Adsorption Of Lead (II) And Nickel(II) From Wastewater Onto A Nigerian Umbuluko Natural And Composite Clay.

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Abstract:
The workability of using modified and unmodified local clays to sequester Lead (II) and Ni (II) ions from aqueous solutions was studied using natural clay obtained from a site in Umbuluko village in Orumba local government of Anambra State, Nigeria assadsorbent. The exchange of inorganic inter layer cations was achieved using cationic Genamine CTAC. The dried clay composite was produced by using ethenylacetate solution. The standard used in this study is scommercialBentonite clay.
The batch technique was employed and effect of contact time, pH, initial metal ion concentration and temperature on the adsorption process was studied. The data obtained from equilibrium studies were fitted with Langmuir isotherm model.

I.   Introduction

Heavy metals discharged into the environment causes serious soil and water pollution, endangering the quality of water and natural resources used for human consumption. Pb (II), Ni (II), Cd (II), Fe (II) and Cr (II) are among the most hazardous as they tend to accumulate in organisms causing numerous diseases and disorders (Inglezakis et. al., 2003, Bailey et.al., 1993). The threat generated by the presence of heavy metals becomes particularly worrisome because of their non–biodegradability, toxicity, persistence and bio-accumulation tendency (Ajjabi and Chouba, 2009, Jain et. al., 2010,Bulut and Bayasal, 2006).

Also heavy metals, when ingested by living organisms react irreversibly with enzymes and protein, thereby causing various diseases and disorders.

As a result of increased awareness of the ecological effects of toxic metals, their removal from solution has received detailed attention in recent years.

Conventional methods for achieving this include chemical precipitation (Mattock et. al., 2002), ion exchange(Dabrowski et. al., 2004) and electrochemical techniques (Koene and Janssen, 2001). These processes are either ineffective or extremely expensive, especially when the metals are present in solutions of low concentrations.

Alternative metal removal methods which are based on metal- sequestering properties of certain natural materials are being considered recently (Hong et. al., 2008).

Adsorption, as an alternative technique for heavy metal removal has proven to be competitive and effective (Wang et. al., 2009).

Activated carbon has been found to be a good adsorbent and is the most commonly used in wastewater treatment (Zainiet. al., 2010). However, because of its high cost of production and regeneration (Babel and Kurniawan, 2003, Kim, 2004). The development of more economical and effective adsorbents has been the target of recent research, several materials has been tried for the removal of heavy metals from wastewater including seaweeds (Senthikumar et. al., 2006), marine algae (Jalah et. al., 2002), kaewsarn, 2002, derhte (Mathialagan and viraraghavan, 2002), clay (veli and Alyuz, 2007) and clay minerals (Bhattacharyya and Gupta, 2008). Clays attract attention due to the heterogeneity of their surfaces and some have been found to sob ions from solutions and release them later, when the conditions charges (Foresteir et. al., 2010). There are about thirty different types of "pure" clays but most natural clays are mixtures of these different types along with other weathered minerals (Ivan and velimin , 1998). Studies have shown that natural clay is an appropriate adsorbent for heavy metal removal due to its efficiency, low cost and availability(Ivan and velimin, 1998), the adsorption

capabilities of natural clay are attributable to their high surface area and exchange capacities (Cuevas et. al., 2009), including the presence of negative charges on the clay mineral structure which can attract positively charged metal ions (Babel and kurniawan, 2003). Clays are two-dimensional structure (Jiang et. al., 2002). Members of smectite group include the dioctahedral minerals montomorillonite, bentonite, beidelite and trioctahedral minerals hectorite (Lirich) (Liu et. al., 2007). The structure of clay will be neutral if:

(1)   An octahedral element contains trivalent cations (usually Al(III) and Fe (III) on two octahedral positions with the vacation in the third octahedral;

(2)   divalentcations (usually Fe(II),Mg (II), Mn (II) occupy all octahedral positions; (3) tetrahedral structural elements contains a Si (IV) tetrahedral layer.

In general, modified clays can be divided into pillared layered clays, organoclays,nanocomposite, acid- and salt- induced, thermally induced and mechanically induced modified clays. (Basak et. al., 2012).

A negatively charged structure can be obtained: (1) By substitution of Si (IV) with Al (III) in a tetrahedral position; (2) By substitution of cations with lower charges with Al (III) or Mg (II) In an octahedral position and in the presence of holes which create negative charge synthesis of nanocomposites can be achieved in the following ways:

(1)Polymenzation in situ (synthesis of thermosetting resin – clay; (2) use of organic solvents (organoclay swells in an organic solvent); intercalating by melting. There are numerous examples of clay modifications, for instance, Wyoming montmorillonite was modified using ultrasonic and hydrothermal methods and cationic surfactant, octadecyltrimethylammonium bromide (ODTMA). Bentonite was modified using dyes, TBAC and CTAB (Xi et. al., 2005, Vilasovaet. al., 2003).

Bentonite was modified using the monomer ethenylacetate (Stojiljkovic et. al., 2013).

Water pollution is caused by industrial effluents which contain heavy metals like Lead (II) and Nickel(II).

Lead is a very toxic metal which causes kidney damage, problems in the reproductive system, liver, brain, central nervous system, blood and blood vessels. It can lead to mental retardation in children.

Acute inhalation and exposure to Nickel produces headache, nausea, respiratory disorder, asthmatic conditions and death (Goyer, 1991, Rendal et. al., 1994).

The aim of the work is the organic modification of Umbuluko--Orumba natural clay using the monomer ethenylacetate, investigation of its properties, influence of temperature on its properties and checking adsorptive properties of the composite for the removal of $Pb^{2+}$and Ni^{2+} from wastewater.

II.   Materials And Methods

Preparation and characterization of Adsorbent:

The natural clay sample was obtained from Umbuluko, Orumba in Anambra State, the raw clay sample were wet refined and sieved to remove impurities and particles, it was dried in an oven at 373K and ground to powder to pass through 250µm sieves, The chemical composition of the clay sample was determined by fourier Transform Infrared Spectrometer (FTIR), X-ray Diffractometer (XRD), Electron Dispersive X-ray (EDX) and Scanning Electron Microscopy (SEM) (Celik, 2010).

