ISOTHERMS, KINETICS AND THERMODYNAMIC STUDIES OF ADSORPTION OF Cd AND Ni FROM TEXTILE EFFLUENT WITH ACID MODIFIED CLAY

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ABSTRACT

Locally sourced acid modified clay was used as an adsorbent for the removal of Cd (II) and Ni (II) ions from textile wastewater. The adsorption of Cd (II) and Ni (II) was performed using the batch method. The hydrochloric acid (HA) and acetic acid (AA) modified clay was characterized by XRF, Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The effect of variables such as contact time, adsorbent dosage, temperature and pH were investigated. Equilibrium isotherms, kinetic and thermo-dynamic behaviour of the processes were studied. The results from XRF, SEM and FTIR studies of adsorbents show changes in composition, rough porous structure and difference in the intensity of the spectra. The equilibrium of the adsorption process was achieved at 50 and 90 min for HA and AA, respectively. The maximum removal of Cd (II) and Ni (II) by HA was recorded at optimum conditions of 50 min, 0.3g adsorbent dosage, temperature of 45ºC and pH 7, while for AA the maximum uptake was attained at 90 min, 0.4g adsorbent dosage, temperature of 45ºC and pH 6. The pH at point of zero charges (pH_{pzc}) was 2.0 and 3.0 for HA and AA respectively. The experimental data fitted well to Langmuir isotherm showed adsorption capacity of HA for Cd (II):10.49 mg g^{-1} and Ni (II):14.06 mg g^{-1}, and AA for Cd (II):40.01 mg g^{-1} and Ni (II):11.23 mg g^{-1}, respectively. The kinetic analyses revealed that the pseudo-second-order model fitted well to the acquired experimental data. The thermodynamic behaviour of metal ion adsorption onto modified clay was found to be spontaneous and endothermic. The result obtained show that modified clay can effectively remove cadmium and nickel from aqueous solution.
Keywords: adsorption, textile effluent, isotherms, kinetics.

INTRODUCTION

The presence of toxic heavy metals in wastewater has been attributed to human and industrial activities, which has raised considerable public concern regarding the negative consequences on plants, animals (aquatic and terrestrial) and human lives [1, 2]. Most of these heavy metals such as nickel, cadmium, and chromium are known to be carcinogenic agents and may represent a serious threat to the living population because of their non-degradable, persistent, and accumulative nature.

These result in a rising global concern about water pollution because of heavy deleterious metals and a great awareness in respect to the treatment of the industrial wastewater received from effluents discharge areas as it eventually returns to the water bodies. Many of the deleterious metal ions found in industrial wastewater, including those of cadmium, chromium, nickel, zinc, lead, and copper, result from various activities [3]. Cd (II) and Ni (II) ions are toxic heavy metals which are widely used in industry, particularly the electroplating and battery industries. The chronic toxicity of these

metal ions to humans and the environment has been well documented, in the United States, the safe level of Cd (II) and Ni (II) in drinking water has been set at 0.01 mg L^{-1} and 0.020 mg L^{-1} respectively [4]. High concentrations of nickel in humans can cause health problems such as heart and liver damages, skin irritation, headache, dermatitis and nasal cancer [5, 6]. The presence of cadmium, nickel and others metals in the aqueous environment has a potentially damaging effect on human physiology and other biological systems when the acceptable levels are exceeded.

Several treatment techniques have been employed to separate some of these heavy metals from wastewater like chemical precipitation, coagulation, nano-filtration, evaporation, solvent extraction, ion exchange, electrochemical treatment, and membrane filtration and adsorption process [7]. Due to high efficiency, low cost, simple operation, eco-friendliness and simple operating conditions, adsorption is applied as a general purification process in many industries [8, 9]. The adsorption of Fe (III) and Cr (VI) in wastewater is a significant challenge. The adsorption technique is the easiest method used in the decontamination of heavy metals in discharged effluents. Some of its economic and technological advantages are: it is cheap and easy to operate, accessible and available, profitable and efficient, and effective than other techniques [10, 11]. For these reasons, more focus has been directed towards the research on the development of novel and effective adsorbents in recent years. Various traditional and non-traditional adsorbents have been employed to remove heavy metals. They include tree bark, clay, activated carbon [12 - 14].

Clay is a natural material that has a great tendency to serve as an adsorbent in removing heavy metals from wastewater. The application of kaolin as an adsorbent is determined by its low-cost, availability, abundance, shape-selective properties, and pore size. In fact, it is an excellent material for adsorption [3]. This material is available in large quantity and also has a high surface area. Previous studies reported that acid modification of local clay samples enhanced its adsorption for heavy metals [15]. Therefore, it becomes necessary to improve the adsorption capacity and expand local clay application beyond fine art and local pottery work. Thus, this study will characterize clay treated with hydrochloric and acetic acids to improve the utilization and commercial value of the local clay. The sourcing of natural material

from local sources is advantageous because it will support the local economy and help lower environmental impact [16]. Recently, rapid removal of both cadmium and nickel from water/wastewater has been proven to be possible by the use of activated carbon-based adsorbent.

Therefore, this work is being focused on the preparation of adsorbents from locally sourced clay such as Umunze clay which is also a kaolinite clay and can serve as a promising starting ingredient for modification. After modification, the resultant modified clay was characterized to gain insight into its properties and used for removal of cadmium and nickel ions from aqueous solution, and equilibrium isotherms, kinetics and thermodynamics, were investigated. For this purpose, real effluents from a textile industry were selected and acid-treated local clay was used for the treatment.

EXPERIMENTAL
Materials

The clay was obtained from Umunze in Anambra State, Nigeria. All chemicals used in this study, including acetic acid (CH_3COOH), hydrochloric acid (HCl) and distilled water were analytical grade, purchased from Sigma-Aldrich and used as received. Industrial effluent used for analysis was supplied by a local textile factory.

