



Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions

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ABSTRACT

Surface properties of montmorillonite (MMT) and its adsorption characteristics for heavy metals have been investigated with nickel and copper as sorbate from aqueous solutions. Employing the potentiometric and mass titration techniques in batch experimental methods, the point of zero charge (PZC) and point of zero net proton charge (PZNPC) of MMT edges at different ionic strengths present pH_{PZC} and pH_{PZNPC} to be 3.4 ± 0.2 . A crossing point was observed for the proton adsorption vs. pH curves at different ionic strengths of KCl electrolyte and in investigating MMT remediation potentialities as sorbent for heavy metals polluted waters, the effects of heavy metal concentration, pH, MMT dosage, reaction time and temperature for Cu^{2+} and Ni^{2+} uptake were studied. The sorption of metal ions by MMT was pH dependent and the adsorption kinetics revealed sorption rate could be well fitted by the pseudo-second-order rate model. The data according to mass transfer and intraparticle diffusion models confirmed diffusion of solutes inside the clay particles as the rate-controlling step and more important for the adsorption rate than the external mass transfer. Adsorption isotherms showed that the uptake of Cu^{2+} and Ni^{2+} could be described by the Langmuir model and from calculations on thermodynamic parameters, the positive ΔG° values at different temperatures suggest that the sorption of both metal ions were non-spontaneous. Change in enthalpy (ΔH°) for Ni^{2+} and Cu^{2+} were 28.9 and 13.27 kJ/mol K respectively, hence an endothermic diffusion process, as ion uptake increased with increase in temperature. Values of ΔS° indicate low randomness at the solid/solution interface during the uptake of both Cu^{2+} and Ni^{2+} by MMT. Montmorillonite has a considerable potential for the removal of heavy metal cationic species from aqueous solution and wastewater.

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1. Introduction

Discharge as aqueous effluents from various industrial activities of chemical processing outfits may contain heavy metals which are non-biodegradable and toxic priority pollutants [1]. Presence of heavy metals in human environment is of a major concern due to their tendency to accumulate in living organisms, and by that find their way into the human body causing various diseases and disorders. The sustainability of any human community hinges on adequate supply of potable water, which conforms to the acceptable standard. This makes removal of heavy metal species in wastewater an essential factor for environmental and human health protection.

Ni^{2+} and Cu^{2+} as representatives of these heavy metals are chosen for this study as they are present in many industrial effluents. Copper pollution arises from copper mining and smelting, brass

manufacture, electroplating industries and excessive use of Cu-based agri-chemicals. Exposure to high levels of copper in water and diet can lead to diseases of the liver and kidney [2]. Nickel is a toxic heavy metal widely used in zinc base casting, silver refineries, electroplating and storage battery industries. The chronic toxicity of nickel to humans and the environment has been well reported, high concentration of Ni^{2+} causes cancer of lungs, nose and bone [3].

Methods for removal of heavy metal species from wastewaters have been the subject of different researches, in order to improve on environmental remediation technologies. Removal of heavy metals from aqueous effluents can be achieved by chemical precipitation, ion exchange, adsorption, membrane separation, and electrodialysis [4,5]. Of all the various water-treatment techniques, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness [4–8]. The ingrained drawback of this method is the high cost and tedious procedure for the regeneration of the conventional sorbent (i.e., activated carbon), hence it needs the development of cheaper and equally effective substitutes. Attention has been focused on the development of the

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Nomenclature

S_0	surface charge density ($C\text{ cm}^{-2}$)
F	Faraday constant
Γ_{H^+}	adsorbed amounts of H^+ (mol cm^{-2})
Γ_{OH^-}	adsorbed amounts of OH^- ions (mol cm^{-2})
C_e	equilibrium concentration of solution (mg/L)
C_0	initial heavy metal concentration (mg/L)
a	fraction of solute adsorbed at any time t
ΔG°	change in Gibb's free energy of adsorption (kJ/mol)
ΔH°	change in enthalpy of adsorption (kJ/mol)
ΔS°	change in entropy of adsorption (kJ/mol K)
K_F	Freundlich isotherm constant related to adsorption capacity ($(\text{mg/g})(\text{L/mg})^{1/n}$)
K_L	intensity of adsorption (L/mg)
m	clay mass (g)
n	Freundlich isotherm constant related to adsorption intensity
b	Langmuir isotherm constant
R_L	dimensionless separation factor
q	amount of heavy metal adsorbed at time t (mg/g)
q_e	amount of adsorbed heavy metal per unit clay mass (mg/g)
Q_0	maximum adsorption capacity (mg/g)
R^2	correlation coefficient
R	gas constant (J mol/K)
V	volume of solution (L)
K_d	Van't Hoff equilibrium constant
T	absolute temperature (K)
t	time (min)

substitutes from natural clay materials. This shift in attention is predicated on the surface properties of these materials. Clay particles are strongly anisotropic and exhibit faces and edges, which are very different in surface area and in chemical behavior [9]. It has been reported that the abundance of clay minerals and their low cost has posed them a strong candidate as adsorbent for removal of heavy metal from wastewater. Premised on this fact, a number of mechanisms have been supposed to be active in the sorption of heavy metals by these sorbents. Some of these mechanisms are chemisorptions, physical adsorption and micro-precipitation which involve (i) an ion exchange reaction at permanent-charge sites and, (ii) formation of complexes with surface hydroxyl groups at edge-sites [10–13]. The adsorption capacity of clay minerals can be enhanced by replacing the natural exchangeable cations with organic molecules forming the so called “organoclays” [14].

Montmorillonitic smectites, $\{(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}\}$ are one of the natural clay minerals that has specific surface chemical properties. The adsorption of Cd^{2+} , Zn^{2+} , Pb^{2+} onto natural clays have been studied [15–19]. Owing to the crystal-chemical features of MMT, heavy metal retention by the mineral can occur by adsorption and/or cation exchange reaction. The ability of MMT, to adsorb heavy metal ions from water is significant for the removal of toxic pollutants from the environment [20]. MMT clays at layer edges have variable surface charge, i.e., they partially behave as oxide surfaces [21]. The acid–base reactions of the surface hydroxyl groups are equally responsible for the charge formation on the surface of metal oxide in electrolyte solutions [22]. The PZC is an important characteristic of a solid phase immersed in a liquid medium and by knowing the PZC, conclusions on the sign of surface charge can be made, e.g., metal oxides are positively charged at $\text{pH} < \text{pH}_{\text{PZC}}$ and negatively charged at $\text{pH} > \text{pH}_{\text{PZC}}$, which gives a better understanding of adsorption

phenomena. Knowledge of surface properties of MMT, is very important and fundamental for the determination of the characteristics of the surface functional groups and their interactions with ions from aqueous solutions.

