Enhancing Adsorption Capacity of a Kaolinite Mineral through Acid Activation and Manual Blending with a 2:1 Clay

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ABSTRACT: The efficiencies of raw and modified kaolinite mineral in removing selected heavy metal ions from their respective aqueous solutions were investigated. The mineral was modified through two different methods; i) activation with HNO3, H2SO4, H3PO4, CH3COOH and C2H5O2 acids to form NK, SK, PK, AK and OK acid activated clays respectively and ii) preparations of 3:1 and 1:1 Kaolinite: Bentonite blends to form UBK and EBK composites respectively through manual blending. The adsorbents were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red Spectroscopy (FTIR) and Brunauer Emmett Teller (BET) analysis for surface area determination. The surface area increased in some of the modified clays from 114.9457 m2/g (RK) to 288.685 m2/g (EBK), 205.92 m2/g (UBK), 162.227 m2/g (NK), 151.335 m2/g (SK), and 115.837 m2/g (OK) but reduced to 113.872 m2/g (PK) and 112.865 m2/g (AK) after modification. Adsorption studies were subsequently conducted out to remove Pb2+, Cd2+ and Ni2+ ions from synthetic solutions. Pb2+ was found to be most removed (383.5 mg g−1 (RK), 591.13 mg g−1 (EBK), 576.61 mg g−1 (UBK), 475 mg g−1 (NK), 450 mg g−1 (SK), and 425 mg g−1 (PK), 375 mg g−1 (OK) and 375 mg g−1 (AK)) with highest removals on the composites.

KEYWORDS: Kaolinite, Bentonite, Composites, Adsorption, Heavy metals

I. INTRODUCTION

Industrial wastewaters have been found to contain heavy metal ions such as lead, cadmium, chromium and nickel amongst others (Berihun and Solomon, 2017, Huang et al., 2020, Dim et al., 2021, Aziz et al., 2023). The metals bioaccumulate because of their non-susceptibility to biodegradation and also exhibit carcinogenic tendencies causing them to be considered as hazardous pollutants. Thus, their removal from industrial wastewaters before their discharge into the water environment is highly necessary (Khalfa et al., 2020, Balali-Mood et al., 2021, Razzak et al., 2022). To accomplish this feat, various wastewater treatment techniques have been evaluated out of which adsorption is proposed to be the most preferable due to reasonable costs of design and operation (Uddin, 2017, Dim et al., 2021, Malima et al., 2021).

Activated carbon remains the choice adsorbent for adsorption of pollutants from wastewaters but the costly methods of operation and regeneration challenges necessitated the current growth spurt in the search for alternative cheaper adsorbents (Crini et al., 2019, Almeida-Naranjo et al., 2023). Several materials have been evaluated as suitable alternatives but most of them have been discovered to be accompanied by challenges such as low adsorption capacities, premature fouling, short half-life among others all of which have made their industrial use for remediation purposes impractical (Aragaw and Bogale, 2021). All of these justify the increasing attention focused on natural minerals especially clays because of their local availability, natural abundance, and modification potentials (Ngulube et al., 2017, Li et al., 2020)

Adsorption of pollutants on natural clay minerals have been successfully carried out and it has also been demonstrated to be enhanced by the modification of the clay surfaces (Mudzielwana et al., 2019). Modified clays are however not without their own shortcomings, but acid activated clays have been found to provide the most advantages associated with modification. This is due to their ease and low cost of production (Özcan and Özcan, 2004, Mohammed-Azizi et al., 2013, Lawal et al., 2020).

Kaolinite clay, being a 1:1 mineral has mostly been reported in literature to possess lower capabilities than 2:1 clay minerals in wastewater treatments and to give better performance in its raw than the activated form (Bhattacharyya and Gupta, 2008). However, Kaolin deposits are reported to be widespread throughout Nigeria such that most states in the country have at least one known deposit which makes it to be easily accessible (Badmus and Olatinsu, 2009, Adeniyi et al., 2020). Thus, it is necessary to find a way of improving its abilities as an adsorbent through simple and practical methods.

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such as acid activation or formation of composite with 2:1 mineral that has higher adsorptive abilities.

In this study, Kaolinite mineral was purified through sedimentation after which some purified samples were modified with (0.1M) acetic, oxalic, nitric, sulphuric and phosphoric acids. Some parts of the clay were also used to form 3:1 and 1:1 Kaolinite:Bentonite composites with Bentonite mineral through manual blending of both. The raw as well as modified clays were characterized by Brunauer Emmett Teller (BET) surface area analysis, Fourier Transform Infra-red (FTIR), X-ray Diffractogram (XRD), and Scanning Electron Microscope (SEM). Preliminary experiments were conducted on the raw clay to establish optimum conditions for the removal of Pb\(^{2+}\), Cd\(^{2+}\) and Ni\(^{2+}\)ions from their respective aqueous solutions. The optimum operating conditions obtained were used for subsequent evaluations on the modified clays.

II. THEORETICAL ANALYSIS

A. Adsorption Isotherms

The experimental data was tested with different adsorption isotherm models to determine the maximum adsorption capacities of the Kaolinite and understand the relationship between the adsorbent and adsorbate at equilibrium (Akpomie and Dawodu, 2016, Pathania et al. 2017, Omer et al. 2018). The data was fitted into Langmuir, Freundlich, Dubinin-Radushkevich (DBR) and Fowler-Guggenheim (FG) models using the linearized forms of their equations as presented in Eqs. 1 to 4 respectively:

\[
\frac{C_e}{q_e} = \frac{1}{K_d q_m} + \frac{1}{q_m} C_e
\]

(1)

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

(2)

\[
\ln q_e = \ln q_{m} - k_{ads} e^2
\]

(3)

\[
\ln \left(\frac{C_e}{\theta}\right) = -\ln K_F + 2W\theta \left(\frac{1}{\theta}\right)
\]

(4)

