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Effect Of Organic Modification On The Structural And Adsorptive Properties Of A Nigerian Ajegunle Natural Clay And Its Application For Removal Of Lead And Nickel.

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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 Ajegunle, Ilaje local government of Ondo State, Nigeria as adsorbent. 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 a commercial Bentonite clay.

The batch technique was employed and effect of contact time, PH, initial metal ion concentration and temperature on the adsorption process were studied. The data obtained from equilibrium studies were fitted with Langmuir isotherm model.

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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 (Zaini et. 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 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) divalent cations (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, organo- clays, 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, Vilasova et. al., 2003).

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

Water pollution is caused by industrial influent 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 was the organic modification of Ajegunle- Ilaje 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+} from wastewaters.

II. MATERIALS AND METHODS

Preparation and characterization of Adsorbent:

The natural clay sample was obtained from Ajegunle – Ilaje ,Ondo State, the raw clay sample were wet refined and sieved to remove impurites and particles, it was dried in an oven at

373K and ground to power to pass through 250mm sieves, the point of Zero charge (PZC) was determined using the PH drift method (Eggleston and Jordan, 1998). 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 1000mg L^{-1} Pb (II) and Ni (II) ion 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.

$$qe = \frac{(Ci - Cf)}{M} \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (1)$$

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 mg L^{-1}, C_e 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 valve determined.

III. RESULTS AND DISCUSSIONS

Organic modifications of Ajegunle – Ilaje clay with ethenylacetate using hexadecyl trimethyl ammonium chloride (Genamine CTAC).

Ajegunle – Ilaje clay was organically modified using monomer ethenyl acetate considering that the clay is completely inorganic materials, it was made compatible with organic compound during modification. It was necessary to modify its surface. To achieve this, a compatibility tools was necessary which usually consist of the group of cation- active materials (alkyl ammonium derivative). During the process of organically modifying Ajegunle – Ilaje clay with ethenylacetate, the cationic surfactant hexadecyltrimethyl ammonium chloride was use as compatibility tool. The reaction of cationic exchange was achieved by mixing the aqueous dispersion of Ajegunle – Ilaje clay 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 cause a change of hydrophilic properties of the silicate surface. Also, the reaction of the cationic exchange indicate the distance between inter layers was increased by several nanometers. 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 the monomer ethenyl acetate by the mechanism 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 interlayers cations.

CHARACTERIZATION OF ADSORBENTS:

Fourier Transform Infrared (FTIR) Analysis

Spectra of natural and modified Ajegunle clay (Figs. 1a,b) were obtained and analysed. Adsorption bands at around 3610cm^{-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 783cm^{-1} are consequences of Si – O valence vibrations. Deformation vibrations Si – O – Al in the infrared spectrum appeared at around 536cm^{-1}

With the addition of monomer ethenyl acetate, adsorption bands of increased intensity occurred at around 2929cm^{-1}, which have its origin from vibration of methylene group of ethenyl acetate. Analysis of 1R spectra confirmed that the monomer is strongly associated with Ajegunle 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

X – ray diffractometer (XRD) Analysis

XRD analysis of Ajegunle natural clay and the clay composite were analysed (Fig. 2a and b). 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, CaO, Fe_2O_3, FeO and TiO_2, in the natural clay. The basal spacing was 3.357A^o and the diffraction peak was 26.528, (Fig 2a)

The compounds found in the composite clay were SiO_2, Al_2O_3, Fe_2O_3 and FeO. Basal spacing was 5.44A^0 while diffraction peak was 17.225. Magnesium and Titanium were absent in the composite..

Basal spacing of the composite was higher than that of the natural Ajegunle clay. This is due to the intercalation of the ethenylacetate monomer molecule in the composite clay.