In this study, attempt was made to evaluate MMT surface properties such as point of zero charge (PZC), point of zero net proton charge (PZNPC) and surface charge density in relation to its potentialities as sorbent for heavy metals removal in aqueous bodies.

2. Experimental

2.1. Surface properties

2.1.1. MMT clay

Analytical grade of MMT was purchased from Aldrich Chemicals. Clay fraction passed through a $150\ \mu\text{m}$ sieve was used as received, unwashed powder. Its surface area as determined by the EGME method [23] was found to be $699\ \text{m}^2/\text{g}$ and from extraction with ammonium acetate a CEC of $89\ \text{meq}/100\ \text{g}$ was obtained. The surface charge properties of the MMT clay suspensions were evaluated by two methods, i.e., potentiometric acid–base titration [10,24] and mass titration [25].

2.1.2. Potentiometric titrations

Acid–base potentiometric titration was used to measure the surface proton adsorption. $100\ \text{mL}$ distilled water was initially adjusted to a high pH using $0.01\ \text{M}$ NaOH and then titration began with small increments of $0.01\ \text{M}$ HCl, until pH was 2.57 . Titration was repeated with $20\ \text{g}$ of MMT clay present in the same volume of distilled water. Experiments for charge determination were carried out under ambient temperature using $20\ \text{g}$ MMT in $100\ \text{mL}$ of KCl electrolyte concentration of 0.01 and $0.001\ \text{M}$, the resulting dispersion was allowed to equilibrate for $6\ \text{h}$ with continuous stirring. The suspension was then titrated with a standard NaOH solution, and the pH was measured and recorded when the potential variation was lower than $1\ \text{mV}$. Titration was stopped when the pH was around 10 , and then, to check reversibility, the same suspension was titrated with a standard HCl solution. In all cases, pH was measured using a digital pH meter (Orion EA 940). From the potentiometric titration results, the net surface charge density, S_0 , was calculated using Eq. (1) [26].

$$S_0 = F(\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}) \quad (1)$$

where the surface charge S_0 is in C cm^{-2} , F is the Faraday constant. Γ_{H^+} and Γ_{OH^-} are the adsorbed amounts of H^+ and OH^- ions (mol cm^{-2}) during titration. In this manner, the dependence of the surface charge density on pH and electrolyte concentration was obtained.

Verification on the point of zero charge was carried out using the technique of [19]. Initial pH values (pH_i) of $20\ \text{mL}$ of KCl solutions (concentrations 10^{-3} and $10^{-2}\ \text{M}$) were adjusted in pH range of 3.1 – 10 using $0.01\ \text{M}$ of HCl or NaOH. Then, $0.05\ \text{g}$ of MMT was added to each sample. Equilibration was carried out by shaking, in a rotary incubator at $200\ \text{rpm}$ for $2\ \text{h}$ at $25 \pm 1\ ^\circ\text{C}$. The dispersions were then filtered and the final pH of the solutions (pH_f) was determined, point of zero charge was found from a plot of pH_f vs. pH_i .

2.1.3. Mass titration

According to methods described by Avena and Pauli [25], the mass titration experiments were performed to determine the point of zero net proton charge of the clay at the same conditions of potentiometric titration by following the pH drift until a steady value is obtained. Each addition of $0.05\ \text{g}$ of dry MMT sample were added to $30\ \text{mL}$ of KCl solution at a given ionic strength, $I = 0.01\ \text{M}$, having a pH between 2.4 and 5.1 . After each addition, the pH was recorded

after an equilibrium time. It was verified that the pH reached a constant value for exactly 10 min after each addition of the mineral. Then, a new amount of sample was introduced to change pH; this procedure was repeated until a pH was found where no pH change occurs with further addition of the sample. For a clay or oxide free of contamination [27], this pH value has been shown to be a good approximation to the PZNC of oxide or clay surfaces.

2.2. Batch mode adsorption studies

Stock solutions of 1000 mg/L were prepared by dissolving appropriate quantities of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ respectively in a liter of double distilled water. Working solutions were prepared by diluting each stock solution to give the desired concentrations and followed by batch adsorption studies at $25 \pm 1^\circ\text{C}$ in a thermostated rotary shaker to investigate the sorption processes. Known mass of MMT was added to a 50 mL of the metal ions solution, thoroughly mixed, and allowing sufficient time for equilibrium. Fast filtration followed and remaining metal ion concentrations were determined directly in the supernatant solution by Flame atomic absorption spectrometry. The amount of adsorption at equilibrium q_e (mg/g) was calculated according to the expression:

$$q_e(\text{mg/g}) = \left[\frac{(C_0 - C_e)V}{m} \right] \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L), V the volume of solution (L), m the weight of MMT (g).

Different adsorbent doses in 50 mL of 100 mg/L metal ion solutions were agitated for equilibrium time. The kinetics of adsorption was determined by analyzing adsorption of metal ions from the aqueous solution at different time intervals. For adsorption isotherms, MMT dosage of 1 g was introduced to 50 mL of 50–300 mg/L of Cu^{2+} and Ni^{2+} solutions at 298 K. And in the thermodynamic studies, adsorptions of 100 mg/L of each metal ions by 1 g of MMT were carried out at 298, 308 and 318K, respectively.

3. Results and discussion

3.1. Acid–base potentiometric titration

In the acid–base potentiometric titration of MMT with distilled water as electrolyte, PZC was found to be around a pH of 3.6 (Fig. 1). Equally of note, was the fast equilibration observed for successive increments of HCl during the titration process. This may suggest a relatively short time adsorption experiments, making negligible effects of other processes such as dissolution that could affect proton adsorption data especially at low pH [26]. The fast equilibration, leading to rapid pH stability can be interpreted as a result of reactions between protons and hydroxylated surface sites which are known to be very fast reactions. This same behavior was observed during the acid–base potentiometric titrations with different KCl electrolyte concentrations to measure the proton adsorption.