Preparation of modified clay (MC)

The clay sample was thoroughly washed with distilled water to remove dust and other impurities. It was thereafter heated at 105°C for 24 h in an oven. The dried clay was crushed into smaller particles by mortar and pestle and ground into powder form. The powdered clay was sieved to a particle size of 125 μm. To activate the powder, an aliquot of 50 g of the powder clay was soaked in 50 mL of 1.0, 2.5, 4.0 and 5.5 M of both HCl and CH_3COOH acid solutions and left overnight for full impregnation. The eight modified samples were then taken for BET analysis to check which concentration gives the highest surface area for further experiment.

Characterization of modified clay

The textural characteristics of modified clay, including specific surface area, pore volume and pore diameter were determined by the BET method using a Quantachrome instrument (Nova station A, version 11.03, USA) based on the principle of adsorption/desorption of nitrogen at 77 K and 60/60 s (ads/des) equilibrium

time. The surface morphology and elemental composition of the samples were simultaneously examined using a scanning electron microscopic-energy dispersive X-ray (SEM-EDX, JEOLJSM 7600F) spectroscopy. The surface functional groups present on the MC samples was determined by a Fourier transform infrared (FTIR) spectrophotometer (IR Affinity 1S, Shimadzu, Japan).

Determination of pH at point of zero charge (pHpzc)

Point of zero charge (pzc) of an adsorbent is a parameter that determines the net surface charge of the ion in solution. The pH at pzc (pHpzc) is the value of pH at which the total external and internal surface of the ion is fixed at zero [17]. The point of zero charge (pH$_{pzc}$) of the adsorbent was determined by the salt addition method. Adsorbent in a quantity of 0.1 g was added to 100 mL of 0.1M KNO$_3$ solution and both were mixed in six conical flasks at 25°C which were securely capped immediately. The pH of solution was adjusted from pH initial (pHi) of 1.0 to 8.0 by adding several 0.1M HCl and NaOH solution. The content in each flask was then agitated in an isothermal water bath shaker at 150 rpm for 36 h and the final pH (pHf) of each solution was carefully measured. The difference between the initial and final pH (pHf - pHi) of each solution was thereafter determined. The plot of (pHf - pHi) versus pHi was constructed and the pHpzc was obtained as the intercept on an x-axis [18].

Batch adsorption studies

The influence of contact time (10 - 120 min), pH (2 - 12), adsorbent dosage (0.1 - 0.5 g) and temperature (25 - 45°C) on the adsorption process were investigated. The batch mode adsorption experiments were conducted by bringing into contact the 50 mL of wastewater effluent with a specified quantity of modified clay in a set of each 250 mL conical flasks. The solution pH was adjusted to the required value and the content of each flask was agitated in a water bath shaker (SearchTech Instrument) operating at related temperature and a constant stirring rate of 190 rpm. After the equilibrium was attained, each sample was decanted allow to dry for 30 min. The concentration of un-adsorbed Cd (II) and Ni (II) were then determined by an atomic absorption spectrophotometer (AAS, Buck Scientific 210VGP, USA). The Cd (II) and Ni (II) ions removal efficiency, R (%) and equilibrium amount of metal ions adsorbed, q$_e$, mg g^{-1}, were calculated by equations (1) and (2): Metal removal

$$R, \% = \left(\frac{C_0 - C_e}{C_e} \right) \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{2}$$

where C$_o$ and C$_e$ (mg L^{-1}) are the initial and equilibrium concentration of the effluent waste; V is the volume of the solution; M (g) is the mass of adsorbents.

Equilibrium adsorption isotherm

The correlation between the amount of metal ion adsorbed onto and the equilibrium concentration of metal ion in the aqueous phase was evaluated using three parameter isotherm models. The experimental data acquired was analysed by Langmuir, Freundlich and Temkin models. The Langmuir isotherm model is employed based on assumption of monolayer adsorption of adsorbate on homogeneous active sites and thus saturation is attained, beyond which no further attachment of on adsorbent takes place. It also operates with the assumption that there is no interaction between the adsorbed molecules on adjacent sites [19]. The non-linear model which was used by Ho & Mackay [20] as presented in equation (3).

$$q_e = \frac{C_e q_{max} b}{1 + b C_e} \tag{3}$$

where, C$_e$ (mg L^{-1}) is the equilibrium concentration of metal ions adsorbed; q$_e$ (mg g^{-1}) is the amount of metal ions adsorbed; b (l mg^{-1} metal) is the Langmuir isotherm constant. Two derivatives of the Langmuir equation are equation (4).

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{1}{q_o} C_e \tag{4}$$

The separation factor (R$_L$) whose value determines the nature of the isotherm shape is an important feature of the Langmuir isotherm. It represents favourable (0 < R$_L$ < 1), unfavourable (R$_L$ > 1), linear (R$_L$ = 1) or irreversible adsorption (R$_L$ = 0). The dimensionless parameter is given by equation (5).

$$R_L = \frac{1}{1 + bCo} \tag{5}$$

where b is the Langmuir constant; Co (mg L^{-1}) is the highest metal ion adsorbed concentration.

The Freundlich isotherm is the oldest known two-parameter adsorption model, which is applied for multilayer, heterogeneous adsorption sites and is expressed as follows in equations (6) and (7).

$$q_e = k_F C_e^{\frac{1}{n}} \qquad (6)$$

$$log \, q_e = log \, K_F + \frac{1}{n} log c_e \qquad (7)$$

where q_e (mg g^{-1}) is the amount adsorbed at equilibrium; C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate; K_F and n are the Freundlich equilibrium coefficients. The value of n gives information on favourability of adsorption process; K_F is the adsorption capacity of the adsorbate.