PREPARATION OF METAL SOLUTIONS:

All reagents used were AR grade and were used as sourced without further purification. Stock solutions of $1000mgL^{-1}$ Pb(II) and Ni(II) ions were prepared from $Pb(NO_3)_2$ and $NiSO_4.6H_20$ respectively, by dissolving appropriate amount of solid salt in de-ionized water. 0.1MHCL and 0.1M KOH solution were used for pH adjustment (Mishra and Patel, 2009).

Batch Adsorption experiment:

Batch adsorption experiments were carried out to determine the effect of contact time, pH, initial metal ion concentration and adsorbent dose on the metal uptake. The data obtained were used to calculate the adsorbed metal quantity using the mass balance expression.

(1)

Where $q_e$is the amount of heavy metal ions adsorbed per unit weight of clay in mgg^{-1}, $C_i$is the initial metal ion concentration in mgL^{-1}, $C_f$is the final metal ion concentration in mgL^{-1}, V is the volume of solution treated in L and M is the dry mass of clay in g.

All the adsorption experiments were done in triplicates and the mean value determined.

III. Results And Discussions

Organic modifications of Umbuluko – Orumba clay with ethenylacetate using hexadecyltrimethyl ammonium chloride (Genamine CTAC):

Umbuluko – Orumba clay was organically modified using monomer ethenylacetate considering that the clay has inorganic ions in between its interlayers, which were made compatible with organic compound during modification. To achieve organic modification, a compatibility tool was necessary which usually consist of the group of cation-active materials (alkyl ammonium derivative). During the process of organically modifying Umbuluko – Orumba clay withethenylacetate, the cationic surfactant hexadecyltrimethylammoniumchloride was used as compatibility tool. The reaction of cationic exchange was achieved by mixing the aqueous dispersion ofUmbuluko – Orumbaclay and the surfactant solution and the product filtered

The filtered product was washed many times. During the reaction, an exchange of alkylammnium ions of surfactant with the ion situated between clay plates occured which led tp a change of hydrophilic properties of the silicate surface. Also, the reaction of the cationic exchange indicate that the distance between inter layers was increased by severalnanometers. This was due to the vertical orientation of the chains of the surfactant when the available volume of clay grew significantly. The increased width of interlayers between plates of clay enabled interlayer adsorption of themonomer, ethenylacetate bythemechanism of direct incorporation. Therefore, a good geometrical package of monomers into the interlayer of clay was achieved by the influence of Vander Waals interactions making hydrogen bonds between the oxymethylene group of the monomer and the clay surface, as well as the effect of an ion-dipole interaction of the oxymethylene group and the interlayerscations.

CHARACTERIZATION OF ADSORBENTS:

Fourier Transform Infrared (FTIR) Analysis

Spectra of natural and modified Umbuluko clay (Figs.1a and 1b) were obtained and read. Adsorption bands at around $3606cm^{-1}$ in both natural and modified clays can be attributed to the valence vibration of the OH group d the presence of interlayer water ($3492cm^{-1}$). The quantity of adsorbed water in the clay is attributed to the deformation vibration of the H – O – H group (around $1643cm^{-1}$). Bands at around $1030cm^{-1}$ and $779cm^{-1}$ are consequences of Si – O valence vibrations.

With the addition of monomer ethenylacetate, adsorption bands of increased intensity occurred at around $2929cm^{-1}$, which has its origin from vibration of methylene group of ethenylacetate. Analysis of 1R spectra confirmed that the monomer is strongly associated with Umbuluko clay when put in its interlayer space. The result of this is the formation of a new composite which because of the different structure relative to the natural clay and the monomer will have different properties
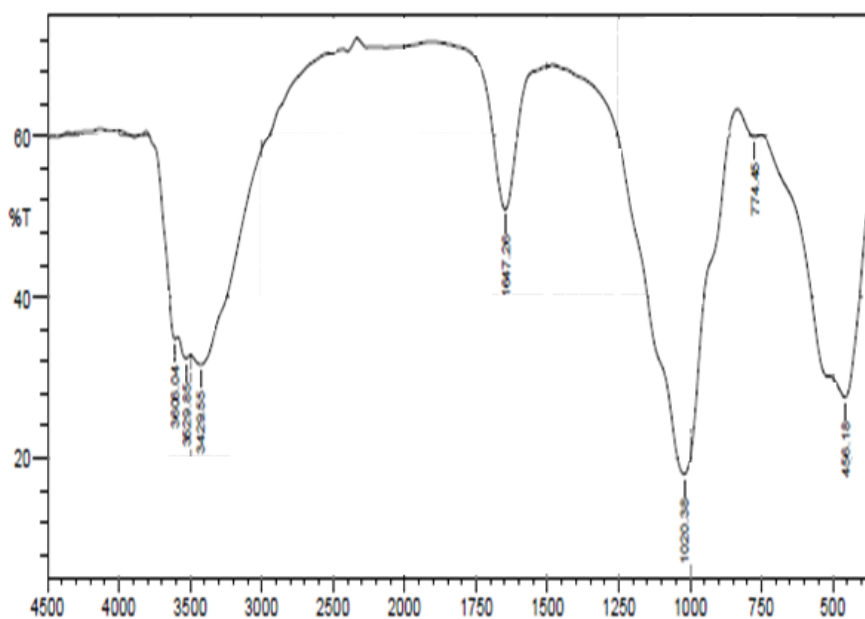
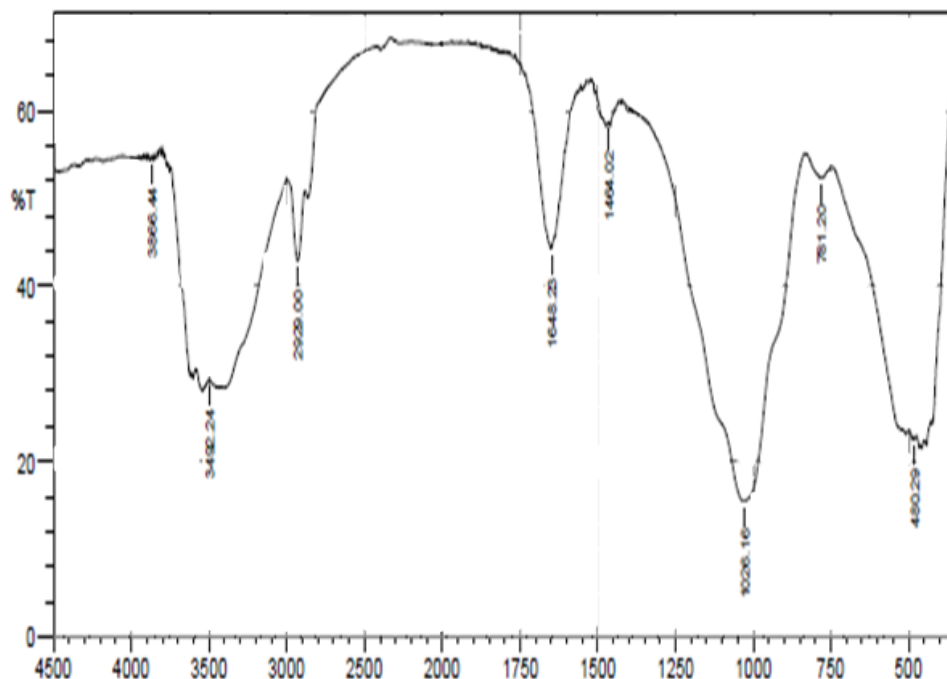