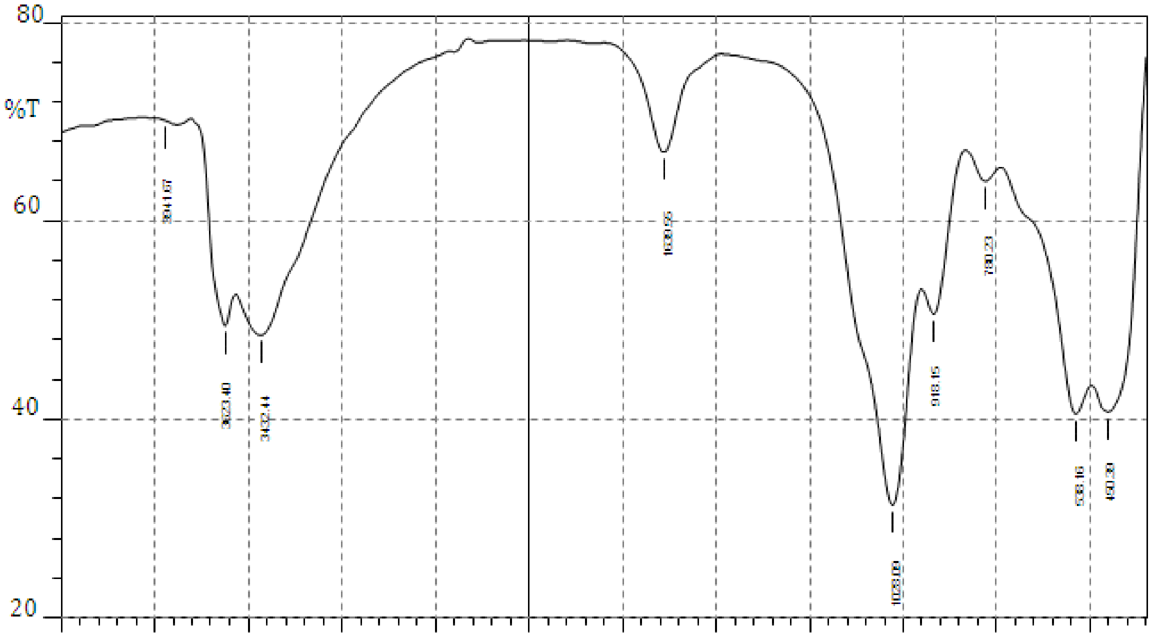

Fig 1a: 1R spectrum of Ajegunle natural clay

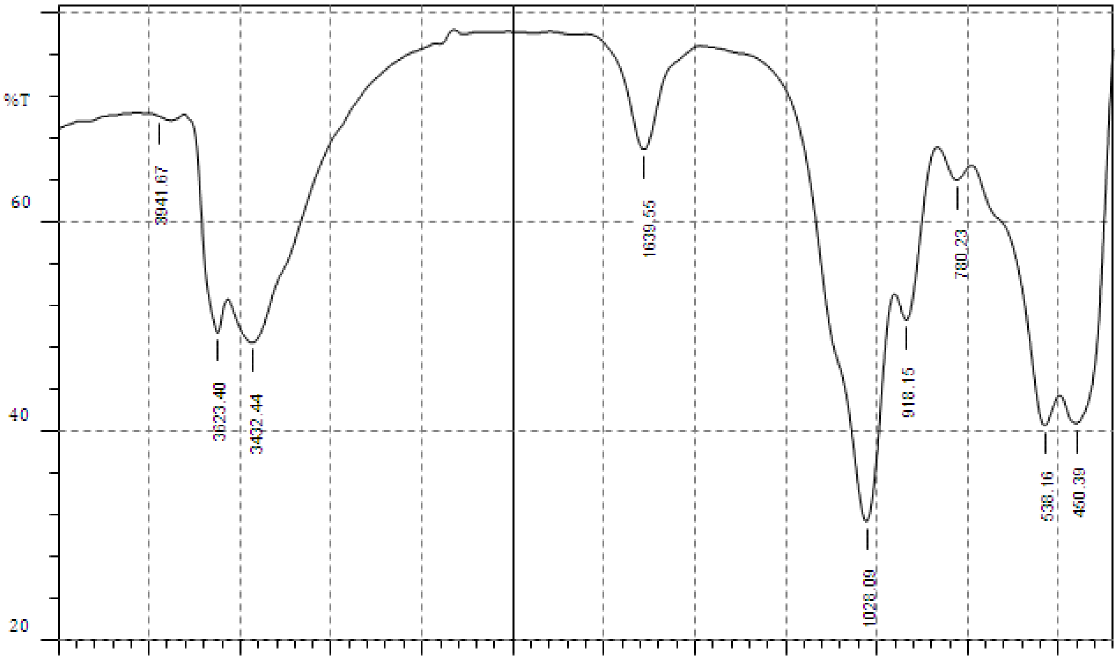

Fig.1b: 1R spectrum of Ajegunle composite clay.