Temkin considered the effect of the adsorbate interaction on adsorption and proposed the model known as Temkin isotherm, which can be expressed as:

$$q_e = B \ln(k_T C_e) \qquad (8)$$

where K_T is the equilibrium binding constant corresponding to the maximum binding energy; B is related to the heat of adsorption (equation 9); q_e (mg g^{-1}) is the experimental adsorption capacity; Ce (mg L^{-1}) is the concentration of the metal ion adsorbed at equilibrium position.

$$B = \frac{RT}{b_T} \qquad (9)$$

where $1/b_T$ indicates the adsorption potential of the adsorbent; R is the universal gas constant (8.314 J/kmol); T is the temperature in Kelvin (K).

Adsorption kinetics

Pseudo-first-order, pseudo-second-order and intra-particle diffusion models were applied to evaluate the experimental data in order to gain insight into the controlling mechanism of the adsorption of Cd (II) and Ni (II) onto modified clay. The linear forms of the pseudo-first-order and pseudo-second-order [20] and are given in equations (10 - 11), respectively.

$$log \, (q_e - q_t) = log \, q_e - \frac{k}{2.303} t \qquad (10)$$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (11)$$

where q_e (mg g^{-1}) is the amount of metals ion adsorbed at equilibrium; q_t (mg g^{-1}) is the amount of metals ion adsorbed at time t; k_1 (min^{-1}) is the pseudo-first-order rate constant; k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order constant.

Adsorption thermodynamic study

The thermodynamic behaviour of Cd (II) and Ni (II) adsorption onto modified clay was evaluated based on the thermodynamic parameters including standard Gibbs free energy change, ΔG^o (kJ/mol), enthalpy change, ΔH^o (kJ mol^{-1}), and entropy change, ΔS^o (J mol^{-1} K^{-1}) which were determined using the following equations (12 - 14).

$$\Delta G^o = -RT \ln K_{eq} \qquad (12)$$

$$K_{eq} = \frac{C_{ad}}{Ce} \qquad (13)$$

$$\ln k_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (14)$$

where C_{ad} is the adsorbed metal ions concentration on the surface of the adsorbent; K_{eq} is equilibrium constant; T (K) is the temperature; R (8.314 J mol^{-1} K^{-1}) is the gas constant.

RESULTS AND DISCUSSION
Characterization of modified clay

The results of XRF chemical composition analyses conducted on the raw clay (RC) and modified clay (HA and AA) are presented in Table 1. The findings reveal that the major constituents in the clay are Silica (SiO_2), Alumina (Al_2O_3) and iron oxide (Fe_2O_3) containing an approximate percentage of 49.75 %, 9.20 %, and 6.94 %, respectively. The composition of minor elements such as copper, nickel, zinc, chromium, titanium, calcium and manganese oxides were low which was conform with chemical analysis of clay [21] and is in agreement with the values obtained by Gupta and Bhattacharyya [22]. From Table 1 the contents of the natural clay Al_2O_3, Fe_2O_3, MgO, CaO were 12.88, 6.88, 1.50, and 0.36 wt.%., it can be seen from second column that Al_2O_3, Fe_2O_3, MgO, CaO contents decreased, while silicon oxide (SiO_2) content increased after treatment with HCl and CH_3COOH. The percentage of SiO_2 is 67.82 % for the raw clay but after treatment with HCl and CH_3COOH, it increased to 70.27 % and 68.21 %. The SiO_2 content of the clay activated with HCl and acetic

Table 1. Chemical characterization of adsorbents.

Composition	Weight (%) RC	Weight (%) HA	Weight (%) AA
SiO_2	67.82	70.27	68.21
Al_2O_3	12.88	12.32	12.55
Fe_2O_3	6.68	5.17	6.42
Cr_2O_3	0.02	0.01	0.02
TiO_2	1.48	1.42	1.42
CaO	0.36	0.24	0.26
MgO	1.50	1.17	1.32
Na_2O	0.15	0.16	-----
MnO	0.14	0.02	0.10
V_2O_5	0.03	0.01	0.04
K_2O	0.51	0.49	0.51
P_2O_5	0.12	0.12	0.13
LOI	7.92	7.79	8.31

was higher than that of the natural clay. The increase in SiO_2 content can be explained by the depletion of the interlayer and octahedral cations after acid activation. The increase in SiO_2 content after acid activation was investigated by Siddiqui and reported that the high silica content might have some bearing on the adsorption efficiency [23].

It was observed that exchangeable cation, such as Ca^{2+}, was the easiest to be removed after treatment with HCl and CH_3COOH, as they are located out of the kaolinite lattice (between layers). For both acids, the dissolution of the octahedral cations (such as Al^{3+}, Fe^{3+}, and Mg^{2+}) were increased. Yusuff et al., reported that Al^{3+} was the most difficult oxide to be dissolved by HCl activated clays, compared to Fe^{3+} and Mg^{2+} [24]. This is attributed to the fact that, in the clay mineral's structure, Al^{3+} occupies the centre of the ribbons while Mg^{2+} is located at the edges of the octahedral ribbons [25]. Another factor that promotes the rapid decrease in Mg^{2+} content is that MgO is more soluble in acidic media than Al_2O_3. The loss on ignition values indicated that the clay has low carbonaceous matter and high mineral matter contents.

BET analysis

The textural properties of modified clay including surface area, total pore volume and average pore radius are presented in Table 2. The BET surface areas of modified clay were found to be larger than that of raw clay (RC) 84.223 m^2 g^{-1} compared to the value of 88.05 m^2 g^{-1} reported for treated clay [3].

Scanning electron microscopy

The scanning electron microscope (SEM) images before and after modification are depicted in Fig. 1. It displayed asymmetrical size cavities and the wide distribution of pore size. However, the better performance showed by HA was due to removal of adsorbed gases paving way for those available pores needed for mass transfer and high removal, meanwhile Fig. 1 revealed the SEM analysis of AA and this shows agglomeration into smaller crystallite.