Where, \(q_e\) and \(C_e\) are the solid phase concentration (mg g\(^{-1}\)) and equilibrium concentration of the metal ions (mg L\(^{-1}\)) respectively, \(q_m\) is the maximum adsorption capacity (mg g\(^{-1}\)) while \(K_L\) (L mg\(^{-1}\)) is an empirical Langmuir constant associated with the affinity of the binding site. In Eqn. (2), \(K_F\) and \(n\) and \(\alpha\) and \(\beta\) are Freundlich constants related to adsorption capacity and heterogeneity of sorption respectively. In the DBR linearized equation, \(c\) denotes the Polanyi potential and is given as [RTln(1+ 1/Ce)], \(q_m\) is the theoretical saturation capacity (mg g\(^{-1}\)) and \(k_{ads}\) is a constant related to mean free energy of adsorption per mole of the adsorbate (mol\(^2\)/kJ J\(^{-1}\)) (Hamdouou and Naffrechoux, 2007; Foo and Hameed, 2010, Bahl et al, 2012, Nordin et al., 2020, Nandiyanto, 2020). For FG isotherm (Eqn. 4), the values ln [(Ce (1-\(\theta\)))/\(\theta\)] were plotted against \(\theta\) and the values of \(W\) (the interaction energy between adsorbed molecules kJmol\(^{-1}\)) and \(K_F\) (Fowler–Guggenheim equilibrium adsorption constant (L mg\(^{-1}\)) were determined.

B. Kinetics Studies of Adsorption Data

Kinetic modelling of the adsorption data was accomplished using pseudo first order, pseudo second order, and elovich models through the appropriate plots to determine the values of important kinetic parameters. The model whose regression coefficient R\(^2\) was closest to unity and whose experimental values correlated closely to calculated parameters was used to determine the controlling mechanism of the sorption process (Sukpreabprom et al., 2014, Akpomie and Dawodu, 2016, Pathania et al., 2017, Omer et al., 2018).

1) Pseudo first order model

The linearized Lagergren’s equation was used to test for pseudo first order kinetics:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}
\]

(5)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
\]

(6)

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t.
\]

(7)

\[
q_t = k_{ad} t^{1/2} + C_t
\]

(8)

Where, \(k_1\) and \(k_2\) are the pseudo first and pseudo second order rate constants (min\(^{-1}\)), \(k_{ad}\) is the intraparticle diffusion rate constant, \(q_e\) and \(q_t\) are amounts of adsorbates adsorbed at time \(t\) and equilibrium respectively (mg g\(^{-1}\)) while \(\alpha\) and \(\beta\) are constants that represent the initial adsorption rate (mg min g\(^{-1}\)) as well as the extent of surface coverage (g mg\(^{-1}\)). (Abechi et al., 2011, Boparai et al., 2011).

2) Thermodynamic Studies

Thermodynamic parameters such as changes in free energy change (∆G), enthalpy (∆H) and entropy (∆S) were estimated from the data using the Eqns. 9-12 (Boparai et al, 2011, Al-Anber 2011):

\[
\Delta G = -RT\ln K
\]

(9)

\[
\Delta G = \Delta H - T\Delta S
\]

(10)

Substitution of equation 9 in to 10 gives the vant’ Hoff equation (Levine, 2009; Omer et al 2018):

\[
\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]

(11)

K was calculated as follows:

\[
K = \frac{q_e}{C_e} \times M_{adsorbate} \times C
\]

(12)

In Eqn. 12, \(M\) is the molecular weight of the adsorbed species, and \(C\) is the concentration of the solution (Omer et al (2018)). The plot of lnK against 1/T at the different temperatures enabled the determination of the thermodynamic parameters (Sukpreabprom et al, 2014, Akpomie and Dawodu 2016, Pathania et al., 2017, Omer et al., (2018)).

III. MATERIALS AND METHODS/METHODOLOGY/EXPERIMENTAL PROCEDURE

A. Materials

The 2:1 clay mineral used in the study was Bentonite and it was obtained from Afuze deposit, Edo State while the kaolinite was sourced from Share, Kwaara state, Nigeria. The chemical reagents that were used include: Cadmium sulphate (CdSO\(_4\)·8H\(_2\)O; Molecular weight (MW); 208.47g mol\(^{-1}\), 99.99%); Lead nitrate (Pb(NO\(_3\))\(_2\); MW; 331.21g mol\(^{-1}\), 99.0%); Nickel sulphate (NiSO\(_4\)·6H\(_2\)O ; MW; 154.76 g mol\(^{-1}\), 99.99%); Nitric acid (HNO\(_3\); MW; 63.01 g mol\(^{-1}\), 90%); Phosphoric acid ( MW ; 98.00 g mol\(^{-1}\), 85%); Hydrochloric acid (MW; 36.46 g mol\(^{-1}\), 97%), Sodium hydroxide (MW; 40.0 g mol\(^{-1}\), 98%); Acetic acid (MW; 60.05g mol\(^{-1}\), 98%) and...
Oxalic acid (MW: 90.03 g mol$^{-1}$, 85%). All reagents were of analytical grade and obtained from BDH Limited, England and Merck, Germany.

B. Experimental Procedure

1) Purification of Kaolinite Clay Mineral

A purification method previously described (Ho et al., 2001; Bhatt et al., 2012) was adopted and modified. It entailed the soaking of 10g of clay in 500 ml of de-ionized water in a 5 L cylindrical plastic container and allowing the resulting suspension to stay undisturbed for 24 hrs. The mixture was subsequently subjected manual stirring for 30 min and left to equilibrate for additional 4 hrs for sedimentation of impurities to occur. The pure clay was separated through careful decantation and subsequent centrifugation using (KUBOTA-6500) at 4000 rpm for 20 min. The wet recovered clay was dried at 80 °C, ground, labelled and stored in airtight sample bottles. The purification method was repeated several until considerable quantity was sufficiently purified.