Titration consumption was significantly pronounced at basic pH than at acidic pH and proton adsorption decreases as the electrolyte concentration increases. In Fig. 2, the PZNPC, which in this case correspond to the pH where titration curves crossed at different ionic strengths and as well the pH where the surface charge is zero, now, shifted to a lower pH value of 3.4, showing the influence of ionic strength. The 2:1 MMT has high permanent layer charge and negligible variable charge. Sets of curves shifted in the direction of lower pH with increasing KCl concentration, which also indicate the presence of permanent charges. The extent of proton accumulation on the surface of MMT particles is always greater at lower ionic strength; this trait is similar to those of other clay materials in literatures [25,28,29].

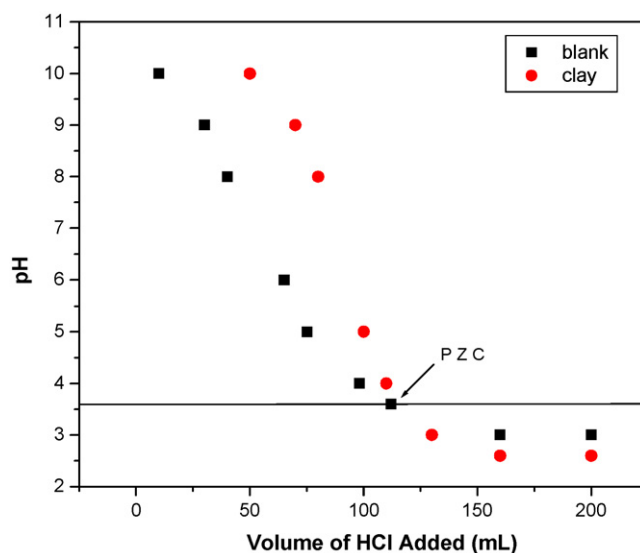


Fig. 1. Potentiometric titration curves for blank distilled water and MMT in distilled water.

From a non-titration method, in which the dependence of final pH (pH_f) vs. initial pH (pH_i) was plotted in Fig. 3, the value of the point of zero charge was obtained as the pH value at which the curve plateau, i.e., the curve inflexion appeared. At this pH value, a change in surface charge from positive to negative or vice versa occurs [19]. According to Fig. 3, the plateau obtained at a pH value of 3.4 ± 0.1 corresponds to the point of zero charge of the MMT smectite powder. Shift of the curves towards lower pH_{PZC} with increasing ionic strength for the KCl solutions may be attributed to the formation of $\text{SO}^- \cdot \text{K}^+$ surface complexes due to coulombic interactions. It is generally assumed that oxygen surface groups have the potential to react with ions in solution (electrolyte cation) to yield surface complexes, such surface reactions may be described by the affinity of surface sites for solutes and the coulombic interaction between the surface charge and the dissolved ions. This behavior is exhibited by materials carrying structural negative charge and it is attributed to H^+ adsorption and H^+ /cation exchange on variable charge sites [25,28,30]. According to [31] the observed trend in this work is common for 2:1 clays and can be interpreted in two different ways: either the PZNPC is located at very acidic pH, or other

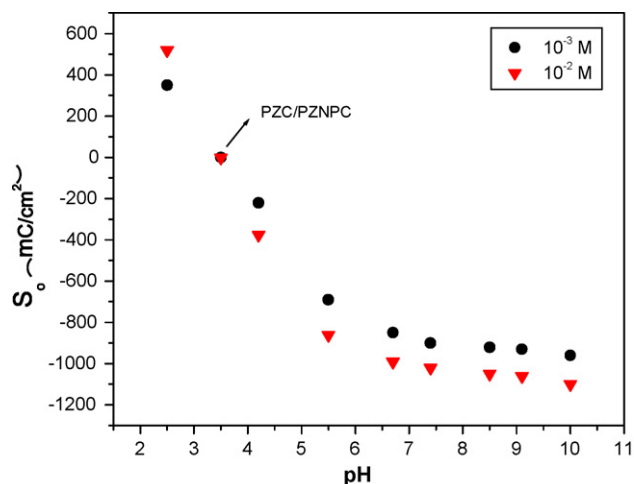


Fig. 2. Surface charge density of MMT as a function of pH for different KCl concentrations.

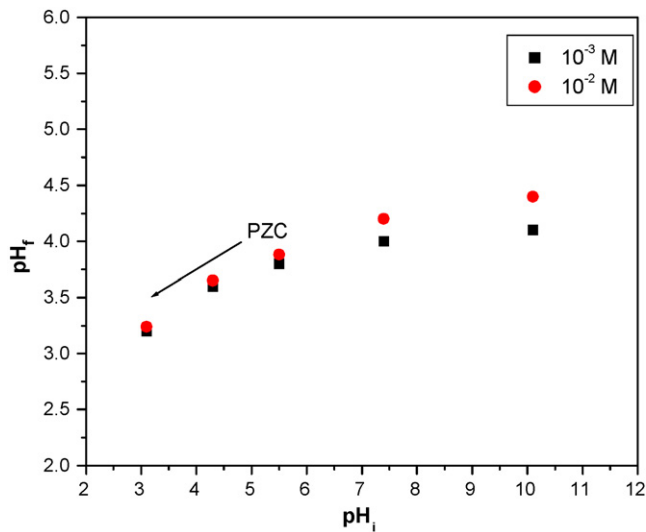


Fig. 3. Dependence of pH_f on pH_i during equilibration of 0.05 g MMT with KCl at different concentrations.

titrant-consuming reactions such as ion exchange or dissolution occur.

3.2. Mass titration

Mass titration data performed at two KCl concentrations was presented in Fig. 4. The pH gradually changes with addition of solid and asymptotically approaches a limiting value. The direction of the pH variation depends on the pH of the starting KCl solution. Therefore, the pH where solid addition does not produce any change in the pH of the initial KCl solution can be estimated by interpolation. This is the pH where proton adsorption is zero (PZNPC) [31]. If mineral is added to a solution at the pH of PZNPC, no change in pH should occur. The PZNPC estimated this way is marked with arrow in Fig. 4. The release of Si-OH and Al-OH caused by MMT dissolution (generally at pH 3–4) into the aqueous solution was not significant and assumed negligible during the titration experiments, this observation was also reported in previous studies as cited by [26].