Fourier transform infrared

Fourier transform infrared (FTIR) spectral analysis was carried out to identify the different functional groups

Table 2. BET results of raw and activated clay.

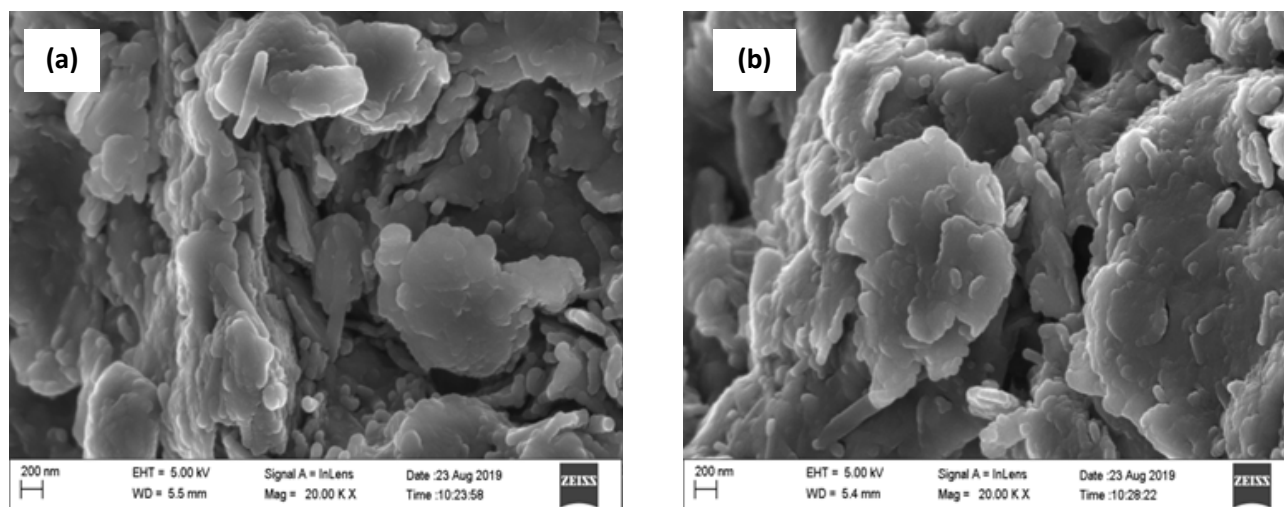| Samples	Surface area (m^2 g^{-1})	Pore volume (cc g^{-1})	Pore size (nm)
RC	84.223	0.0527	2.115
HA	389.370	0.2168	2.116
AA	319.955	0.2285	2.126

Fig. 1. SEM images of (a) HA and (b) AA.

present in clay and after acid, modifications as well as after adsorption. Fig. 2 shows FTIR spectra in the range of 500 cm^{-1} - 4000 cm^{-1} wave number. The different functional groups which are present in the given samples are OH stretching, CH, C=C, and C-O stretching. FTIR spectra of given raw clay sample show that the broad and intense peak at 3893 cm^{-1} to 3763 cm^{-1} was attributed to the stretching of OH group due to inter- and intra-molecular hydrogen bonding of polymeric compounds such as alcohols or phenols. The Si – O stretching and bending as well as the OH bending absorption in the range of 1020 – 425 cm^{-1} shows more about the kaolinite and montmorillonite minerals present in the clay samples. This represents dissociated silanol groups (-Si-O) in the tetrahedral sheets. The appearance of double bands at around (908 cm^{-1} and 689 cm^{-1}) represents –Al$_2$-OH and Si – O stretching an indication of montmorillonite

and quartz clay minerals respectively [26]. During acid activation of clay, the protons penetrate the clay layers attacking the OH groups causing the alteration in the adsorption bands attributed to the OH vibrations and octahedral cations [5]. The intensity of stretching bands observed at 3619 cm^{-1} decrease to 3538 cm^{-1} with acid activation. The acid treatment resulted in the increasing peak sharpness associated with the water adsorbed in the kaolinite minerals at 3414 cm^{-1} (H-O-H). The FTIR spectra of the activated clay showed either a reduction or shift in wave number and intensity of peaks. For instance, wave number 3839 cm^{-1} and 3836 cm^{-1} were shifted to 3619 cm^{-1} and 3414 cm^{-1} which indicates the involvement of H-O-H molecule. The participation of montmorillonite mineral and silanol groups (-Si-O) were confirmed by the resulted shift in wave number from 1020 to 908 cm^{-1} and 781 to 712 cm-1, respectively [27].
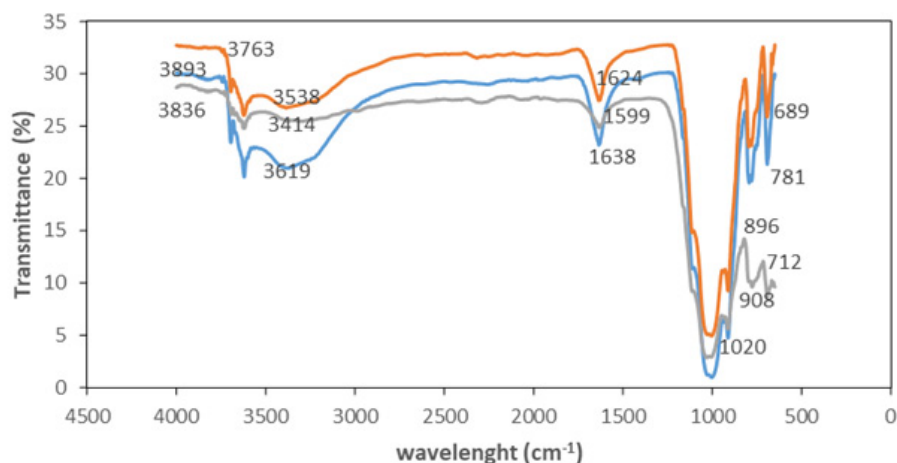