2) Acid Modification

An acid-activation method earlier described (Ozcan and Ozcan, 2004, Akpomie and Dawodu, 2016) was modified and adopted. A 250 ml of 0.1 M acid was added to 50 g of purified clay in a 500 ml beaker and magnetically stirred for 30 min. The wet acid modified clay was recovered through the same process as the wet purified form earlier described. The clay was subsequently washed thoroughly with de-ionized water until pH 7 was attained. The moist acid-activated clay was dried in an oven at 105 °C for 2 hrs, appropriately labelled and stored.

3) Preparation of Composites of Kaolinite and Bentonite Minerals

A method already described in literature (Daniel-Mkpume et al., 2011; Edoziuno et al., 2016) was modified and used for the preparation of the clay composites. Appropriate amounts of the purified clays to obtain 25:75% and 50:50% composites of Bentonite: Kaolinite mixtures were weighed into two separate 250 ml beakers. Just enough de-ionized water to make slurries was added in each after which the mixtures were stirred vigorously until homogeneity was achieved. This was followed by drying in the oven at 120 °C for 2 hrs after which the samples were ground and kept in air-tight bottle.

4) Characterization of raw and modified clays

The mineral constituents of the different clay samples were analyzed by measurements using a multipurpose Bruker D8-Advanced X-ray diffractometer with continuous operations of 0-0 scan locked in coupled mode with Cu-Kα radiation at i-Themba Labs, South Africa. The surface of the Bentonite clay was imaged by Hitachi SU 8230, model Oxford LINK ISIS at Georgia Institute of Technology, (USA). Fourier Transform Infrared (FTIR) spectra were generated with Shimadzu IR Affinity-1S spectrophotometer through mull technique at the University of Cape Town, South Africa. The surface areas of the adsorbents were estimated via Nitrogen adsorption/desorption isotherms measurements at -196°C on a Micromeritics Tristar 3020 Porosimeter also at the University of Cape Town, South Africa. The total specific surface area ($S_{BET}$) was determined by the Brunauer-Emmet-Teller (BET) method while the t-plot method was used for the determination of the micropore volume. The total pore volume was calculated at the relative pressure $p/p_0$ of 0.97 while the pore size distribution was evaluated through the Barrett-Joyner-Halenda (BJH) method.

5) Adsorption Analysis

Stock solutions of the heavy metal ions were prepared through the dissolution of required amount of respective metal salt (Pb(NO$_3$)$_2$, NiSO$_4$ · 6H$_2$O, CdSO$_4$ · 8H$_2$O,) in appropriate volume of deionized water. Subsequently, a 100 ml of varying concentrations (10-250 mg L$^{-1}$) of metal solution was introduced into 6 different 250 ml conical flasks and pH adjustments (2 to 4.5 for Pb and 2-7 for Ni and Cd) of the solutions were achieved by dropwise addition of dil. nitric acid (HNO$_3$) and sodium hydroxide (NaOH) when necessary. A 40 mg of raw kaolinite clay was added into each flask after which they were placed in a rotary shaker at 250 rpm at varying conditions of temperature 30 – 60°C, and time (10 min – 3.5h). At the end of each time interval, the contents of the flasks were centrifuged at 3000 rpm for 20 min and then filtered. The residual concentrations of the metals in the supernatant solutions were determined by Atomic Absorption Spectroscopy using a Buck 200 spectrophotometer at ROTAS Soil Lab Limited, Ibadan, Nigeria.

The amounts of the metal ions adsorbed were determined using Eqn. (13):

$$ q_e = \frac{C_0 - C_e}{m} \times V \tag{13} $$

Where; $q_e$ is the quantity of metal adsorbed (mg g$^{-1}$). $C_0$ is the initial concentration of the metal in the aqueous solution (mg L$^{-1}$) $C_e$ is the concentration of the ions at equilibrium (mg L$^{-1}$) $m$ is the mass of the adsorbent (g) V is the volume of metal solution used (L)

IV. RESULTS AND DISCUSSION

A. Characterization of raw and modified adsorbents

1) Results of XRD Analysis

The XRD spectrum in Figure 1a confirms the identity of the raw kaolinite mineral by identifying peaks at 20 positions (12.34, 19.82, 24.8, 38.38 and 61.96) (Kumar and Lingfa, 2020; Moretti et al., 2020). It also suggests high purity of the clay as Kaolinite is the only identified crystalline phase in the sample indicating the absence of other crystalline phases like quartz and mica (Hai et al., 2015).

It can be observed form Figure 1b that the acid-activated kaolinites retained the structure and crystallinity of the raw clay with insignificant lowering of intensities of the assigned peaks. This implies that de-crystallization of the clay during acid treatment occurred which is a confirmation of the interaction of the acids with the clay surface (Novakovic et al., 2008). Decline in intensity has previously been reported to be
greatly influenced by the strength of the acid (Kumar et al., 2013) and this was also the case in this study as the trend was found to be SK > NK > PK ~ OK > AK.

The typical characteristics of bentonite as a 2:1 mineral to naturally occur with associated minerals is represented by its XRD spectrum in Figure 1c. The composition of the clay includes dominant phases of sodium montmorillonite (Na-Bentonite) at (2θ = 8.47, 19.79, 34.95, 54.27, 62.13 and 71.15), kaolinite at (2θ = 12.3, 19.82, 38.38 and 61.96) and quartz at (2θ = 21, 26.58, 39.38, 50, 51 & 60). It also contains trace amounts of goethite, microcline as and albite high. Quartz is a common impurity found in clay minerals (Olise et al., 2018, Ihekweme et al., 2020). As evident from Figure 1d, the peaks of the raw kaolinite mineral remain unchanged in U-BK having higher intensities for kaolinite peaks but lower for quartz as well as the montmorillonite peaks, but the peaks are narrower in E-BK. Nontronite, and other associated minerals were also found in E-BK while they are absent in U-BK probably due to the higher amount of the 2:1 mineral in the former. The presence of these minerals might not be detrimental to the adsorption characteristics of the clay composites as adsorption studies have been carried out successfully on some of them especially nontronite (Gupta et al, 2006, Guerra et al, 2016, Ye and Fu, 2019) and goethite (Adegoke et al., 2014, Adebayo et al., 2020).

