorbents when compared to other stripping agents such as HNO$_3$, H$_2$SO$_4$ and NaOH [52,53]. As a result HCl and distilled water (DW) were used as stripping agents in this study. The effect of DW and different concentrations of HCl (0.05–1.0 M) on the desorption of Ni(II) and Mn(II) from their loaded UUC is shown in Fig. 11a. As observed, optimum adsorption of up to 92.8% of Ni(II) and 90% of Mn(II) was achieved at 0.1 M HCl concentration. This result is significant because it will help elucidate the right concentration of the stripping agent to be applied during desorption of metals from UUC. The high percentage desorption of both metal ions indicates the suitability of UUC as a good potential adsorbent. Furthermore, the fact that up to 32.6% of Ni(II) and 30.1% of Mn(II) were desorbed using DW alone suggests that physical adsorption must have played a major role in the adsorption process [54].

Stability is generally important when the same adsorbent is re-used in multiple adsorptions and desorption cycles. Therefore the reusability of adsorbent was examined based on adsorption/desorption ability. This was done by performing three cycles of adsorption–desorption studies using 0.1 M HCl as stripping agent as illustrated in Fig. 11b. It was observed that the adsorption of both metal ions after the first cycle remained the same as the initial adsorption before desorption. This may be due to the acid treatment of UUC by the desorbing agent during desorption which activates the pores of the adsorbent [55]. However, the percentage adsorption decreased slightly for both metal ions from the 1st to 3rd cycle. This decrease may be due to the destructive effect of the stripping agent and mass loss of the adsorbent during desorption [56]. In addition, resident of metal ions in UUC (irreversible binding) resulted in a decrease in the number of available adsorption sites [57].

4. Conclusions

The unmodified Ugwuoba montmorillonite clay (UUC) was found to be useful as a low-cost adsorbent for the removal of Ni(II) and Mn(II) ions from aqueous solution. Optimum removal for both metal ions was obtained at pH of 6.0 and a contact time of 180 min was utilized for equilibrium removal. Among the adsorption isotherm model tested, the Freundlich model gave the best fit to the experimental data for both metal ions, indicating a heterogeneous surface of UUC which was also confirmed by the scatchard plot analysis. The kinetic data followed the first order kinetic model and showed the presence of intraparticle diffusion mechanism. However, the data did not fit the pseudo-second order model, which indicates the likelihood of a physical adsorption mechanism. The occurrence of physical adsorption was confirmed by the value of $\Delta H^0$ obtained from thermodynamic study. Thermodynamic studies showed an endothermic process as increase in percentage removal of both metal ions with temperature and positive $\Delta H^0$ were obtained. Thermodynamic parameters also indicated a dissociative mechanism and a spontaneous adsorption process.

References


Mechanism on the sorption of heavy metals from binary-solution