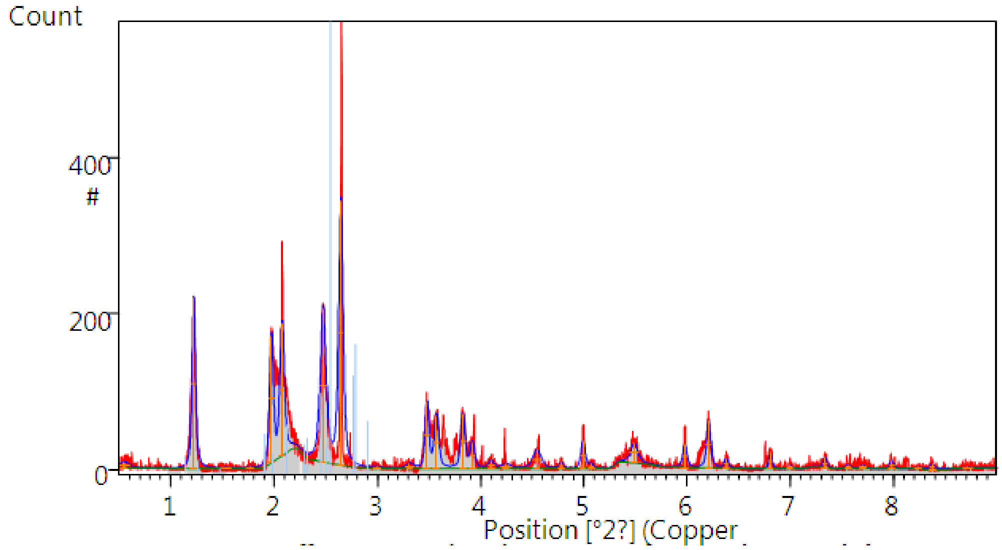

Fig. 2a: X-ray Diffractometer (XRD) spectrum of Ajegunle natural clay.

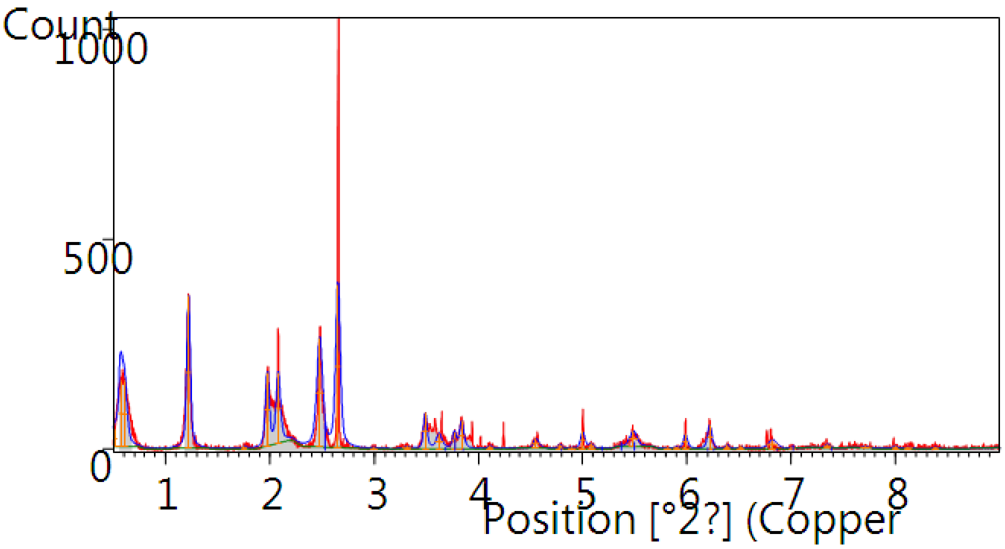

Fig. 2b: X-ray Diffractometer (XRD) spectrum of Ajegunle composite clay.