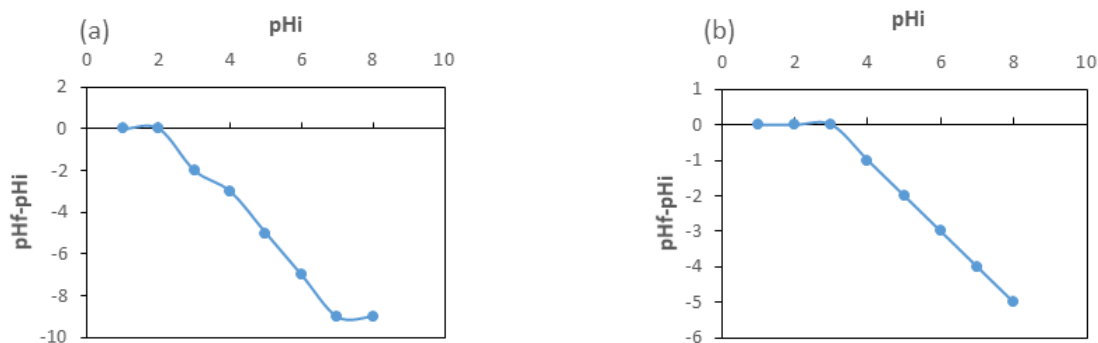Fig. 2. FTIR spectra of (a) RC (blue) (b) HA (grey) and (c) AA (yellow).

Fig. 3. Effect of pH$_{pzc}$ on adsorption of Ni (II) and Cd (II) onto (a) HA and (b) AA at agitation speed = 190 rpm, mass = 0.1 g, and temperature = 25°C.

Determination of point of zero charge

The value of pH$_{pzc}$ on the surface of prepared HA and AA was determined to be 2 and 3 as shown in Fig. 3. This value helps to determine whether the surface of the adsorbent is positively or negatively charged. The result indicates that metal ions adsorption is favourable at pH value higher than pH$_{pzc}$, while anion adsorption is favoured at pH values lower than pH$_{pzc}$ [28]. Due to the presence of functional group such as OH− group, cationic adsorption is favoured at pHc > pH$_{pzc}$, whereas, anionic adsorption is favoured at pH < pH$_{pzc}$ where the surface becomes positively charged [29].

Effect of contact time

The effect of contact time (10 - 120 min) on Cd (II) and Ni (II) removal efficiency and the amount of adsorbed at equilibrium was investigated. When the contact time increased from 50 to 120 min, the removal efficiency of both metal ions from effluent wastewater increased from 38.47 % to 85.6 % for HA and from 22.08 % to 69.43 % for AA as seen in Fig. 4. A rapid removal

of both heavy metal ions occurs during the first 10 min of the interaction. This observation may be attributed to the presence of more than enough surface adsorption sites on the surface that facilitated rapid attachment of metal ion on surface and penetration into the adsorbent pores in a short period [18, 26, 30].

Effect of adsorbent dosage

Adsorbent dosage is an important factor affecting the adsorption process by determining the amount of adsorbate removed [31]. In the present study, the effect of adsorbent on the removal of Cd (II) and Ni (II) from aqueous solution was determined by changing the adsorbent doses from 0.1 to 0.5 g at 40°C, for a contact time of 50 and 90 min and at fixed pH of 7. As shown in Fig. 5, the removal efficiency increased from 82.06 % to 98.97 % for HA and it increased from 45 % to 65 % for AA. The discrepancy between the binding sites and holding capacity of the adsorbent makes it less efficient towards the removal of both heavy metal ions at low adsorbent dosage. However, when the adsorbent
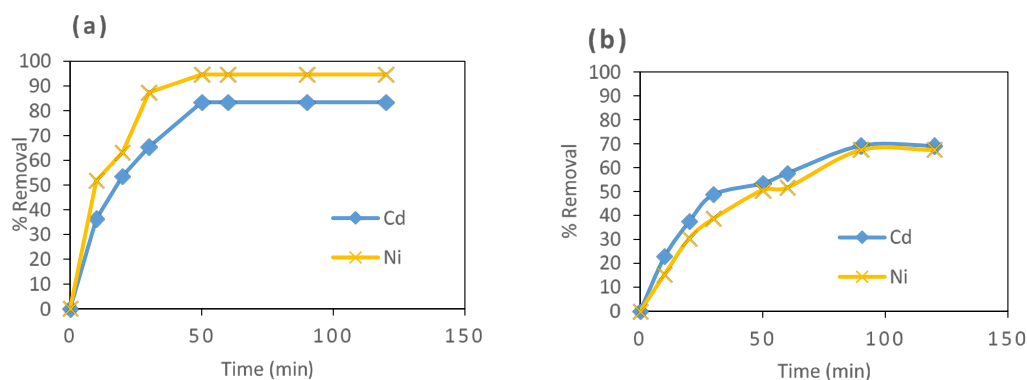

Fig. 4. Effect of contact time on adsorption of Ni (II) and Cd (II) onto (a) HA and (b) AA at agitation speed = 190 rpm, mass = 0.1 g, and temperature = 25°C.
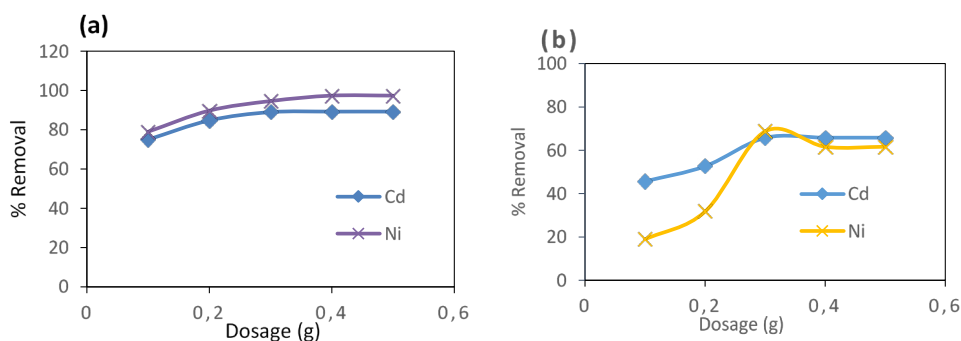
Fig. 5. Effect of adsorbent dosage on adsorption of Ni (II) and Cd (II) onto (a) HA and (b) AA at agitation speed = 190 rpm, mass = 0.1 g, and temperature = 25°C.