Fig.1a: FTIR SPECTRUM OF UMBULUKO NATURAL CLAY

Fig.1b: FTIR SPECTRUM OF UMBULUKO COMPOSITE CLAY

X – raydiffractometer (XRD) Analysis

XRD analysis of Umbuluko natural and composite clay was carried out (Figs.2a and 2b). The percentage of the compounds found in each of the adsorbent is depicted in Table 1.

The following compounds were identified: SiO_2, Al_2O_3, MgO, Fe_2O_3 as the major constituents(Folleto et. al., 2006, Falaras et. al.,2000, Njiribeaker and Nwaya, 2000) with traces of CaO in the natural clay. After modification of the natural clay, the silica content and the magnesia content of the adsorbents reduced, depicting that they must have been involved in the modification process. These compounds are the adsorbate species removal when natural clay is used in adsorption process (Solener et. al.,2008),(Fig. 2b).
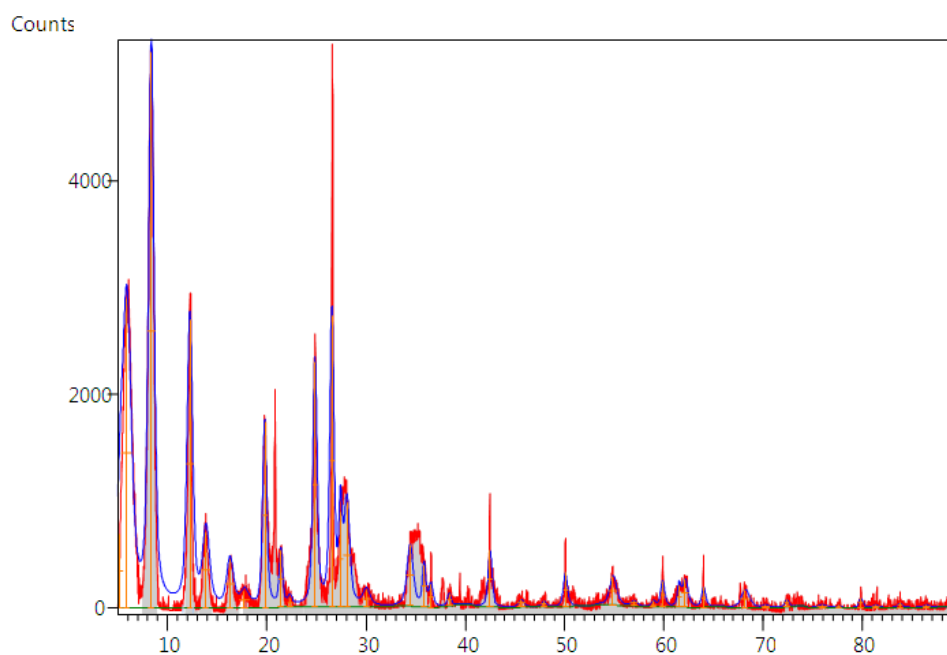

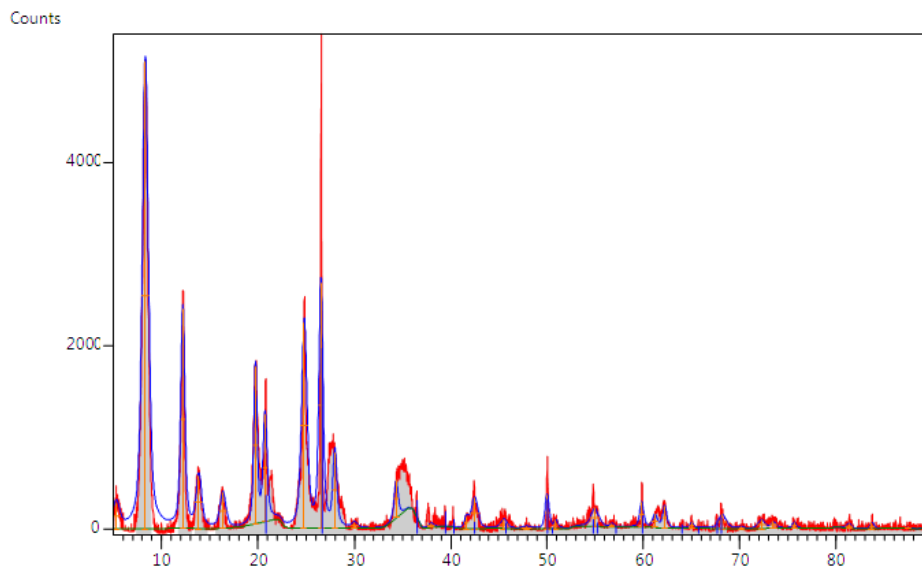**Fig. 2a: X-ray Diffractogram (XRD) spectrum of Umbuluko natural clay.**

Fig. 2b: X-ray Diffractogram(XRD) spectrum of Umbulukocomposite clay.

Table 1:Percentage composition of Umbuluko natural and composite clay.

Compound	SiO$_2$	Al$_2$O$_3$	TiO$_2$	MgO	Fe$_2$O$_3$	FeO	CaO	H$_2$O
Percentage in natural clay	44.08	18.98	2.13	14.50	15.94	8.76	5.18	2.59
Percentage in composite clay	30.76	12.13	17.96	5.62	18.35	7.32	0.0	2.15

Energy Dispersive X- ray Analysis.