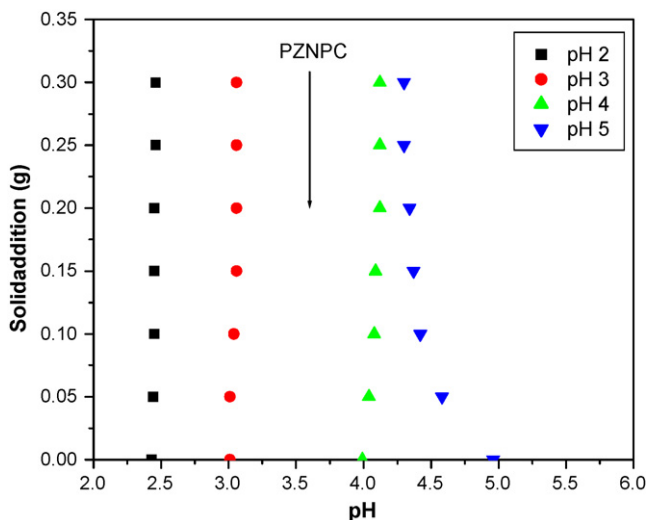


Fig. 4. Mass titration curves for MMT obtained at $I = 10^{-2}$ M; each solid addition correspond to 0.05 g dry MMT.

Table 1

Physicochemical parameters of the MMT clay used.

Properties	Values
CEC	89 meq/100 g
PZNC	3.4 ± 0.2
Specific surface area	$699 \text{ m}^2/\text{g}$
Particle size	$150 \mu\text{m}$

3.3. Clay surface charge effect

Montmorillonite clay mineral possess two kinds of electrical charges a variable (pH dependent) charge resulting from proton adsorption/desorption reaction of surface sites $M_{\text{surf}}\text{-OH}$ and a structural negative charge from X^- sites resulting from isomorphous substitution within the clay structure. The physicochemical parameters of MMT clay used in this study are summarized in Table 1. Adsorption of ions on charged surfaces can be described to involve both a coordination reaction at specific surface sites and an electrostatic interaction between adsorbing ions and the charged surface [10–13]. Data from potentiometric titration and adsorption isotherms suggest two dominant sorption reactions in the study: cation exchange at permanent negatively charged sites on the siloxane faces including interlayer regions of MMT, with the interlayer region accounting for the relatively slow sorption, and inner-sphere surface complex formation at variable charge surface hydroxyl groups ($M_{\text{surf}}\text{-OH}$) at the crystal edges. Fig. 5 showed, Cu^{2+} and Ni^{2+} were sorbed by MMT at lower pH and sorption does not involve significant displacement of protons which is one of the features of metal ion uptake. Metal ions exchange may have occurred not only on external faces, but also within the interlayer regions. As the surface of MMT is more protonated at low pH, H^+ competes with metal ion resulting in active sites less able to retain heavy metal ions, this may be explained by the surface complexation reactions which are influenced by the electrostatic attraction between negatively charged groups at MMT surface and the metal ions. The sorption of Cu^{2+} and Ni^{2+} by MMT at higher pH is similar to metal ion uptake onto oxide surfaces [13,25,32,33] that is, sorption increases to near 100% over a narrow pH range [34]. According to a simultaneous ion exchange on the particle face and protonation/deprotonation processes at the edges, metal ion uptake of the sorption processes may be expressed by:

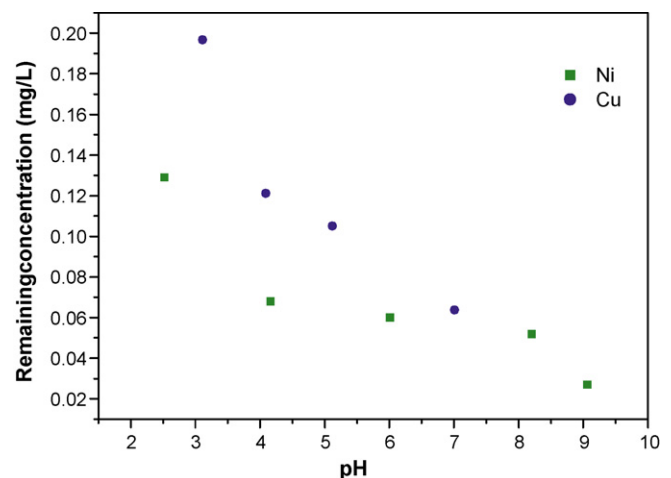
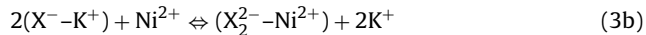
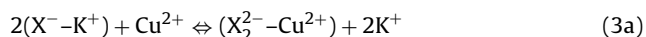


Fig. 5. Remaining concentrations of Cu^{2+} and Ni^{2+} in solution according to pH (amount of adsorbate: 1 g; 25°C ; 200 rpm; metal ion [Cu and Ni] = 100 mg/L).

(i) cation exchange reactions at the permanent negative charge of faces or interlayer region of MMT



(ii) formation of copper and nickel hydroxyl surface complex at the variable charge surface hydroxyl groups



Assessment of acid–base properties of MMT particles from experimental data, are usually performed by potentiometric titration, some results from previous studies were summarized by Kriaa et al. [28] and it clearly shows that published experimental potentiometric data vary significantly (PZNPC values vary from 2.6 to 8.5) according to experimental conditions selected by authors [28,29,31,35]. Differences in values may have arose from factors like purification protocol, storage conditions of purified clays, analytical conditions selected for titration such as stability criteria, effects of gas atmosphere in the titration reactor, solid liquid ratio, equilibrium conditions and ionic strength. It is evident that such variability would have influence on the determination of PZC value and as a consequence prevents comparisons and generalization of published results. According to [36,37] PZC can be defined as PZNPC.