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

Compound	SiO_2	Al_2O_3	TiO_2	MgO	Fe_2O_3	FeO	CaO	H_2O
% in nat.clay	45.9	20.7	15.4	7.8	1.7	4.7	-	3.7
% in comp.clay	38.5	12.3	18	10.3	5.6	-	15.4	-

Energy Dispersion X- ray Analysis.

The results of the energy Dispersion X – ray (EDX) analysis of Ajegunle natural clay and its composite clay are presented in Figs. 3a and b. The figures clearly indicate that the 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_2O_3.MgO etc) and organic matter" it was observed that Mg and Al that were present in unmodified Ajegunle natural clay were not available in the composite clay . These metals (Mg & 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.

$C_{19}H_{42}CLN$ + clay _ $MgCl_2$ + $C_{19}H_{42}N$ – clay -------- 3.1
$C_{19}H_{42}CLN$ + clay _ $AlCl_3$ + $C_{19}H_{42}Cl$ – clay -------- 3.2

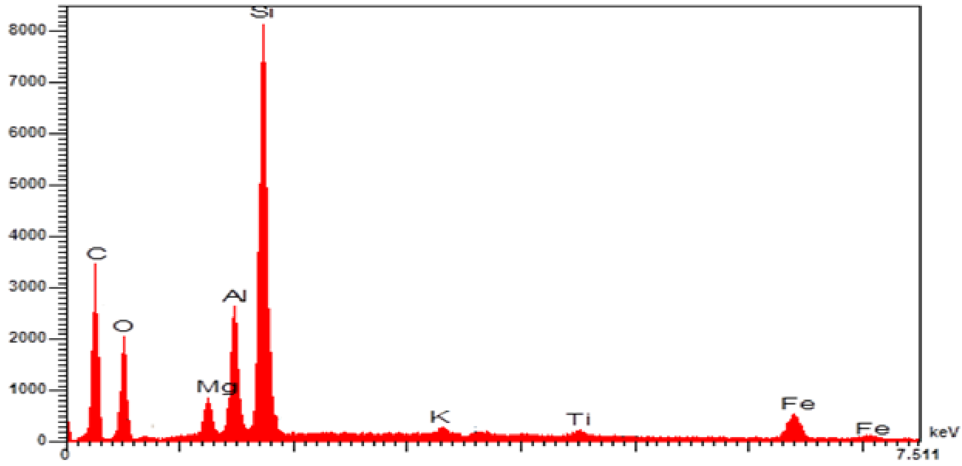

Fig.3a: Energy Dispersion X-ray (EDX) of Ajegunle natural clayy

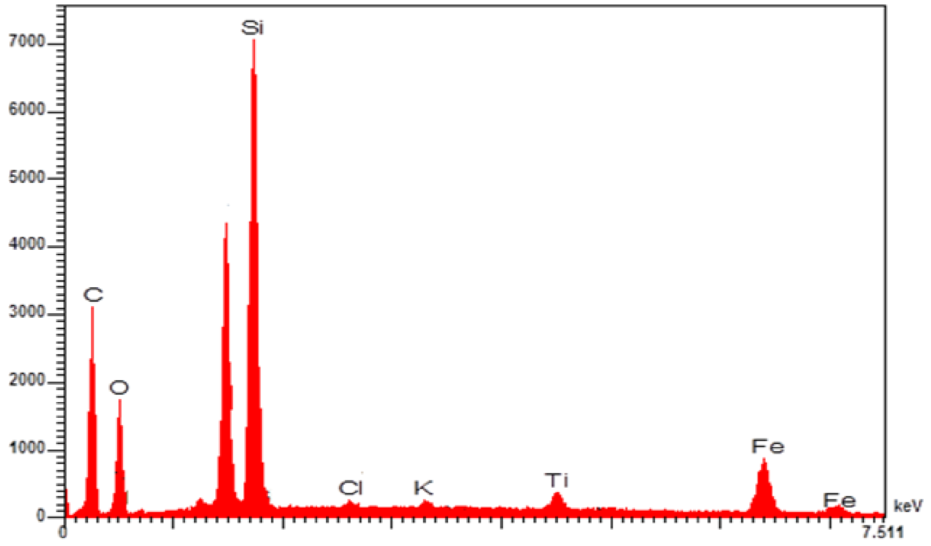

Fig.3b: Energy Dispersion X-ray (EDX) of Ajegunle Composite clay.