The results of the energy Dispersive X – ray (EDX) analysis ofUmbulukonatural clay and its composite clay are presented in Figs.3a and 3b. The figures clearly indicate thatthe clay was carbonaceous since carbon was present in large amount than other elements in the clay sample, this is followed by oxygen and silicon (Table2). The spectra reveal that C, O, Si and Fe are present in the clay swamp. This agrees with the report of Pinnavia (1983) who stated that "Natural clay may be composed of mixture of fine grained clay minerals and clay sized crystals of other minerals such as quartz (SiO$_2$), carbonate and metal oxides (Al$_2$O$_3$.MgO etc) and organic matter" it was observed that Mg and Al that were present in Umbuluko natural clay were not available in the composite clay . These metals (Mg and Al) could have formed salts with the chloride ion from the surfactant (according to equation 3.1 and 3.2) which would have been washed down in the process of preparing the composite clay.
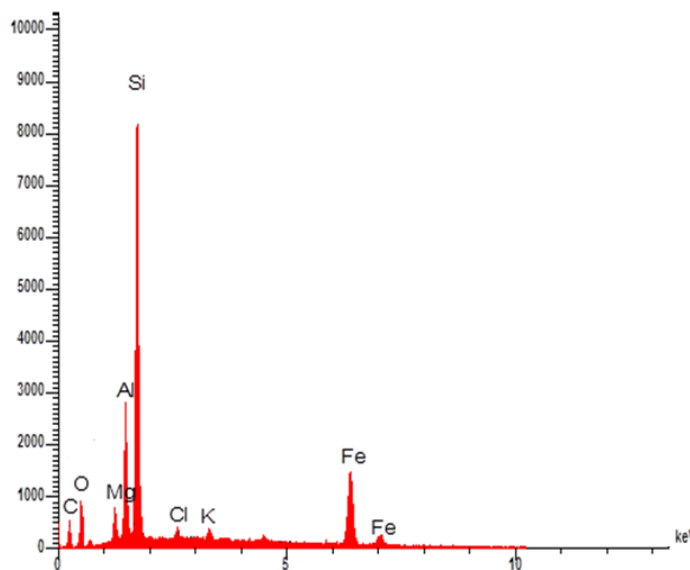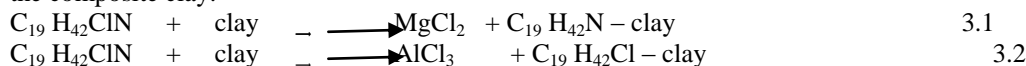
$$C_{19}H_{42}ClN \quad + \quad clay \quad \longrightarrow MgCl_2 \quad + C_{19}H_{42}N - clay \qquad\qquad 3.1$$
$$C_{19}H_{42}ClN \quad + \quad clay \quad \longrightarrow AlCl_3 \qquad + C_{19}H_{42}Cl - clay \qquad\qquad 3.2$$

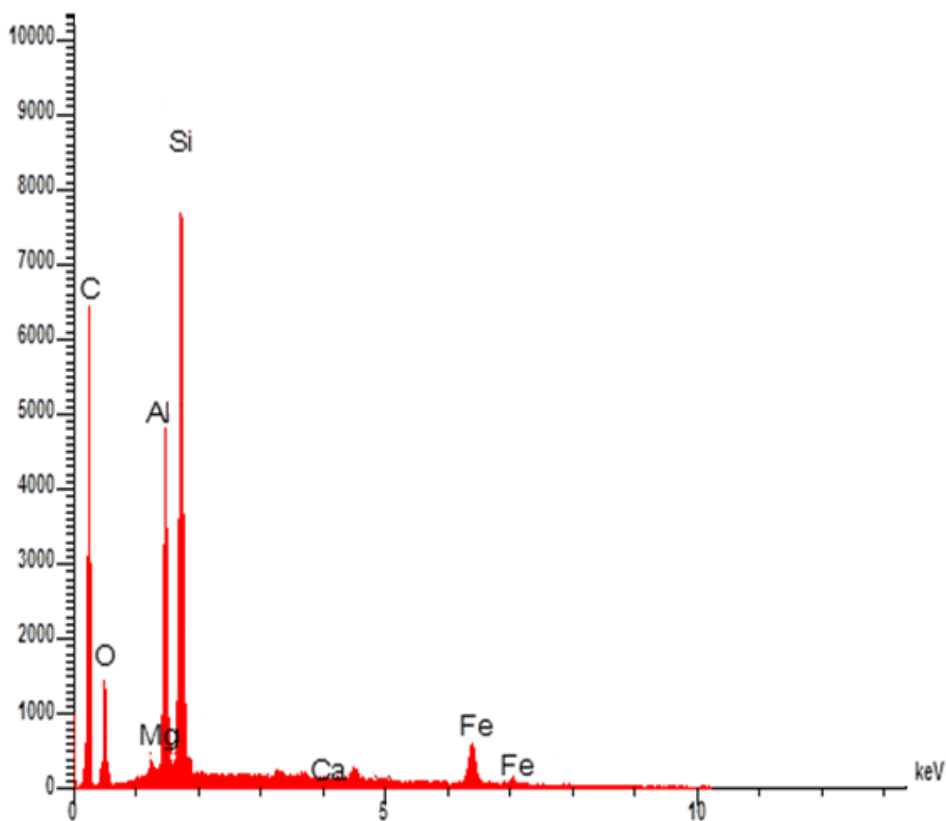**Fig.3a: Energy Dispersive X-ray (EDX) of Umbuluko natural clay.**

Fig.3b: Energy Dispersive X-ray (EDX) of Umbuluko composite clay.

**Table 2: Chemical composition of Umbuluko natural and composite clay**

| Element	C	O	Mg	Al	Si	K	Fe	Cl
% in natural clay	68.72	15.8	1.06	5.51	7.49	0.13	2.95	-
% in composite clay	68.15	14.68	0.0	4.13	6.44	0.77	2.49	0.62

SEM Analysis

A scanning electronic microscope JSM – 5300 (Joel, Japan) was used for the investigation of the upper composite layers of Umbulukonatural clay and its composite clay.

From the obtained SEM record (plate 1a and b), we can clearly see the layered clay structure and group of particles which vary in shape, magnitude and spatial abundance. The SEM image of Umbulukonatural clay (Plate 1a) shows about four large pores which are arranged towards the edges. The SEM image of the composite clay (plate 1b) shows a very large crack at the upper right hand edge of the micrograph and another large crack at the lower right hand edge of the micrograph.