dosage is increased, more Cd (II) and Ni (II) ions were retained by excess surface center which have not yet been saturated [32]. Therefore, an adsorbent dosage of 0.4 g for HA and 0.3 g for AA was chosen for the subsequent studies.

Effect of temperature

The influence of temperature on the adsorption process was studied within the temperature range of 25°C – 45°C. The removal efficiency of both metal ions from aqueous solution increased from 50.52 % at 25°C to 85.22 % at 45°C as shown in Fig. 6. Both metal ions uptake increased with temperature and the positive effect of temperature on removal of both metal ions from the effluent is an indication that active sites present on the surface increased and thus improved adsorption performance [33].

Effect of pH

The effect of pH on the adsorption of metal ions from effluent wastewater was also investigated over a pH range of 2 - 12 while keeping other variables con-

stant: 0.1 g adsorbent dosage, the temperature of 25°C and a contact time of 50 min and 90 min. The removal efficiency of the metal ion was 32.63 % at pH 6 increased to 54.36 % at pH 7.0, while that of acetic acid showed a similar trend as shown in Fig. 7. The result confirmed with the result obtained by Salleh [34], and Dim and Termtanun [35].

Adsorption isotherms

The data obtained from the batch adsorption experiments were analysed by Langmuir, Freundlich and Temkin isotherms. The validity of the models was compared, to the value of the linear correlation coefficient (R^2). The adsorption parameters of three models (equations 3, 6 and 8) were used. The plot obtained from the experimental data was compared with those obtained from the Langmuir, Freundlich and Temkin isotherm models in Table 3 and also depicted in Figs. 8 and 9 respectively. The values of R^2 suggest that the Langmuir isotherm provides the best conformity with experimental data when compared to the Freundlich and Temkin models. Thus, it indicates that both adsorbents contain uniform
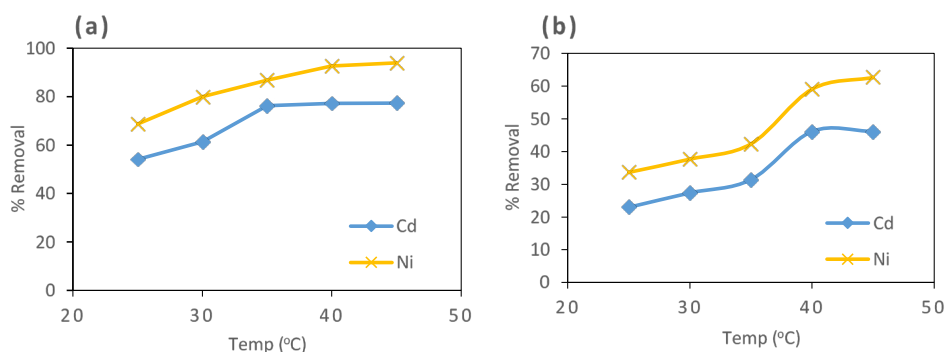

Fig. 6. Effect of temperature on adsorption of Ni (II) and Cd (II) onto (a) HA and (b) AA at agitation speed = 190 rpm and mass = 0.1 g.
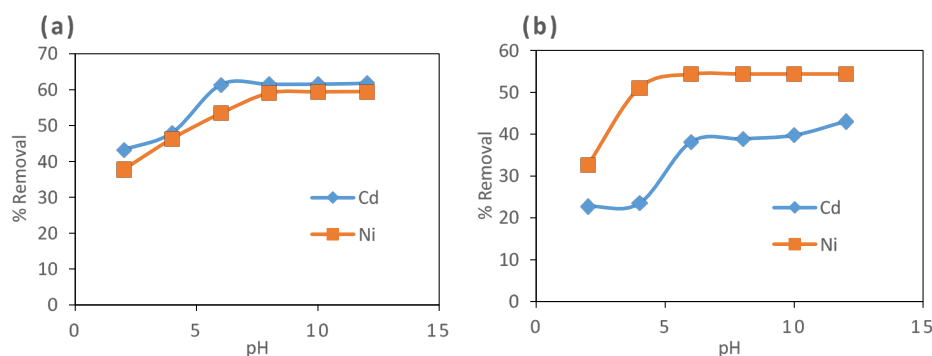
Fig. 7. Effect of pH on adsorption of Ni (II) and Cd (II) onto (a) HA and (b) AA at agitation speed = 190 rpm, mass = 0.1 g, and temperature = 25°C.

adsorption sites and thus enables the anion species to form a monolayer. A similar result was reported for Cd (II) and Ni (II) removal by kaolinite clay [36], ball clay [37], beidellite clay [38]. The value of separation factor (R_L), which was obtained is less than one which indicated that the adsorption of the two-metal ion onto HA and AA is a favourable process as shown in Table 3.