Table 2: Chemical composition of Ajegunle natural and composite clay

Element	C	O	Mg	Al	Si	K	Fe	Cl	Br
% in nat.clay	58.78	24.49	1.07	2.99	8.94	0.42	2.87	-	-
% in comp.clay.	58.27	19.64	-	-	8.06	0.22	4.62	0.19	8.25

SEM Analysis

A scanning electronic microscope JSM – 5300 (Joel, Japan) was used for the investigation of the upper composite layers of the Ajegunle natural 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 Ajegunle natural 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.

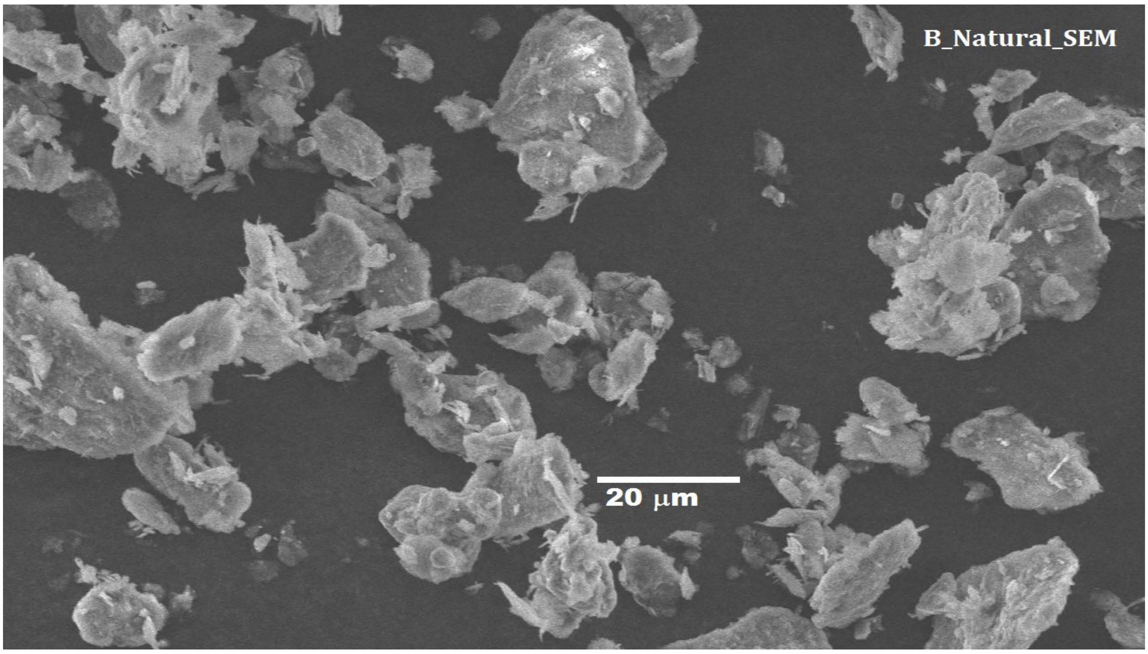

Plate 1b: Scanning Electron Micrograph of Ajegunle composite clay.