The difference in the morphological characteristics of these materials will actually account for the differences in their adsorption capacities. The large cracks observed in the composite clay might be one of the contributing factors to its higher metal adsorption efficiencies than the natural clay.
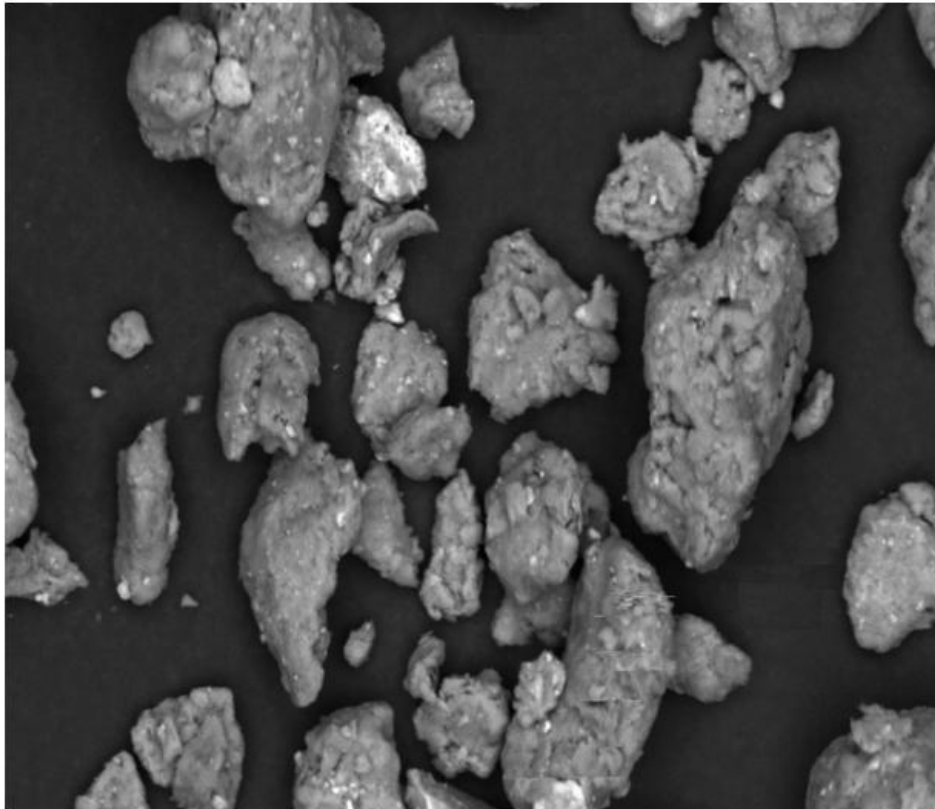
Plate 1a: Scanning Electron Micrograph of Umbulukonatural clay.
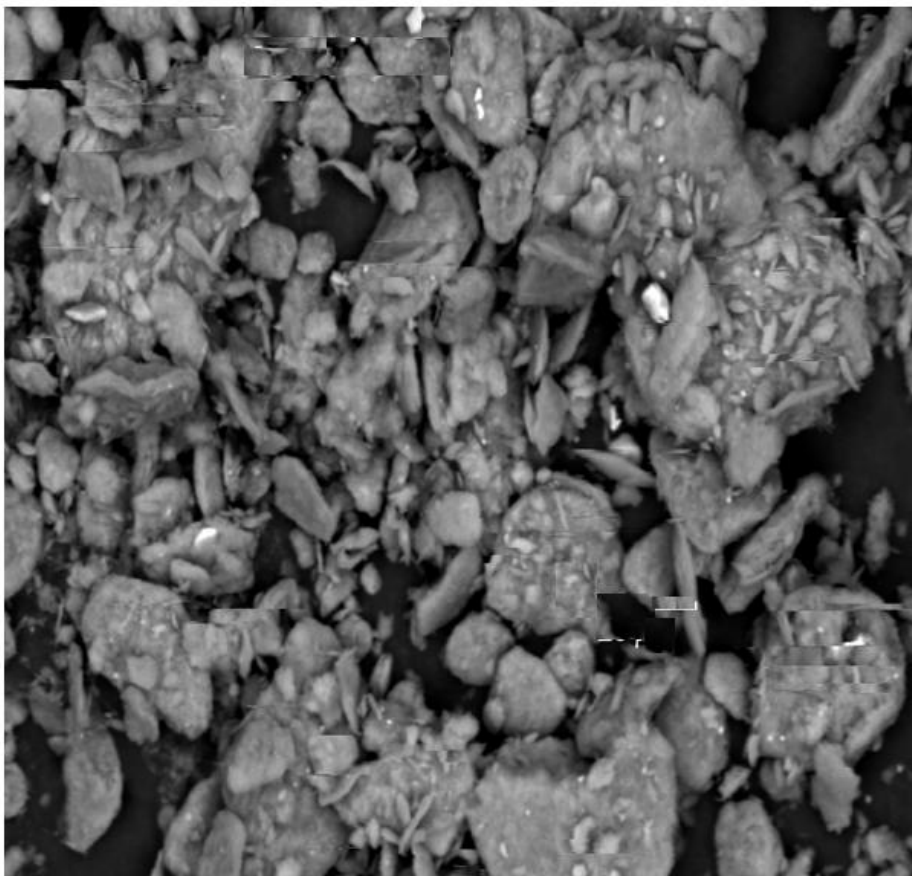
Plate 1b: Scanning Electron Micrograph of Umbuluko composite clay.

EFFECT Of pH ON ADSORPTION OF METALS:

The effect of the initial pH on adsorption of Pb (II) and Ni (II) onto the Umbuluko natural clay and the composite clay was studied at optimumcontact time of 40minutes and temperature of 298K. This is illustrated in Figs. 4a and b. The results reveal that the adsorption capacity of the clay increased with increasing pH, attaining a maximum value at pH 8.0 for Ni (II) and a maximum value at pH 6.0 for Pb (II) which decreases with further increase in pH.