3.4. Adsorption studies

Adsorption processes are affected by several conditions, such as initial pH, initial metal ion concentration and sorbent amount. The effect of hydrogen ion concentration on removal of Cu^{2+} and Ni^{2+} ions from solutions were studied at pH ranging from 2.45 to 9.6, Cu^{2+} and Ni^{2+} precipitates at pH higher than 8.2. Fig. 5 summarizes the sorption of Cu^{2+} and Ni^{2+} onto MMT at various pH values, showing that the sorption of metal ions strongly decreases with the acidity of the solution. Removal was enhanced at pH above pH_{PZC} , explaining the nature of the chemical interactions of the metal ions with the active site of MMT surface. Metal removal depends on these active sites as well as on the nature of the metal ions in the solution. However, as the pH is lowered, the hydrogen ions compete with the metal ions for the sorption sites in the sorbent and may hinder the binding of positively charged metal ions. As the pH increases, more negatively charged surfaces become available therefore leading to greater metal uptake, even at precipitation pH. With increase in sorbent dosage, adsorption increased (Fig. 6). Keeping sorbate concentration fixed and increasing the amount of the sorbent, makes a large number of sites available for a fixed concentration of metal ion, hence the increase in extent of adsorption. Time dependence experiments for metal ions removal were investigated to understand adsorption behavior of MMT with Cu^{2+} and Ni^{2+} . Figs. 7 and 8 present the plot of the metal ion sorbed q_e (mg/g) as a function of the time. From the figures, maximum adsorbed amount for Cu^{2+} was achieved within 50–100 min while for Ni^{2+} it was between 100 and 150 min. Increasing concentration gradient, acts as increasing driving force, and in turn leads to an increasing equilibrium sorption until sorbent saturation is achieved. Amount sorbed for Ni^{2+} is higher compared with Cu^{2+} and sorption behavior of MMT for Ni^{2+} fits more to patterns of other natural sorbent as compared to Cu^{2+} .

3.4.1. Kinetics

The kinetics of the adsorption process was analyzed using the pseudo-first-order and pseudo-second-order equations, to model the kinetics of Cu^{2+} and Ni^{2+} adsorption onto MMT.

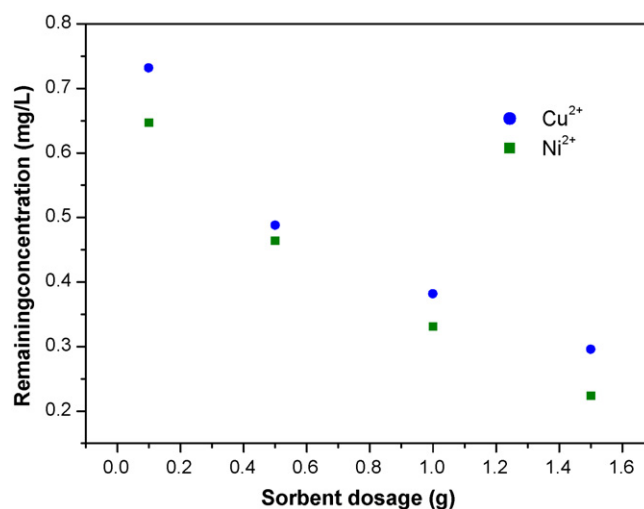


Fig. 6. Adsorption of Cu^{2+} and Ni^{2+} onto MMT according to sorbent dosage (25 °C; 200 rpm; metal ion [Cu and Ni] = 100 mg/L).

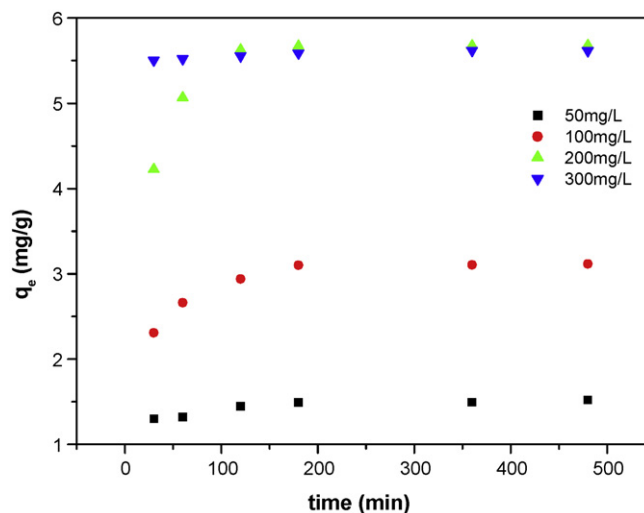


Fig. 7. Equilibrium sorbed amount of Ni^{2+} according to adsorption time for various initial concentrations.

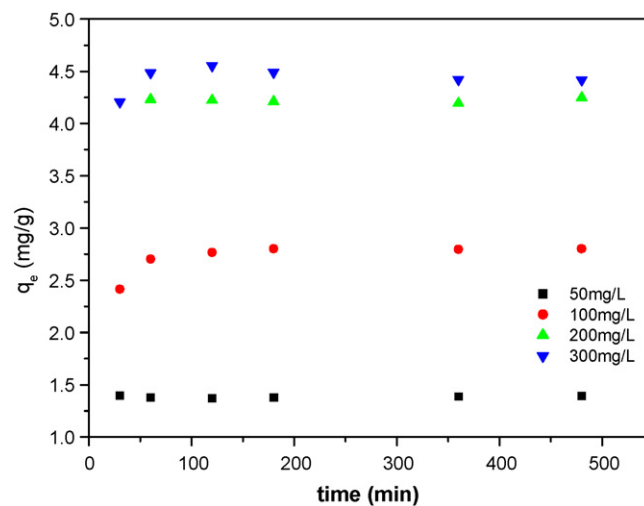


Fig. 8. Equilibrium sorbed amount of Cu^{2+} according to adsorption time for various initial concentrations.

Table 2
Kinetic parameters for Cu²⁺ and Ni²⁺ sorption onto MMT at different concentrations.

Metal ion	Initial concentration (mg/L)	q_e Exp. (mg/g)	First-order kinetics			Second-order kinetics		
			k_1	q_e Cal. (mg/g)	R^2	k_2 (g/mg/min)	q_e Cal. (mg/g)	R^2
Ni ²⁺	50	1.52	0.003	2.56	0.887	0.305	1.53	0.998
	100	3.11	0.0024	4.36	0.721	0.211	3.15	0.999
	200	5.68	0.0021	5.66	0.583	0.198	5.70	0.998
	300	5.61	0.0014	6.05	0.688	0.175	5.62	0.999
Cu ²⁺	50	1.39	0.007	2.46	0.782	0.781	1.39	1
	100	2.80	0.004	3.12	0.894	0.416	2.81	0.998
	200	4.25	0.004	3.76	0.791	0.357	4.27	0.998
	300	4.42	0.003	3.92	0.811	0.326	4.44	0.998

3.4.1.1. *Pseudo-first-order model.* The Lagergren's (pseudo-first-order) rate equation employed is given by:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (4)$$

where k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}), q is the amount of metal ion adsorbed at various times (mg/g), and q_e is the amount of metal ion adsorbed onto adsorbent at equilibrium (mg/g). After integrating with the initial conditions, the equation becomes [38]:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (5)$$

3.4.1.2. *Pseudo-second-order model.* The pseudo-second-order model can be represented in the following form [38]:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (6)$$

where k_2 is the rate constant of pseudo-second-order model (g/mg/min). After integrating with the initial conditions, the form can be obtained as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Slopes and intercepts of plots of $\log(q_e - q)$ vs. t were obtained for both Cu²⁺ and Ni²⁺ ions to determine the first-order rate constant k_1 and equilibrium adsorption amount q_e (plots not shown) but the correlation coefficients for the first-order kinetic model at different concentrations were relatively low and the calculated q_e values obtained from the first-order kinetic model failed to match the experimental q_e values, both indicating that the adsorptions of Cu²⁺ and Ni²⁺ ions onto MMT were not of first-order reaction. Results of the model are shown in Table 2.