3) Fourier Transform Infrared Spectroscopy Analysis Results

The spectrum of the raw Kaolinite is shown in Figure 3a from which the functional groups present were identified. The absorption bands at 3687.90, 3622.32 and 3618.46 cm⁻¹ correspond to the inner surface –OH stretching vibrations specific to Kaolinite minerals and further affirms the clay as kaolinite (Sdiri et al., 2011, Bukalo et al., 2017, Alshameri et al., 2018, Ihekweme et al., 2020). The Al – Al – OH and Si – O – Si stretching vibrations are suggested by absorption bands at 1006.84, 1026.13 and 1114.86 cm⁻¹ and 3618.46 cm⁻¹ (octahedral sheet) respectively (Bertagnolli and da Silva (2012); Al-Ashameri et al., 2018, Unuabonah et al, 2008, Madejova et al, 2002 and Panda et al, 2010). The absorption
Figure 1b Comparison of the raw and acid-activated clays' XRD spectra

Figure 1c: XRD spectrum of raw Bentonite (RB)
Figure 2: Scanning Electron Micrograph images of Raw kaolinite, AK, NK, SK, PK, OK, UBK, EBK, RB and RK

Figure 1d: Compared view of the XRD spectra of the raw clays and composites
bands at 462.92, 682.80, and 532.35 cm\(^{-1}\) indicate bending vibrations of Si – O – Si and Si – Al – O and groups (Novakovic et al., 2008), Bertagnolli and da Silva (2012) and Ozdes et al., 2011).

The spectra in Figure 3b shows no appreciable changes in the absorption bands of the clay after acid treatment. However, further careful study of the FTIR raw data indicated that absorption bands at 3687.90, 3622.32 and 3618.46 cm\(^{-1}\) attributed to –OH stretching vibrations were retained only in acid activated clays SK, OK and PK but at reduced intensities. However, there was shift of the absorption band at 3687.90 cm\(^{-1}\) to 3689.83 cm\(^{-1}\) and 3684.04 cm\(^{-1}\) in NK and AK respectively. The absorption band at 1114.86 cm\(^{-1}\) was retained in most of the acid clays with lowered intensities except for NK where the intensity was higher. The absorption band at 1026.13 cm\(^{-1}\) shifted to 1028.06 cm\(^{-1}\) in NK while that at 1006.84 cm\(^{-1}\) shifted 1002.98 cm\(^{-1}\) in SK, OK and PK. The trio S–K, P–K and O–K exhibited shifts of the Al – Al – OH stretching vibrations at 914.26 cm\(^{-1}\) to 910.40 cm\(^{-1}\) and to 912.33 cm\(^{-1}\) in NK. There was a reduction in intensity of the absorption band at 790.81 cm\(^{-1}\) that was retained in all the acid activated samples except in NK where there was a shift 788.89 cm\(^{-1}\). The band at 682.80 cm\(^{-1}\) was maintained but with higher intensity in NK and a shift to 678.94 cm\(^{-1}\) in AK, OK, PK and SK with reduced intensities. In PK, OK and SK, the absorption band 532.35 cm\(^{-1}\) moved to 528.50 cm\(^{-1}\) and 534.28 cm\(^{-1}\) in NK but remained in AK. The 462 cm\(^{-1}\) absorption band assigned to Si – O – Si remained intact after acid treatment in most of the acid activated samples except in NK where it shifted to 464.84 cm\(^{-1}\). The changes in intensities of original bands identified in the raw clay and movements of some to new positions in the acid activated samples suggest the de-alumination of the clay and leaching of replaceable cations which is expected after acid treatment. Similar findings have been reported (Novakovic et al., 2008, Akpomie and Dawodu, 2016 and Ihekweze et al., 2020).

The characteristic bands 3691.75 cm\(^{-1}\) and 3610.45 cm\(^{-1}\) of the kaolinite mineral are visible on the spectral of the composites. However, the intensities of the absorption bands of the clay composites E-BK and U-BK in Figure 3c were lower than those exhibited by the minerals independently over the entire IR region and this has been previously reported (Madejova et al., 2002). In addition, the intensities of the band at 3622.32 cm\(^{-1}\) were higher than those of 3687.90 cm\(^{-1}\) band in both U-BK and E-BK because of the contribution of the bentonite (Madejova et al., 2002). All FTIR bands exhibited by the raw sample RK were retained in U-BK except for Si – O – Si vibration bands at 1026.13 cm\(^{-1}\) and 1006.84 cm\(^{-1}\) that shifted to 1010.70 cm\(^{-1}\) and 1002.98 cm\(^{-1}\) respectively. In E-BK, the smectitic character was more pronounced in the bands 1624 cm\(^{-1}\), 910.40 cm\(^{-1}\) and 912.33 cm\(^{-1}\) that represent –OH bending, Al – Al – OH stretching and Si – O – Al bending vibrations in the parent smectite respectively. Smectites are not usually easily detectable in Kaolinite/Smectite mixtures except at high content which was probably why smectitic character were only detected in the composite with the highest content of montmorillonite (Madejova et al., 2002).

4) **BET analysis results**

A fundamental justification for modification of clay minerals is the improvement of the surface properties through the enhancement of the adsorption area and void capacity; properties that have been reported to be closely proportional to the adsorption tendencies and capacities of clay minerals (Sarma et al., 2016 and Dim et al., 2021). The surface areas of the adsorbents obtained from BET analysis along with their pore volumes and sizes are listed in Table 1a and b.

As can be observed from Table 1a, acid-activated clays NK, SK as well as OK have higher surface areas than the raw while reduction occurred in AK and PK. The order of which is NK (162.227 m\(^2\)/g) > SK (151.335 m\(^2\)/g) > OK (115.837 m\(^2\)/g) > RK (114.946 m\(^2\)/g) > PK (113.872 m\(^2\)/g) > AK (112.865 m\(^2\)/g).