The influence of the solution pH on the adsorption process could be explained on the basis of ion exchange. At low pH, the negative charge on the adsorbent will be occupied by H^+ ions, which will inhibit the approach of positively charged metal ions, consequently reducing metal ions building on the adsorbent surface, causing a decrease in adsorption capacity, as the pH is increased, the adsorbent surface becomes more negatively charged thereby supporting more metals ion adsorption by electrostatic attraction due to columbic forces. Further increase in pH beyond 8 leads to a decrease in the adsorption of metal ions. This is probably due to the formation of anionic hydroxide complexes which decrease the concentration of free metal ions, thereby decreasing the adsorption capacities. This is in line with the observations of other workers (Chantamong et. al., 2001, kaya and Oren, 2005) on comparison of heavy metal adsorption by Thai kaolin and ball clay water.
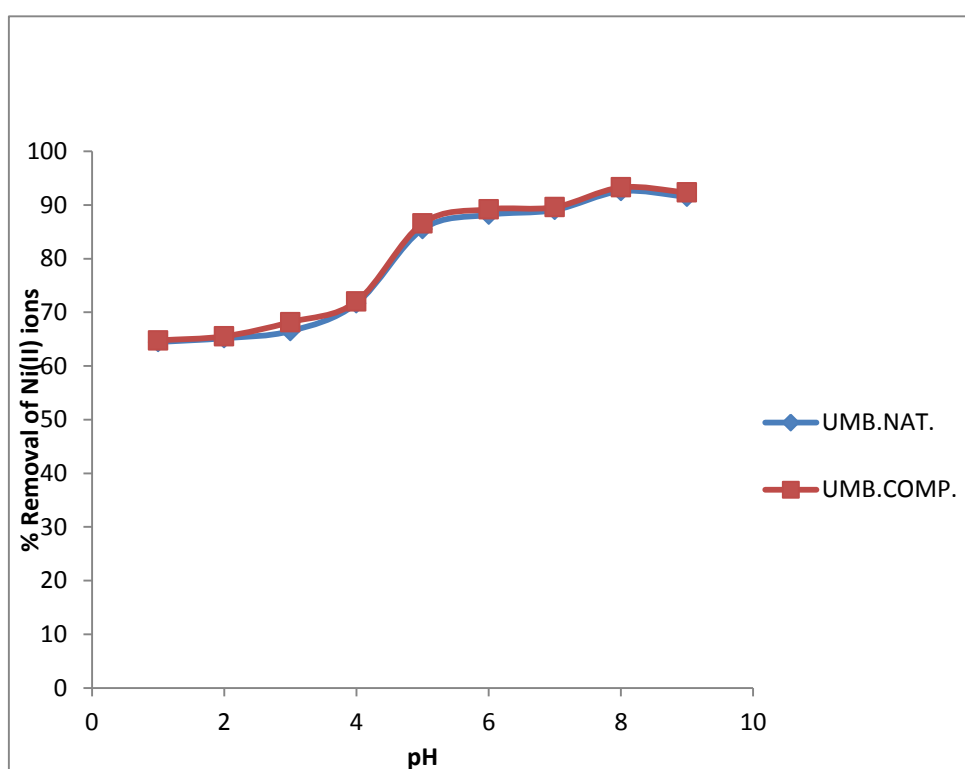

Fig. 4a: Effect of pH on adsorption of Ni^{2+} onto Umbuluko natural and composite clay.

Fig. 4b: Effect of pH on adsorption of Pb^{2+} onto Umbuluko natural and composite clay.

Effect of contact time on adsorption of metals:

The effect of contact time was determined by adding 0.5g of the clay sample (adsorbent) to 50mL of 10 mg L^{-1} solution of Ni (II) and Pb (II) ion in separate conical flasks. The suspensions were maintained at 298k and shaken on a rotary orbital shaker and the samples withdrawn at time intervals of 0-120 minutes and filtered. The concentrations of the metal ions in the filtrates were determined by Atomic Adsorption Spectrophotometer, AAS (Buck Scientific, 2005).

The effect of contact time on adsorption of Ni (II) and Pb (II) onto Umbuluko natural clay and its composite clay is shown in figures 5a and b. The adsorbed metal quantity (qe) increased steadily with time and equilibrium between the metal ions and the clay sample was attained at about 60minutes for unmodified Umbuluko clay and at about 40minutes for the composite clay.

The adsorption rate was rapid in the first 40minutes for unmodified Umbuluko clay and in the first 20minutes for Umbuluko composite clay unitil it decreased gradually to equilibrium. The adsorption rate for unmodified Umbuluko clay was 50.44%, while for the composite clay, it was 82.85%.Umbuluko composite clay showed better adsorption characteristics towards Pb^{2+}and Ni^{2+} ions than thenatural clay. Similar observations were reported by (Stojiljkovic et. al. 2013) on adsorption of lead by modified Bentonite clay.

Fig. 5a: Effect of contact time on adsorption of Ni^{2+} onto Umbuluko natural and composite clay.

Fig. 5b: Effect of contact time on adsorption of Pb^{2+} onto Umbuluko natural and composite clay.

Effect of initial ion concentration on adsorption of metal ion:

Equilibrium experiments were performed by contacting 0.5g of the clay sample with 50mL metal ions having initial concentration in the range 10 to 100 mg L^{-1}. The temperature was maintained at 298k and the suspension shaken for 40 minutes, after which the suspensions were filtered. The filtrate was then analyzed for both Ni (II) and Pb (II) ions.

The dependence of the adsorption capacity of Umbuluko natural clay and composite clay on the equilibrium concentration of Pb(II)and Ni(II) at 298k is presented in Figs. 6a and b. The results reveal that adsorption capacities increased steadily with metal ion concentration. This can be attributed to the increase in the concentration gradient which acts as a driving force for the adsorption process, nevertheless, the increase in adsorption capacity becomes less significant at $C_e>50mgL^{-1}$. This is probably because the active sites on the adsorbent become saturated at this concentration and subsequent increase in concentration does not affect the adsorption capacity. This suggested that adsorption of the ions by Umbulukonatural and composite clay proceeded by a monolayer formation. Similar observation was made by Misthral and Patel (2009). The q$_m$ (mgg^{-1}) parameter again suggested that Umbuluko natural clay exhibits great affinity for Pb(II) and Ni(II) and its composite clay exhibits greater affinity for Pb (II) and Ni(II) than the natural clay, similar results were given by Njoku et. al.,(2014), on heavy metal ion removal by Ezinachi-Okigwe natural clay.