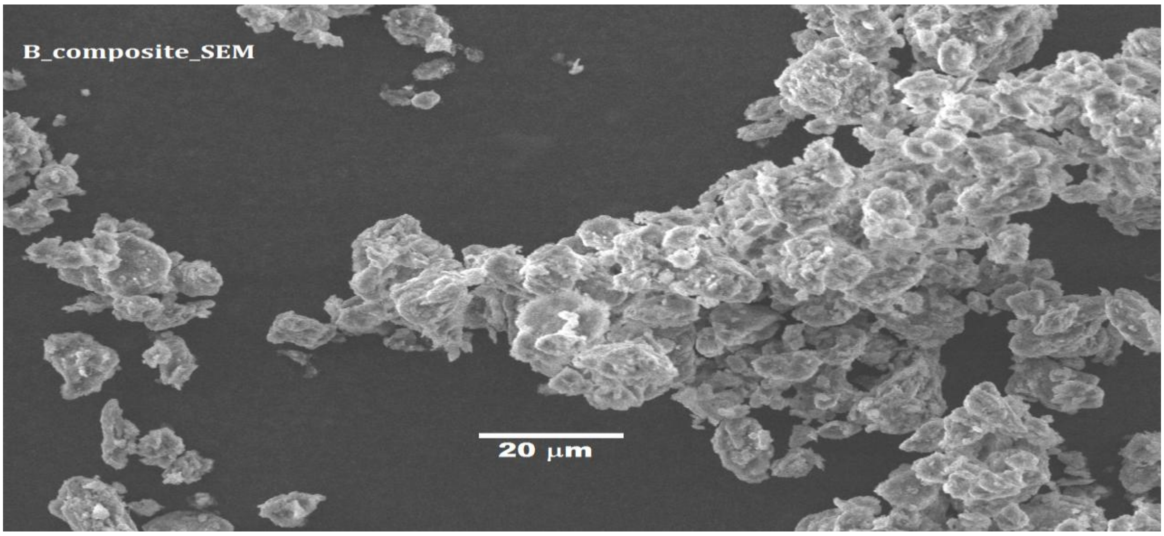

Plate 1b: Scanning Electron Micrograph of Ajegunle composite clay.

EFFECT Of pH ON ADSORPTION OF METALS:

The effect of the initial pH on adsorption of Pb (II) and Ni (II) onto the Ajegunle natural clay and the composite clay was studied at optimum contact 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 decrease 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.

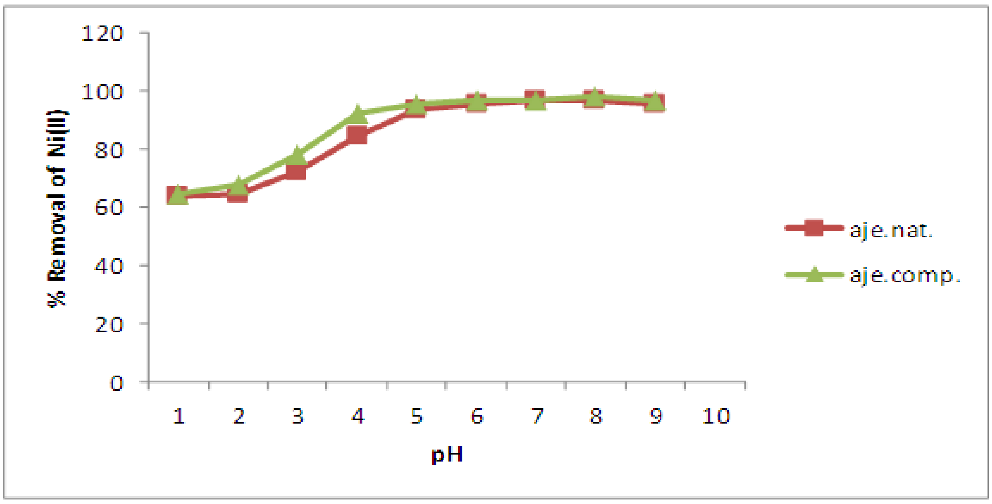

Fig. 4a: Effect of pH on adsorption of Ni^{2+} onto Ajegunle natural and composite clay