![Figure 3a: FTIR spectrum of Raw Kaolinite (RK)](image-url)
The increase was only substantial in strong acid clays NK and SK, moderately so for organic acid clay OK but lowered in the weakest acid clays AK and PK. There was a reduction in the total pore volume of AK (0.51269 cm$^3$/g) from (0.70588 cm$^3$/g) RK but increase in NK (0.80587 cm$^3$/g), SK (0.80055 cm$^3$/g), OK (0.71187 cm$^3$/g) and PK (0.71213 cm$^3$/g).

The acid-activated clays NK (11.84 nm), SK (16.03 nm) have lower pore diameters than RK (23.88 nm) which is less than those of OK (25.14 nm), PK (27.04 nm) and the highest AK (27.56 nm). These alterations in surface area, pore volume and size of the raw clay in the acid-activated clays can be attributed to removal of impurities, replacement of exchangeable cations and generation of Silica. All these allowed more surface creation in most of the acid-activated forms. Reports of the enhancement of surface areas of clay minerals through acid activation have been documented in literature (Kumar et al, 2013, Alvarez, et al 2017, Dim et al, 2021 and Malima et al, 2021).

The surface areas of the composite (UBK (205.92 m$^2$/g) and EBK (288.685 m$^2$/g)) are both higher than that of the raw kaolinite (RK (114.946 m$^2$/g)) but lower than the natural bentonite’s (RB (288.868 m$^2$/g) as can be observed from Table 1b. The pore volume also increased and decreased in the composites as compared with the raw kaolinite and bentonite.
respectively. The pore sizes however are lower in the composites than in the kaolinite but higher than that of the bentonite. This suggests that the introduction of bentonite into kaolinite mineral can increase its surface area (UBK) almost to the magnitude of the raw bentonite (EBK) depending on the amounts of each mineral in the composite. It is also noteworthy that the surface areas of the composites were also higher than those of the acid-activated clays, thus, the surface characteristics of kaolinite can be improved by preparing composites with bentonite mineral.

Table 1a: BET analysis result of raw and acid-Kaolinite

<table>
<thead>
<tr>
<th>Parameter</th>
<th>RK</th>
<th>AK</th>
<th>NK</th>
<th>OK</th>
<th>PK</th>
<th>SK</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area, S_{BET} (m²/g)</td>
<td>114.946</td>
<td>112.865</td>
<td>162.227</td>
<td>115.837</td>
<td>113.872</td>
<td>151.335</td>
</tr>
<tr>
<td>Langmuir surface area (m²/g)</td>
<td>260.374</td>
<td>194.491</td>
<td>274.091</td>
<td>268.049</td>
<td>256.956</td>
<td>267.503</td>
</tr>
<tr>
<td>External specific area (m²/g)</td>
<td>123.275</td>
<td>80.5647</td>
<td>141.733</td>
<td>115.442</td>
<td>112.252</td>
<td>132.453</td>
</tr>
<tr>
<td>Micropore area (m²/g)</td>
<td>19.3005</td>
<td>15.452</td>
<td>20.4937</td>
<td>19.169</td>
<td>20.3941</td>
<td>20.2247</td>
</tr>
<tr>
<td>Micropore volume (cm³/g)</td>
<td>0.00541</td>
<td>0.00617</td>
<td>0.00864</td>
<td>0.00626</td>
<td>0.00635</td>
<td>0.00706</td>
</tr>
<tr>
<td>Total pore volume (cm³/g)</td>
<td>0.70588</td>
<td>0.51269</td>
<td>0.80587</td>
<td>0.71187</td>
<td>0.71213</td>
<td>0.80055</td>
</tr>
<tr>
<td>Pore diameter (nm)</td>
<td>23.88</td>
<td>27.56</td>
<td>11.84</td>
<td>25.14</td>
<td>27.04</td>
<td>16.03</td>
</tr>
</tbody>
</table>

Table 1b: BET Analysis Results of raw and clay composites

<table>
<thead>
<tr>
<th>Parameter</th>
<th>RK</th>
<th>RB</th>
<th>UBK</th>
<th>EBK</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area, S_{BET} (m²/g)</td>
<td>114.946</td>
<td>288.868</td>
<td>205.92</td>
<td>288.685</td>
</tr>
<tr>
<td>Langmuir surface area (m²/g)</td>
<td>260.374</td>
<td>729.109</td>
<td>283.615</td>
<td>686.344</td>
</tr>
<tr>
<td>External specific area (m²/g)</td>
<td>123.275</td>
<td>280.549</td>
<td>280.574</td>
<td>291.659</td>
</tr>
<tr>
<td>Micropore area (m²/g)</td>
<td>19.3005</td>
<td>51.3943</td>
<td>25.128</td>
<td>22.8972</td>
</tr>
<tr>
<td>Micropore volume (cm³/g)</td>
<td>0.00541</td>
<td>0.02365</td>
<td>0.0083</td>
<td>0.0071</td>
</tr>
<tr>
<td>Total pore volume (cm³/g)</td>
<td>0.70588</td>
<td>0.90848</td>
<td>0.72492</td>
<td>0.74956</td>
</tr>
<tr>
<td>Pore diameter (nm)</td>
<td>23.88</td>
<td>11.20</td>
<td>19.35</td>
<td>18.12</td>
</tr>
</tbody>
</table>

B. Adsorption studies

1) Effect of pH

It is highly crucial to investigate the pH dependence of adsorption processes because the pH significantly influences the speciation and degree of ionization of the adsorbate ions as well as the surface charges of adsorbents (Rahmani et al., 2010). In this study, the uptake of the heavy metal ions was found to be enhanced with increase in pH to a maximum of pH 7 for Cd²⁺ as well as Ni³⁺ and pH 4 for Pb²⁺ as shown in Figure 4a.