Fig. 6a: Effect of initial metal concentration on adsorption of Ni^{2+} onto Umbuluko natural and composite clay
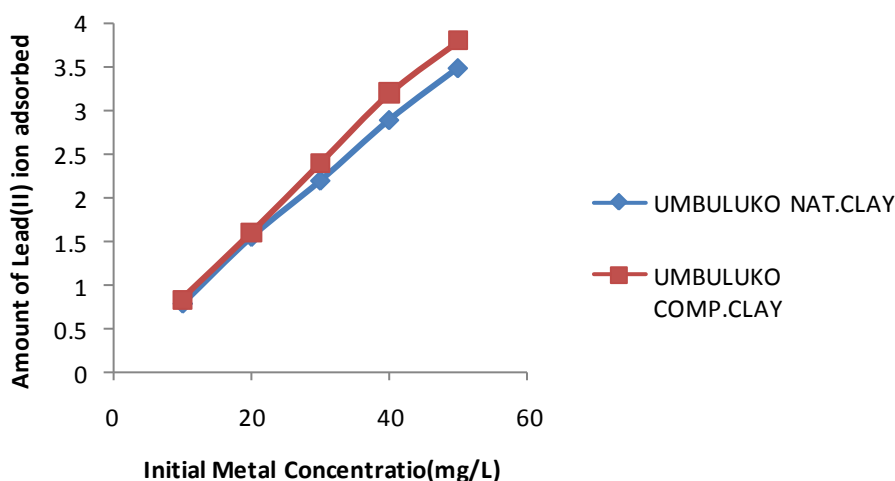
Fig. 6a: Effect of initial metal concentration on adsorption of Pb^{2+} onto Umbuluko natural and composite clay

Adsorption Isotherms:
Langmuir Isotherm:
The experimental data obtained were fitted with the Langmuir adsorption Isotherm. The Langmuir adsorption Isotherm is given by:

(2)

And one of its linear forms is:

(3)

Whereq_e is the equilibrium amount of solute adsorbed per unit weight of adsorbent in mgg^{-1} of clay; C_e is the equilibrium metal concentration in aqueous phase in mgL^{-1}, q_m is the q_e for a complete monolayer in mgg^{-1}, a constant related to adsorption capacity (the maximum amount of metal ion per unit weight of adsorbent) and K_L is a constant related to the affinity of the binding sites and energy of adsorption in Lmg^{-1} and varies with temperature. The equilibrium data for the metal ions over the concentration range studied at 298K were correlated with Langmuir isotherm model by plotting C_e/q_e against C_e. Linear plots obtained are shown in Figs. 7a-d. The Langmuir model parameters,q_m and K_L and the statistical fits of the adsorption data to this model are given in Table 4. The Langmuir model adequately described the adsorption data obtained from Lead(II) and Nickel(II) adsorption onto Umbuluko natural and composite clay. The correlation coefficient, (R^2) for Ni^{2+} - Umbuluko natural clay adsorption and Ni^{2+}- Umbuluko composite clay were respectively 0.7455 and 0.9415. For Pb^{2+}- Umbuluko natural clay adsorption, R^2 was 0.9971 and 0.9981 for Pb^{2+}- Umbuluko composite clay adsorption. Adsorption of Ni^{2+} and Pb^{2+} unto bothUmbuluko natural and composite clay proceeded by a monolayer formation. Similar observation was made by Mishral and Patel (2009). The q_m (mgg^{-1}) parameter again suggests that Umbuluko natural clay exhibits great affinity forPb(II) and Ni(II) and Umbuluko composite clay exhibits greater affinity for Pb (II) and Ni(II) than the natural clay, similar results were given byNjoku et. al.,(2014), for heavy metal ion removal by EzinachiOkigwe natural clay
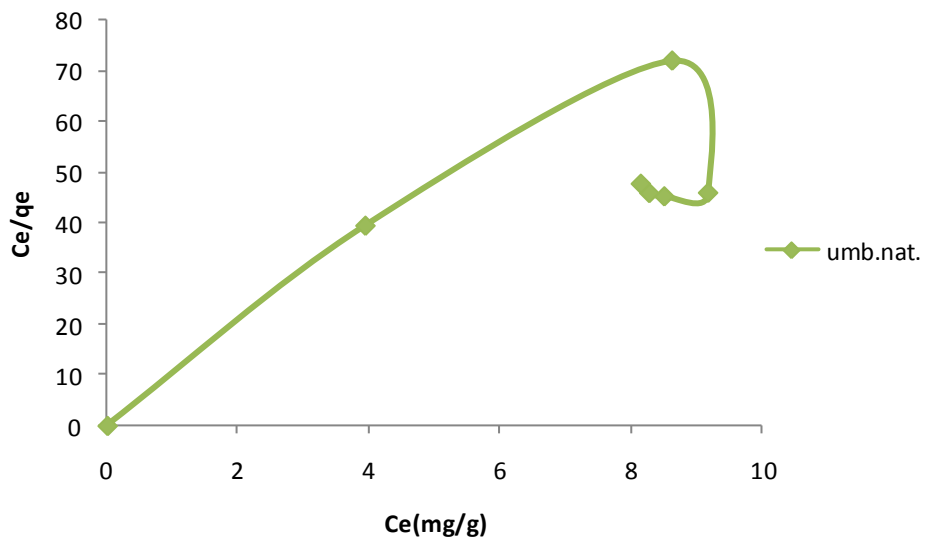
Fig.7a: Langmuir plot for adsorption of Ni(II) ions onto Umbuluko natural clay at 298K
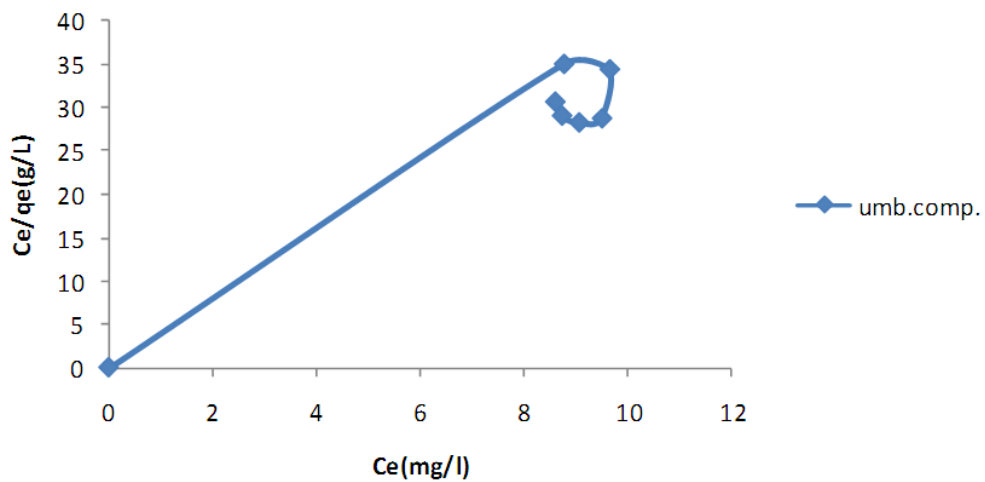