The pseudo-second-order rate constant k_2 and equilibrium adsorption amount q_e for Cu²⁺ and Ni²⁺ ions were determined from the slopes and intercepts of plots of t/q vs. t . The correlation coefficients for the pseudo-second-order kinetic model at different concentrations were above 0.998 and the calculated q_e values were very close to the experimental values. The high correlation coefficients ($R^2 > 0.998$ in all cases) and the agreement of calculated and experimental q_e both demonstrated that the adsorption kinetics of Cu²⁺ and Ni²⁺ onto MMT followed the pseudo-second-order kinetic model. Therefore, the rate-limiting step may be chemical sorption or chemisorption through sharing or exchange of electrons between sorbent and adsorbate. Different works have been carried out using pseudo-second-order kinetics for sorption reactions, and some authors have reported that the kinetics of the sorption of copper and nickel onto modified MMT follows a pseudo-second-order reaction rate [18,39]. Also, the rate constant of pseudo-second-order (k_2), were found decreasing with increasing initial metal ion concentrations that is, time required for the equilibrium adsorption increased, with minute differences as initial metal ions concentration increased (Figs. 7 and 8). As shown in Table 2, from values of q_e , the use of MMT favors the adsorption of Ni²⁺ more than that of

Cu²⁺ ions but the rate of adsorption of Ni²⁺ was slower as compared to Cu²⁺ ions. The longer time of Ni²⁺ adsorption may have allowed more particle diffusion and retention that is more transfer of Ni²⁺ to the active sites of MMT leading to more sorbed Ni²⁺ than Cu²⁺.

3.4.2. Adsorption mechanism

Kinetics data for copper and nickel sorption onto montmorillonite were further studied according mass transfer or intraparticle diffusion model. Sorption kinetics is controlled by different steps [40]:

- (i) solute transfer to the sorbent particle surface (film diffusion);
- (ii) transfer from the sorbent surface to the intraparticle active sites (particle diffusion);
- (iii) retention on the active sites via sorption, complexation or intraparticle precipitation phenomena.

The third step is assumed to be very rapid and can be considered negligible, the slowest of all the steps, is considered as the rate-limiting step for any adsorption process. For design purposes, it is necessary to distinguish between film diffusion and particle diffusion in order to identify the slowest step in the adsorption process. Rate of sorption processes depend on parameters like structural properties of the sorbent (e.g., porosity, specific area and particle size), the properties of the metallic ions (e.g., ionic radius and number of coordination), the concentration of the metallic ions and the interactions between metallic ions and active sites of the sorbent. If intraparticle diffusion has a significant presence in the adsorption process, it is generally characterized by the relationship between specific sorption (q_t) and the square root of time, according to the relation [38]:

$$q_t = \frac{K_i}{m} t^{1/2} \quad (8)$$

where m is the mass of sorbent (g), q_t the amount of solute adsorbed at time t (mg/g) and K_i is the initial rate of intraparticle diffusion ($\text{mg/L s}^{-1/2}$). The rate constant of intraparticle diffusion K_i was determined by plotting q_t (mg/g) as a function of the square root of the time as shown in Fig. 9, which equally presents a non-linear distribution of points, with two distinct portions. The double nature of the plots (*curved and linear*) obtained for the two sorption processes, indicated the existence of intraparticle diffusion in the processes. According to the intraparticle diffusion model, if a plot of the amount of sorbate adsorbed per unit weight of sorbent, q_t , vs. square root of contact time gives a linear plot, it indicates that intraparticle/pore diffusion is the rate-limiting step in the sorption process [40]. The plots obtained in Fig. 9 contrasted the prediction of the intraparticle diffusion model; this indicates that intraparticle/pore diffusion is not the singular rate-limiting step in the adsorption process. The initial curved part is attributed to boundary layer (film) diffusion, the linear, to the intraparticle diffusion and chemical reaction [41]. Owing to the multistep nature of this plot, the linear portions were linearized by the plot

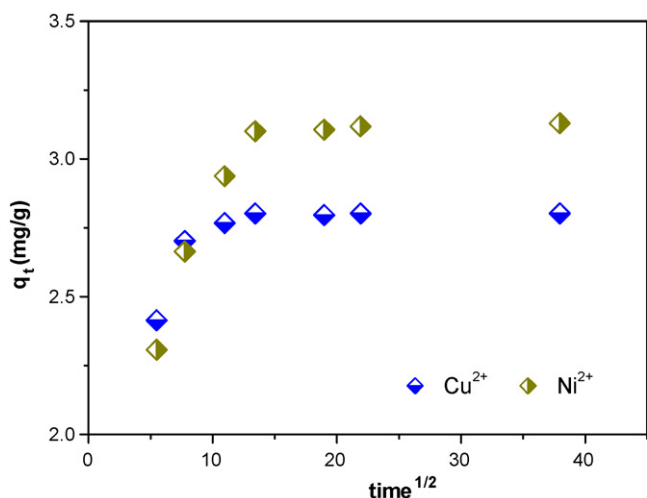


Fig. 9. Sorption of Copper and Nickel onto MMT as a function of square root of time for intraparticle diffusion rate constant determination (metal ion: 100 mg/L; pH ~ 6 for Cu^{2+} and Ni^{2+} ; m : 1 g; T : $25 \pm 1^\circ\text{C}$).

of $-\log[1 - (q/q_e)^2]$ against time as presented in Fig. 10. According to Urano and Tachikawa model [42], if the plots are linear and pass through origin, then the slowest (rate-controlling) step in the adsorption process is the internal diffusion, and vice versa. From Fig. 10, it was observed that the plots were linear but do not pass through the origin, suggesting that the adsorption process is controlled by film diffusion. It can be assumed that the diffusion of the solute inside the clay is more important for the adsorption rate than the external mass transfer.