These findings correlate with earlier reports of effective adsorption of metal ions at higher pH values where less competition for adsorption sites between [H₃O⁺] and the positively ions is obtainable (Ozdas et al., 2011, Sari and Tuzen, 2014, and Mohamed et al., 2019). However, the investigation was not extended beyond pH 7 and 4.5 for Ni³⁺ as well as Cd²⁺ and Pb²⁺ respectively because precipitations of the metals were observed beyond these values especially for Pb²⁺ ions whose precipitation have been reported to occur from pH 5 (Lawal et al., 2020) while other metals have also been found to occur at higher pH values (Rahmani et al., 2010, Dawodu and Akpomie, 2014, El-Naggar et al., 2019). There have been reports where adsorption of the studied metals increased with increasing pH (Barka et al., 2013, Akpomie and Dawodu, 2014, Krika et al., 2016, El-Naggar et al., 2018, Chai et al., 2020).

2) Effect of initial concentration

The optimum pH values (pH 4 for lead and pH 7 for Ni and Cd) obtained from the previous experiments were used for the determination of the effects of the initial concentrations of the heavy metal ions. All other condition were the same as the previous experiments except the concentrations of the metal solutions that were varied between 10-250 mg/L.

As represented by Figure 4b, the quantities of heavy metal ions removed increased with increase in their initial concentrations, and this can be attributed to increased concentration gradient obtainable at higher concentrations that created efficient mass exchange between the solid and liquid.

Figure 4a Influence of pH on the adsorption of heavy metal ions
phases (Akporie and Dawodu, 2014, Mohamed et al., 2019).

However, this was obtainable to a maximum of 150 mg/L for Cd\(^{2+}\) and Ni\(^{2+}\) and 200 mg/L for Pb\(^{2+}\) because no significant change occurred in their removals after these concentrations probably as due saturation of the adsorbent’s active sites at higher adsorbate that could have prevented continued deposition of metal ions on the adsorbent. Related findings have been reported by Ozdes et al., 2011, Ghogomu et al., 2013, Mhamdi et al., 2014 and Khalfa et al., 2020.

The overall assessment shows that the raw kaolinite mineral performed moderately in the adsorption of the studied heavy metal ions with 57% of Cd\(^{2+}\), 60% of Ni\(^{2+}\) and 65% of Pb\(^{2+}\) adsorbed in the order was Cd\(^{2+}\) < Ni\(^{2+}\) < Pb\(^{2+}\). The adsorption of heavy metals has been reported to proceed through two different phenomena: complexation and ion exchange. If complexation is the primary mechanism, several factors come into focus such as the properties of the metals, functional groups present on the adsorbent, and pH of the solution (Chao and Chang, 2012, Saxena et al., 2017).

Conversely, if ion exchange was the case, the uptake of the investigated heavy metal ions would vary directly with the ionic radii, the increasing order of which is: Ni < Cd < Pb (Chao and Chang, 2012). The metal ion with the highest potential to form complexes out of all three metals is Ni\(^{2+}\) while Pb\(^{2+}\) and Cd\(^{2+}\) accomplish relatively higher adsorption tendencies through the ion exchange. The order discovered in this study indicates that the adsorption process was a combination of both pathways. Another factor worth considering is the hydrated radii of the ions (Cd\(^{2+}\) = 0.426 nm, Ni\(^{2+}\) = 0.404 nm and Pb\(^{2+}\) = 0.401 nm), and hydration energy (Ni\(^{2+}\) = -2106 kJ mol\(^{-1}\), Cd\(^{2+}\) = -1807 kJ mol\(^{-1}\), Pb\(^{2+}\) = -1481 kJ mol\(^{-1}\)) (Mobasherpour et al., 2012 and Fan et al., 2021).

C. Isotherm modelling for adsorption of heavy metals on RK

The results obtained from the study of effect of initial concentration at equilibrium time were used for isotherm modelling using four models Fowler-Guggenheim, Langmuir, Freundlich, and Dubinin Radushkevic (DBR) equations as shown in Figures 5a-c while the obtained parameters are presented in Table 2.

It can be noted from Table 2 that the Langmuir isotherm gave the best fit for all the three heavy metals with the highest correlation coefficients of 0.9992, 0.9962 and 0.9927 for Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) respectively. The maximum adsorption capacities for the heavy metals were determined to be 109.89 mg g\(^{-1}\), 126.58 mg g\(^{-1}\) and 263.16 mg g\(^{-1}\) for Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\).
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Figure 4c: Influence of temperature on the adsorption of heavy metal ions on Kaolinite

Figure 4d: Influence of time on the adsorption of heavy metal ions on Kaolinite

Figure 5a: Langmuir plots for the adsorption of heavy metal ions on RK
\[ y = 0.4489x + 3.3792 \quad R^2 = 0.9885 \]
\[ y = 0.2977x + 3.4811 \quad R^2 = 0.8441 \]
\[ y = 0.3848x + 2.952 \quad R^2 = 0.9266 \]

**Figure 5b: Freundlich plots for the adsorption of heavy metal ions on RK**

\[ y = -3E-05x + 5.4434 \quad R^2 = 0.8387 \]
\[ y = -4E-06x + 4.8163 \quad R^2 = 0.9724 \]
\[ y = -8E-07x + 4.6062 \quad R^2 = 0.9392 \]

**Figure 5c: Dubinin Radushkevic plots for the adsorption of heavy metal ions on RK**

\[ \ln qe \] vs. \( \ln Ce(1-\theta)/\theta \)

**Figure 5d: Fowler-Guggenheim plots for adsorption of heavy metal ions on RK**
The E values obtained from the DBR equation were all lower than 8 kJ/mol which suggests that the adsorption of the metal ions was physical in nature and mostly through ion exchange mechanism (Inglezakis and Zorpas, 2011, Hu and Zhang, 2019). The positive w values obtained for the three metals from the FG equation suggest lateral interactions between adsorbed moles which indicate exothermic processes of adsorption. While this assumption correlates with the result obtained from the study of effect of temperature on the adsorption of metal ions Pb$^{2+}$ and Ni$^{2+}$, it is contradictory for Cd$^{2+}$ as an endothermic process was found to be the case for the latter. This is probably due to low correlation co-efficient of its data to the isotherm compared to the other two (Hamdoui and Nefrecoux, 2007, Nandiyanto, 2020).