Fig.7b: Langmuir plot for adsorption of Nickel(II) ions onto Umbulukocomposite clay at 298K
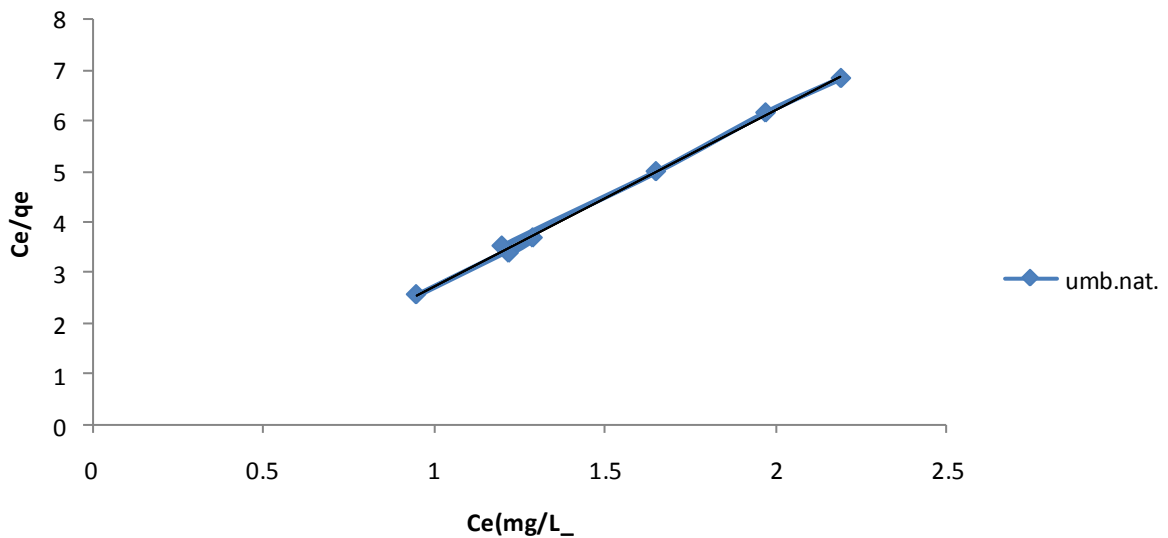

Fig.7c: Langmuir plot for adsorption of Pb(II) ions ontoUmbuluko natural clay at 298K
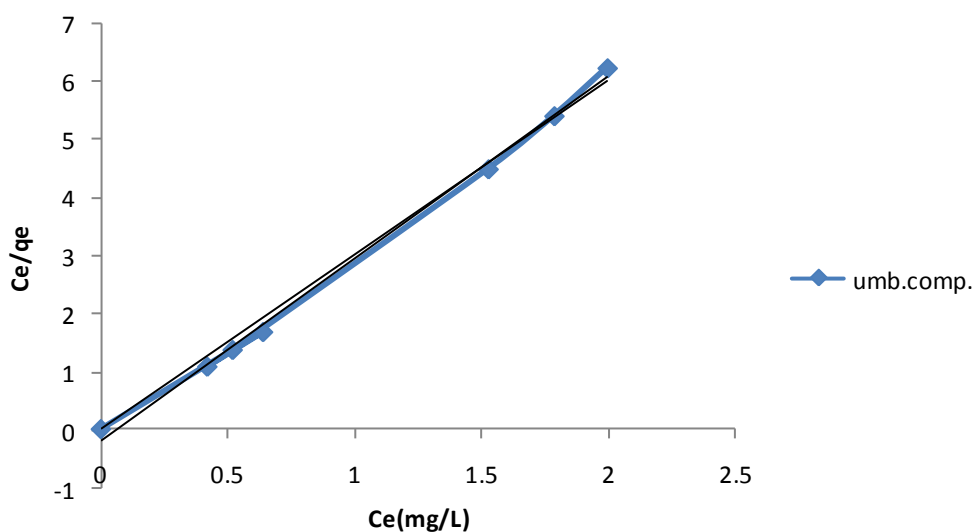
Fig.7d :Langmuir plot for adsorption of Pb(II) ions onto Umbuluko composite clay at 298K

Table 3: Langmuir isotherm parameters for the adsorption of Ni^{2+} and Pb^{2+} onto Umbuluko clay

ADSORBENT-ION	q_e(calc.)	q_e(expt.)	K_L	R^2
Umbuluko Nat.-Ni(II)	0.19	0.2	0.81	0.7355
Umbuluko Comp.-Ni(II)	0.29	0.33	12	0.9415
Umbuluko Nat.-Pb(II)	0.29	0.37	4.59	0.9971
Umbuluko Comp..-Pb(II)	0.32	0.39	16	0.9981

IV.   Conclusion:

The removal of Ni(II) and Pb(II) by Umbuluko natural and composite clay was investigated and the results show high adsorption capacities of the clay samples under optimized conditions. This may be attributable to the high specific area of the adsorbents. The experimental data show that Umbuluko natural clay exhibits great affinity for Ni(II) and Pb(II) with the composite clay exhibiting greater affinity which is confirmed by the q_m values. The ratio of clay to metal ions that yield maximum adsorption at 298K is 0.5g to 50mgL^{-1} for Pb(II). The best results were obtained under optimum conditions of 60minutes shaking time for natural clay and 40minutes shaking time for composite clay. The Langmuir model adequately described the adsorption data with R^2 values of 0.74, 0.94, 0.99 and 0.99 for Ni(II) adsorption and Lead(II) adsorption onto Umbuluko natural and composite clay respectively. This implies that the adsorption of Ni(II) and Pb(II) from its aqueous solution proceeded by monolayer adsorption.

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