The comparison of monolayer adsorption capacities of clay adsorbents for Cd (II) and Ni (II) ions such as acid activated kaolin [39] and Turkish illitic clay [40] shows that HA and AA have adsorption capacities in agreement with other reports (Table 4). Being economical and easily available, modified clay would serve as effective adsorbents for the removal of Cd (II) and Ni (II) from textile wastewater.
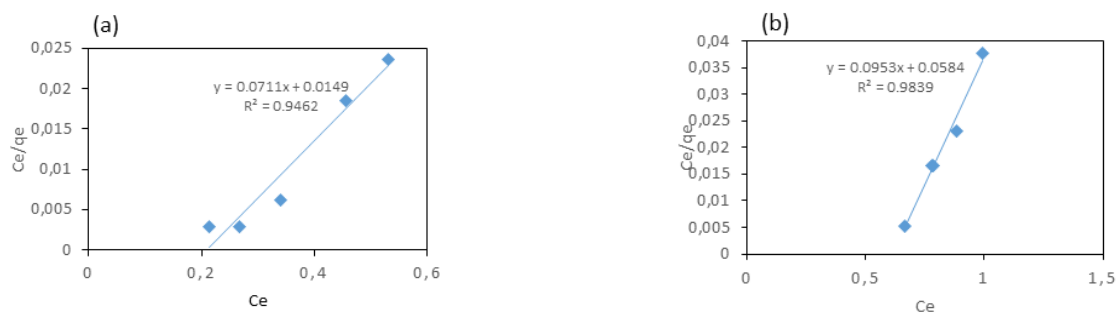

Fig. 8. Langmuir isotherms for (a) Ni (II) and (b) Cd (II) adsorption onto HA.

Table 3. Three-parameter isotherm constants and correlation coefficients.

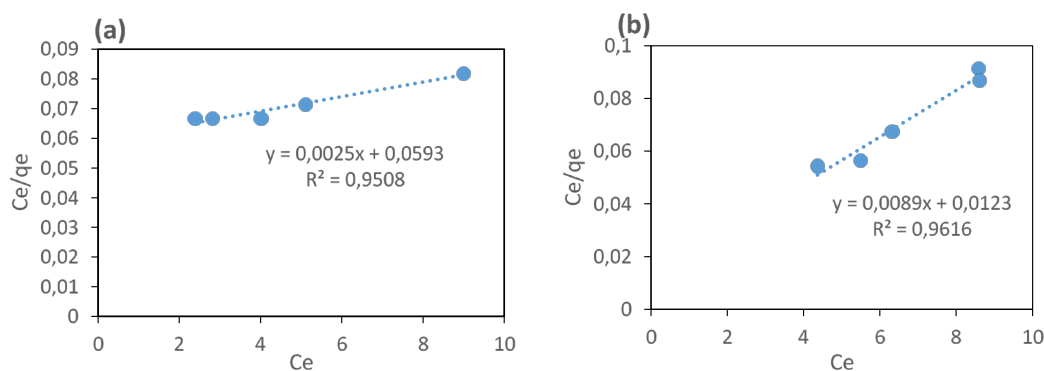| Isotherm	HA		AA	
Parameters	Cd	Ni	Cd	Ni
Langmuir				
q_m(mg g^{-1})	10.49	14.06	40.01	11.23
b (L g^{-1})	0.096	0.075	0.994	0.926
R_L	0.985	0.990	0.788	0.989
R^2	0.9839	0.9462	0.9541	0.9616
Freundlich				
K_F	1.534	2.208	2.406	1.500
n	1.52	0.584	6.623	1.271
R^2	0.7577	0.8994	0.8648	0.6135
Temkin				
A_T	263.78	728.91	16.54	50.23
B_T	$1.18*10^8$	$1.59*10^8$	$1.99*10^8$	$3.16*10^8$
R^2	0.6627	0.9161	0.9637	0.7226

Fig. 9. Langmuir isotherms for (a) Ni (II) and (b) Cd (II) adsorption onto AA.
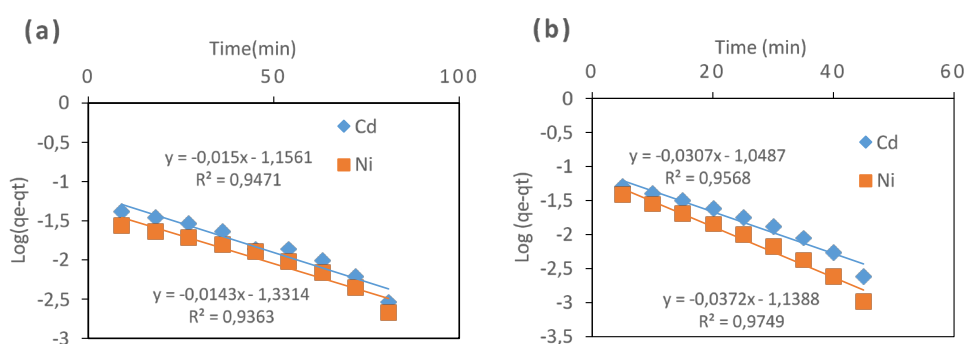

Fig. 10. Pseudo-first order for adsorption of Ni (II) and Cd (II) onto (a) HA and (b) AA.

Adsorption kinetics

Adsorption kinetic parameters were determined following the pseudo-first-order, pseudo-second-order models and are listed in Table 5. The linear plots of models for the two metal ions adsorption onto HA and AA are depicted in Fig. 10 for first order and Fig. 11 for the second order. The best fit model was chosen based on the linear correlation coefficient (R^2). The values of R^2 indicate that the pseudo-first-order model does not fit the adsorption data. However, the R^2 values of 0.999 and 0.997 for Cd and 0.995 and 0.998 for Ni of pseudo-second order model suggests a better fit. Therefore, it may be concluded that the adsorption process of both metal ions by HA and AA are chemisorption controlled [3]. As seen in Fig. 10 the plot of q_t against t = 2 is not linear, indicating that the adsorption process of Cd (II) and Ni (II) onto modified clay involves more than one step.

In the first step, the mass transfer of the adsorbate to the external surface of the adsorbent takes place, which is further evidence supporting a better correlation between pseudo-second-order model.