D. Kinetics of adsorption of heavy metals on R-K

The adsorption data was fitted into three different kinetic models viz pseudo-first order, pseudo-second order and Elvich models as shown in Figures 6a-c. It is apparent from these figures (6a-c) that the pseudo-second order gave the best fit for all the metals. The values of the obtained parameters are presented in Table 4.

The R$^2$ values obtained from the pseudo second order model [0.9628 (Cd), 0.9721 (Ni) and 0.9942 (Pb$^{2+}$)] make it to be the best fit to the data. In addition, the derived qe values (147.06 mg g$^{-1}$, 169.50 mg g$^{-1}$ and 238.10 mg g$^{-1}$ for Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ respectively) from the model are in good agreements with qexp values (155.31 mg g$^{-1}$, 179.58 mg g$^{-1}$ and 250.00 mg g$^{-1}$) for Cd$^{2+}$ Ni$^{2+}$ and Pb$^{2+}$ respectively) values obtained from the experiments.

The major underlying principle of the pseudo-second-order model is that two reactions are occurring simultaneously: a fast reaction that attains equilibrium rapidly and a much slower second one whose likely mechanism is:

\[ \text{Clay} + X(II) \rightarrow \text{Clay} \cdot X(II) \]  

For such reaction as above, the kinetics is greatly influenced by the concentration of X(II) ions in the solution and the number of adsorption sites on the clay surface (Meneguin et al, 2017, Yin et al, 2018, Chai et al, 2020). Several studies have reported the adsorption of the studied metal ions to be best described by pseudo-second order kinetic model (Galindo et al, 2013, Krika et al, 2016, Maged et al, 2020, Kakaei et al, 2020).

The regression coefficients obtained from the Freundlich isotherm were also considerably especially for Pb (0.9885) and Cd (0.9266). The Kc and n parameters of the isotherm give insight into the adsorption capacity as well as intensity of the adsorption respectively. For favourable adsorption, n values must fall within 1-10 (Chand and Pakade, 2015, Omer et al, 2018). The n values from the Freundlich isotherm fall within range that suggests favourable adsorption. In addition, the n values obtained for the three metal ions are all greater than one and these implies the physical nature of the adsorption process (Dada et al, 2021, Nandiyanto, 2020).

---

| Table 2 Parameters obtained from isotherm modelling |
|---------------------------------|------|------|------|
| Isotherm models                | Pb$^{2+}$ | Ni$^{2+}$ | Cd$^{2+}$ |
| Langmuir model                | 263.16 | 126.58 | 109.89 |
| $q_e$ (mg g$^{-1}$)           | 0.085  | 4.158  | 0.152  |
| $R^2$                         | 0.9927 | 0.9962 | 0.9992 |
| Freundlich model              | 29.35  | 32.50  | 19.14  |
| $K_f$ (mg g$^{-1}$)(Lmg/L)$^{1/n}$ | 2.23  | 3.36  | 2.60  |
| N                             | 0.9885 | 0.8441 | 0.9266 |
| R$^2$                         | 0.3E-5 | 4.0E-5 | 8.0E-7 |
| DBR model                     | 231.23 | 123.51 | 100.103|
| $\beta$ (mol$^3$)(kg$^2$)     | 3.0   | 5     | 5     |
| E (kJ/mol)                    | 0.12  | 0.35  | 0.79  |
| R$^2$                         | 0.9392 | 0.9724 | 0.8387 |
| FG model                      | 9.61  | 2.39  | 0.17  |
| KFG (Lmg$^{-1}$)              | 3.05  | 5.15  | 4.23  |
| w (kJmol$^{-1}$)              | 0.9192 | 0.911 | 0.8959 |

---

The dimensionless Langmuir parameter of the equilibrium or adsorption intensity RL was further calculated from the Langmuir equation at the different initial concentrations (C$^0$) investigated in the study and the values are presented in Table 3. Three implications of RL values are favourable adsorption (1 > RL > 0), un-favourable adsorption 1 < RL, linear adsorption RL = 1 and RL = 0 for irreversible adsorption (Ozdes et al 2011, Gebretsadik et al, 2020). From the values presented in Table 3. RL values obtained for all the metals (0.045 - 0.541) for Pb, (0.001-0.023) for Ni and (0.026-0.397) for Cd suggest that their adsorption on the surface of the clay were favourable (Qin et al, 2020, Malima et al, 2021).

Table 3: Dimensionless RL values at different initial concentrations of the three heavy metals

<table>
<thead>
<tr>
<th>C$^0$</th>
<th>RL(Pb)</th>
<th>RL(Ni)</th>
<th>RL(Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.541</td>
<td>0.023</td>
<td>0.397</td>
</tr>
<tr>
<td>0.5</td>
<td>0.191</td>
<td>0.005</td>
<td>0.116</td>
</tr>
<tr>
<td>1.0</td>
<td>0.105</td>
<td>0.002</td>
<td>0.062</td>
</tr>
<tr>
<td>1.5</td>
<td>0.073</td>
<td>0.002</td>
<td>0.042</td>
</tr>
<tr>
<td>2.0</td>
<td>0.056</td>
<td>0.001</td>
<td>0.032</td>
</tr>
<tr>
<td>2.5</td>
<td>0.045</td>
<td>0.001</td>
<td>0.026</td>
</tr>
</tbody>
</table>

The regression coefficients obtained from the Freundlich isotherm were also considerably especially for Pb (0.9885) and Cd (0.9266). The Kc and n parameters of the isotherm give insight into the adsorption capacity as well as intensity of the adsorption respectively. For favourable adsorption, n values must fall within 1-10 (Chand and Pakade, 2015, Omer et al, 2018). The n values from the Freundlich isotherm fall within range that suggests favourable adsorption. In addition, the n values obtained for the three metal ions are all greater than one and these implies the physical nature of the adsorption process (Dada et al, 2021, Nandiyanto, 2020).
Figure 6a: Pseudo-first order plots for adsorption of heavy metal ions on RK