3.4.3. Sorption isotherm

Generally, adsorption isotherms provide vital information in optimizing the use of adsorbents. Descriptions on affinity between sorbates and sorbents, bond energy and adsorption capacity, to mention a few, can be extracted from isotherm equilibrium models applicable to adsorption processes. The two most commonly employed models are the Langmuir and Freundlich isotherms, which have shown to be suitable for describing short-term and monocomponent adsorption of metal ions by different materials [43,44]. The Langmuir adsorption model is based on the sorption on a homogeneous surface by monolayer sorption without interaction between sorbed species. Langmuir model assumes that the adsorptive forces are similar to the forces in the chemical interaction. This

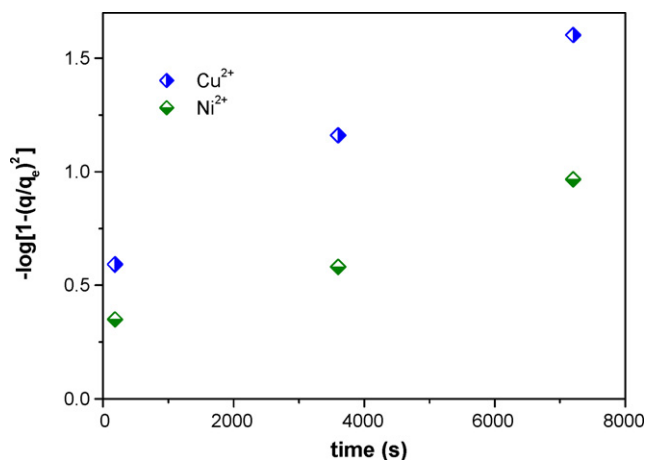


Fig. 10. Boyd plot for the adsorption of Cu^{2+} and Ni^{2+} onto MMT: 100 mg/L; pH ~ 6 for Cu^{2+} and Ni^{2+} ; m : 1 g; T : $25 \pm 1^\circ\text{C}$.

model is described by Eq. (9) [45]:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (9)$$

where Q_0 is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity (mg/g), C_e is the equilibrium concentration of solution (mg/L), K_L is a direct measure of the intensity of adsorption (L/mg) and q_e is the amount adsorbed at equilibrium (mg/g). This equation can be linearized as follows:

$$\frac{1}{q_e} = \left(\frac{1}{K_L Q_0} \right) \left(\frac{1}{C_e} \right) + \frac{1}{Q_0} \quad (10)$$

From the data of $1/q_e$ vs. $1/C_e$, K_L and Q_0 can be determined from the slope and intercept.

The Freundlich adsorption isotherm gives expression on the surface heterogeneity and exponential distribution of the active sites and their energies. The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is given by:

$$q_e = K_F C_e^{1/n} \quad (11)$$

where K_F ($(\text{mg/g})(\text{L/mg})^{1/n}$) and n (dimensionless) are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. This equation can be linearized as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (12)$$

The values of n and K_F were calculated from the slope and intercept of the plot of $\log q_e$ vs. $\log C_e$. On the basis of correlation coefficient R^2 , applicability of the isotherm equations was compared (Table 3). It was clear that the Langmuir model yields a better fit than the Freundlich model for the adsorption of Cu^{2+} and Ni^{2+} ions onto MMT. The strong Langmuir sorption process was supported by the dimensionless separation factor determined for both Cu^{2+} and Ni^{2+} by values less than 1 (Fig. 11). The dimensionless separation factor is given by:

$$R_L = \frac{1}{1 + bC_0} \quad (13)$$

C_0 is the initial concentration of metal ion mg/L; b , the Langmuir isotherm constant. If the value of $R_L < 1$, it indicates a favorable adsorption and if $R_L > 1$ then an unfavorable adsorption. The sorption of Cu^{2+} and Ni^{2+} on MMT was of the range, $0 < R_L < 1$ representing a highly favorable Langmuir adsorption at higher initial

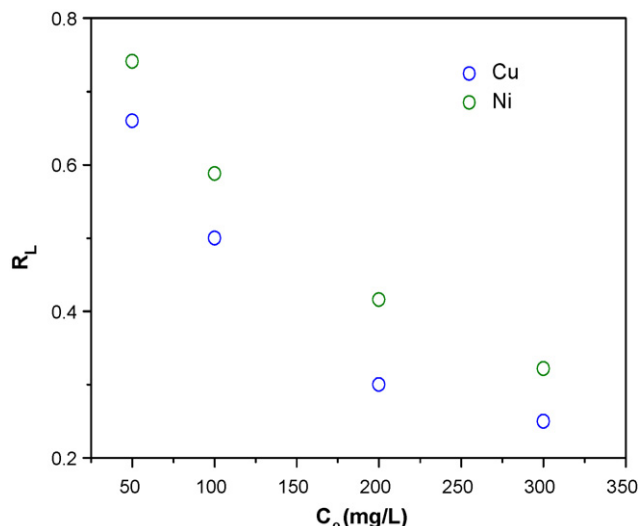


Fig. 11. Separation factor for Cu^{2+} and Ni^{2+} adsorption onto MMT.

Table 3
Freundlich and Langmuir parameters for Cu²⁺ and Ni²⁺ sorption.