Table 4. Adsorptive capacity of some clay adsorbent used to remove Cd (II) and Ni (II) from aqueous medium.

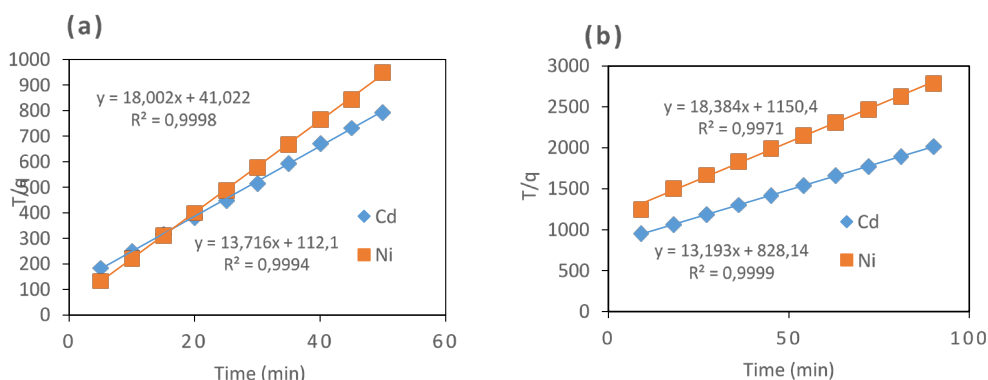| Adsorbent	Adsorbate	q_m (mg g^{-1})	References
HA	Cd (II)	10.49	This study
AA	Cd (II)	40.01	This study
Ball clay	Cd (II)	27.27	[28]
Beidellite clay	Cd (II)	42.00	[29]
Turkish illitic clay	Cd (II)	11.25	[31]
HA	Ni (II)	14.06	This study
AA	Ni (II)	11.23	This study
TBA - Kaolinite	Ni (II)	15.23	[33]
ZrO - Kaolinite	Ni (II)	8.40	[34]
Montmorillonite	Ni (II)	11.20	[14]

Fig. 11. Pseudo-second order for adsorption of Ni (II) and Cd (II) onto (a) HA and (b) AA.

Table 5. Kinetic parameters for adsorption of Cd (II) and Ni (II) onto HA and AA.

Metals	HA				AA			
	Pseudo first order kinetics							
	$q_e exp$ (mg g^{-1})	$q_e cal$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_e exp$ (mg g^{-1})	$q_e cal$ (mg g^{-1})	k_1 (min^{-1})	R^2
Cd	0.0629	0.5873	0.0585	0.9345	0.0446	0.7328	0.0493	0.9753
Ni	0.0533	0.3202	0.0857	0.9748	0.0323	0.3147	0.0345	0.9471
	Pseudo second order kinetics							
	$q_e exp$ (mg g^{-1})	$q_e cal$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2	$q_e exp$ (mg g^{-1})	$q_e cal$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
Cd	0.0629	0.0555	7.914	0.999	0.0446	0.0544	0.2937	0.997
Ni	0.0533	0.0340	0.089	0.995	0.0322	0.0375	0.6584	0.998

Thermodynamic of adsorption

The values of thermodynamic parameters for adsorption of Cd (II) and Ni (II) onto modified clay are listed in Table 6. The negative ΔG^o values determined at all temperatures indicate that the adsorption process is spontaneous and feasible. The positive value of ΔS^o highlights the affinity of modified clay towards the metal ions and also an increased degree of disorder at the adsorbent adsorbate interface [32], and occurrence of some structural changes during the adsorption process [33]. The positive value of ΔH suggests an endothermic nature of the adsorption of both Cd (II) and Ni (II) by the adsorbent over the temperature range of 298 – 318 K. The value of ΔH, which is below the value corresponding to physical adsorption [27].

CONCLUSIONS

Acid modification of Umunze clay shows potential in the adsorption of Cd (II) and Ni (II) from textile wastewater. The BET surface area of modified clay was about four times more than that of raw clay which may be responsible for high adsorption of metal ions. The results showed that the Langmuir isotherm model provided the best fit for equilibrium data, indicating that adsorption process was mainly monolayer. The adsorption kinetics was satisfactorily described by the pseudo-second-order model. Based on the thermodynamic parameters such as enthalpy ($\Delta H°$), entropy ($\Delta S°$), and Gibbs free energy changes ($\Delta G°$), the sorption of Cd (II) and Ni (II) ions onto modified clays is a spontaneous and endothermic process.

Real industrial wastewater was successfully treated this confirmed that modified clay could be a more effective and economical adsorbent for the removal of heavy metal ions from aqueous solution. Therefore, is recommended the modified adsorbent can be used to treat wastewater with concentration range of 0.151 – 0.025 and 0.1125-0.0059 for Cd (II) and Ni (II) respectively. This material sourced locally will support local and national economy and also help to lower environmental pollution.

Table 6. Thermodynamic parameters for adsorption of Cd (II) and Ni (II) onto HA and AA.

HA				
Adsorbate	Temp (ºC)	ΔH (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})	ΔG^o (kJ mol^{-1})
Cd	298	26.5324	0.093009	-1.18413
	303			-1.64917
	308			-2.11422
	313			-2.57926
	318			-3.0443
Ni	298	38.345	0.217261	-26.3989
	303			-27.4852
	308			-28.5715
	313			-29.6578
	318			-30.7441
AA				
Adsorbate	Temp (ºC)	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})	ΔG^o (kJ mol^{-1})
Cd	298	45.63555	0.155389	-0.67032
	303			-1.44726
	308			-2.22416
	313			-3.0011
	318			-3.77805
Ni	298	22.2466	0.101805	-8.09127
	303			-8.60029
	308			-9.10932
	313			-9.61834
	318			-10.1274

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