Figure 6b: Pseudo-second order plots for adsorption of heavy metal ions on RK

Figure 6c: Elovich plots for adsorption of heavy metal ions on RK
Table 4: Kinetic parameters of adsorption of heavy metal ions on RK

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Pb^{2+}</th>
<th>Ni^{2+}</th>
<th>Cd^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>q_{exp} (mg g^{-1})</td>
<td>250.00</td>
<td>179.58</td>
<td>155.31</td>
</tr>
<tr>
<td>Pseudo-first order model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>q_{exp} (mg g^{-1})</td>
<td>46.70</td>
<td>86.91</td>
<td>118.14</td>
</tr>
<tr>
<td>k_1 (min^{-1})</td>
<td>0.9776</td>
<td>0.5793</td>
<td>1.092</td>
</tr>
<tr>
<td>R²</td>
<td>0.7165</td>
<td>0.8344</td>
<td>0.9507</td>
</tr>
<tr>
<td>Pseudo-second order model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>q_{exp} (mg g^{-1})</td>
<td>238.10</td>
<td>169.50</td>
<td>147.06</td>
</tr>
<tr>
<td>k_2 (min^{-1})</td>
<td>0.0882</td>
<td>0.0272</td>
<td>0.004</td>
</tr>
<tr>
<td>R²</td>
<td>0.9942</td>
<td>0.9721</td>
<td>0.9628</td>
</tr>
<tr>
<td>Elovich model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α (mg g^{-1} min^{-1})</td>
<td>1.76E+13</td>
<td>24.60056</td>
<td>176.8555</td>
</tr>
<tr>
<td>β (g mg^{-1})</td>
<td>0.142</td>
<td>0.035413</td>
<td>0.043395</td>
</tr>
<tr>
<td>R²</td>
<td>0.5186</td>
<td>0.7205</td>
<td>0.7673</td>
</tr>
</tbody>
</table>

Table 5: Thermodynamic parameters of adsorption of heavy metal ions on RK

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>ΔH (kJ mol^{-1})</th>
<th>ΔS (J mol^{-1})</th>
<th>ΔG (kJ mol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb^{2+}</td>
<td>-9.96</td>
<td>-21.30</td>
<td>-3.49</td>
</tr>
<tr>
<td>Ni^{2+}</td>
<td>-62.98</td>
<td>-192.12</td>
<td>-2.12</td>
</tr>
<tr>
<td>Cd^{2+}</td>
<td>16.17</td>
<td>57.41</td>
<td>-1.08</td>
</tr>
</tbody>
</table>

Figure 7a: Vant Hoff plot for the adsorption of Pb^{2+} ions on Kaolinite

Figure 7b: Vant Hoff plot for the adsorption of Ni^{2+} ions on Kaolinite

Figure 7c: Vant Hoff plot for the adsorption of Cd^{2+} ions on Kaolinite

F. Comparative adsorption of heavy metal ions on modified clays

The comparison of the performances of the modified clays in adsorbing the metal ions shown in Figure 8 revealed that the composites were more efficient than the raw and acid-activated kaolinite for the adsorption of the heavy metal ions from their respective aqueous solutions. The highest adsorption recorded on them was probably due to the presence of the bentonite that increased the number of exchangeable cations on the composites thus increasing the number of potential active sites for adsorption. As for the acid-activated
clays, the action of the acids on the clay would have occurred on and limited to the existing active sites on the clay. These results suggest that composite formation between Kaolinite and 2:1 clay can sufficiently enhance the adsorption tendencies of the former and provide a more environmentally friendly method of modifying the clay.

In addition, it can be observed from Figure 8b that the composites also performed better than the raw bentonite for Pb$^{2+}$ and Cd$^{2+}$ ions. These also confirm the advantage of manual composite formation between the two clay minerals because the clayey content of the bentonite was increased and thus enhanced its performance compared to the raw form.

V. CONCLUSION

The adsorption characteristics of a Nigerian Kaolinite in its raw and modified forms have been successfully evaluated. Acid modified kaolinites were prepared using inorganic and organic acids while clay composites were prepared by manually blending raw Kaolinite with a bentonite clay. Analytical techniques used for characterization confirmed the clays to be 1:1 (kaolinite) and 2:1 (Bentonite) minerals as well as the changes that occurred in their properties after modification. The BET surface area of the Kaolinite was significantly increased in the strong acid modified clays and the composites. Adsorption studies of three heavy metal ions
were carried out on the raw clay minerals to determine optimum operating conditions of pH, time, initial metal concentration and temperature and time for each metal. The determined conditions were used for investigations on the modified clays. The Langmuir isotherm was found to give the best correlation to the adsorption for the three heavy metal ions while the Pseudo second order model was the best for the kinetics. The Kaolinite was found to be moderate in adsorbing the heavy metal ions in its raw form, but the performance was highly enhanced through modification especially composite formation with a 2:1 mineral. Furthermore, acid activation with dilute acids enhanced the adsorption potentials of the kaolinite clay and for optimum results, dilute strong inorganic acids are recommended but weaker acids as well as organic acids can also be utilized. These results not only confirm the viability of clay minerals as suitable adsorbents for remediation of heavy metals polluted waters but also suggests that composite formation between Kaolinite and a 2:1 clay can sufficiently enhance the adsorption tendencies of the former thus providing a more environmentally friendly method of modifying the clay.

AUTHOR CONTRIBUTIONS
T. O. Abu: Conceptualization, Methodology, Validation, Writing – original draft, Writing – review & editing. H. I. Adegoke: Supervision, Methodology, Writing – review & editing. E. O. Odegunni: Writing – review & editing. M. A. Shehzad: Methodology, Characterization, Writing – review & editing.

REFERENCES