Metal ion	Freundlich isotherm		R ²	Langmuir isotherm		
	1/n	K _F ((mg/g)(L/mg) ^{1/n})		Q ₀ (mg/g)	K _L (L/mg)	R ²
Cu ²⁺	1.036	1.656	0.942	7.616	0.10	0.984
Ni ²⁺	1.100	1.655	0.925	12.886	0.007	0.983

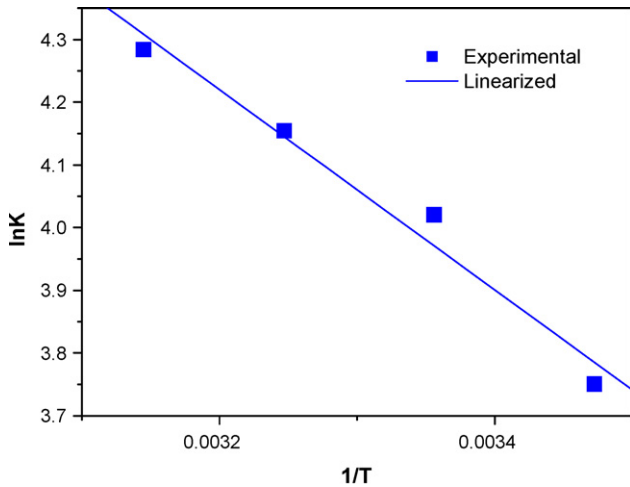


Fig. 12. Plot of $\ln K$ vs. $1/T$ for Cu²⁺.

metal ion concentration. The Freundlich constant K_F indicates the adsorption capacity of the adsorbent and n is a measure of the deviation from linearity of the adsorption. If the value of n is equal to unity, the adsorption is linear. If the value of n is below unity, this implies that the adsorption process is chemical, and if the value of n is above unity, it is physical adsorption [18]. From the $1/n$ values of 1.036 and 1.100 as shown in Table 3, n values at equilibrium were 0.96 and 0.98 for Cu²⁺ and Ni²⁺ respectively, indicating a chemisorption adsorption.

3.4.4. Thermodynamic parameters

The amounts of Cu²⁺ and Ni²⁺ uptakes at 288, 298, 303, and 313 K were calculated to obtain the thermodynamic parameters which were evaluated using the Van't Hoff equation:

$$\log K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (14)$$

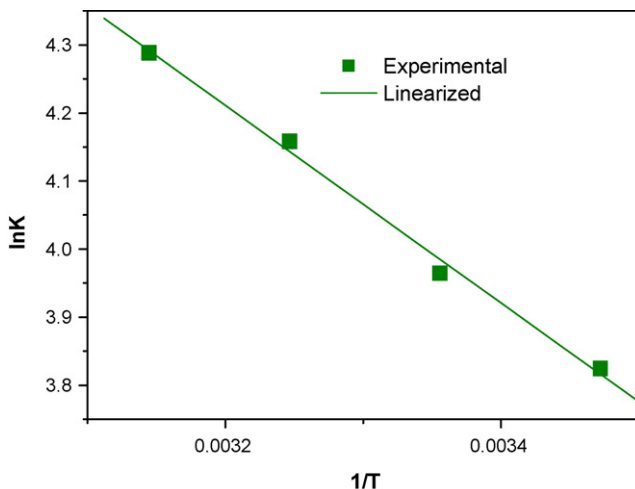


Fig. 13. Plot of $\ln K$ vs. $1/T$ for Ni²⁺.

Table 4
Thermodynamic parameters for Cu²⁺ and Ni²⁺ sorption.

Metal ion	Temp (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)
Cu ²⁺	288	8.979	13.27	0.077
	298	9.950		0.011
	303	10.620		0.0086
	313	11.315		0.0061
Ni ²⁺	288	2.183	28.9	0.0944
	298	4.303		0.0825
	303	5.083		0.0773
	313	6.063		0.0718

The values of $\log K_d$ were defined as follow:

$$K_d = \frac{a}{1-a} \quad (15)$$

where ΔS° and ΔH° are entropy (kJ/mol K) and enthalpy (kJ/mol) change of adsorption, respectively, R is universal gas constant (8.314 J/mol K), and T is the absolute temperature (K). K_d is the equilibrium constant and a is uptake percentage of adsorbate at equilibrium. The values of ΔH° and ΔS° were calculated from the slope and intercept of linear regression of $\ln K_d$ vs. ($1/T$). Values of ΔG° were estimated by:

$$\Delta G^\circ = -RT \ln K_d \quad (16)$$

The plot shown in Figs. 12 and 13 for Cu²⁺ and Ni²⁺ were linear at the range of investigated temperatures. Calculated thermodynamic parameters such as ΔH° , ΔS° and ΔG° are given in Table 4. The positive values of ΔG° indicate that the sorption of Cu²⁺ and Ni²⁺ onto MMT were not spontaneous processes. Change in enthalpy (ΔH°) values is positive, showing that the sorption of Cu²⁺ and Ni²⁺ are endothermic in nature. Both ions uptake increased with the increasing of temperature. The sorption of both ions also require a diffusion process, which is an endothermic process; i.e., the rise of temperatures favors Cu²⁺ and Ni²⁺ transport within the particles of MMT [46]. In another aspect, the exchanges of the metal ions with H⁺ need first the bond breaking of OH, which is one of the possible existing forms of proton in MMT [25,28]. The bond breaking is also an endothermic process. The ΔH° of Ni²⁺ uptake by MMT was larger than that of Cu²⁺, implying, temperature has a more important influence on Ni²⁺ uptake. The positive low values of ΔS° indicate low randomness at the solid/solution interface during the uptake of both Cu²⁺ and Ni²⁺ by MMT.

4. Conclusion

The surface properties and potential use of montmorillonite (MMT) as a sorbent for copper and nickel was studied. Point of zero charge (PZC) and point of zero net proton charge (PZNPC) of edges at different ionic strengths, presented the pH_{PZC} and pH_{PZNPC} to be 3.4 ± 0.2 . The proton adsorption vs. pH curves presents a common crossing point. Adsorption of metal ions were attributed to ion exchange to the permanent charges on the 'silica' faces of MMT and to the binding at the variable charge as well as to the physicochemical mechanisms at the interlayer spacing due to access of the Cu²⁺ and Ni²⁺ and Cu(OH)⁺ and Ni(OH)⁺ species, inferring that Cu²⁺ and Ni²⁺ were sorbed due to the strong interactions with the active sites of the sorbent. This clay was able to remove the metal

ions from aqueous solutions and experimental data fitted well to Langmuir equation showing Ni²⁺ adsorption process is more favorable onto MMT compared to Cu²⁺. The non-spontaneous nature of the sorption process for these species was confirmed from the thermodynamics studies. Sorptions were of a diffusion process with the PZC of MMT revealing an increase in heavy metal removal efficiency as from a pH of 3.4 ± 2 for use as sorbent in aqueous medium. The high selectivity in the bonding of Cu²⁺ and Ni²⁺ suggests MMT may be useful for removal of these toxic heavy metal ions from waste waters. This ability can be explored in treatment technologies since MMT is a cheap, an abundant, and locally available resource.

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