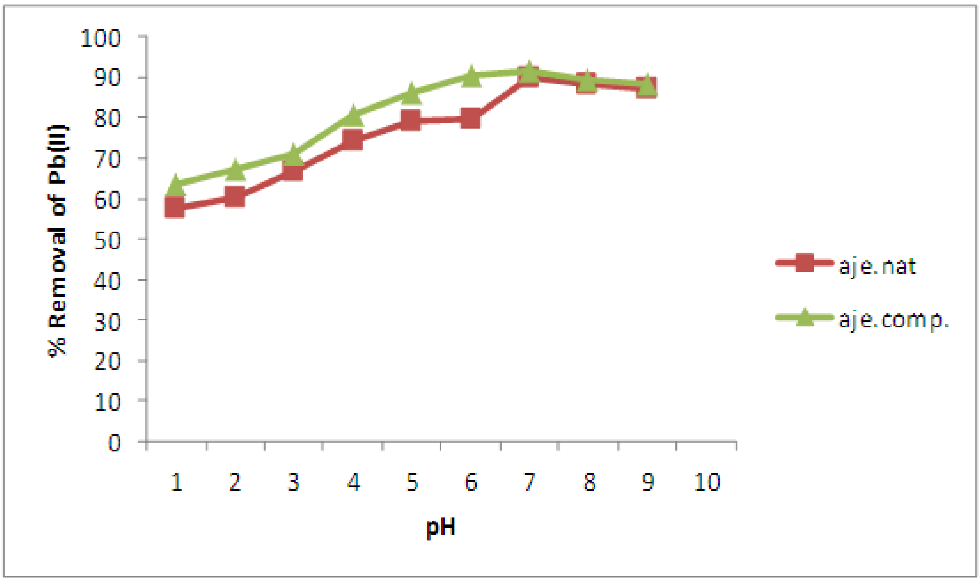

Fig. 4b: Effect of pH on adsorption of Pb^{2+} onto Ajegunle natural and composite clay.

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 Spectrophotometry, AAS (Buck Scientific, 2005).

The effect of contact time on adsorption of Ni (II) and Pb (II) onto Ajegunle 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 Ajegunle clay and at about 40minutes for the composite clay.

The adsorption rate was rapid in the first 40minutes for unmodified Ajegunle clay and in the first 20minutes for Ajegunle composite clay unitil it decreased gradually to equilibrium. The adsorption rate for unmodified Ajegunle clay was 91.47%, while for the composite clay, it was 96.17%. Ajegunle composite clay showed better adsorption characteristics towards $Pb^{2+}$and Ni^{2+} ions than the natural clay. Similar observations were reported by (Stojiljkovic et. al.,2013) on adsorption of lead by modified bentonite clay.

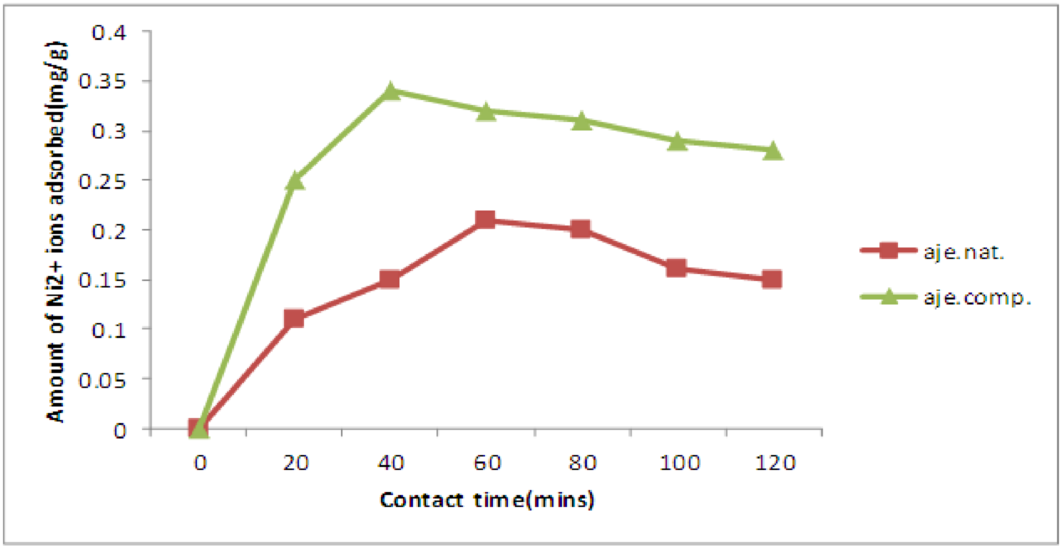

Fig. 5a: Effect of contact time on adsorption of Ni^{2+} onto Ajegunle natural and composite clay.

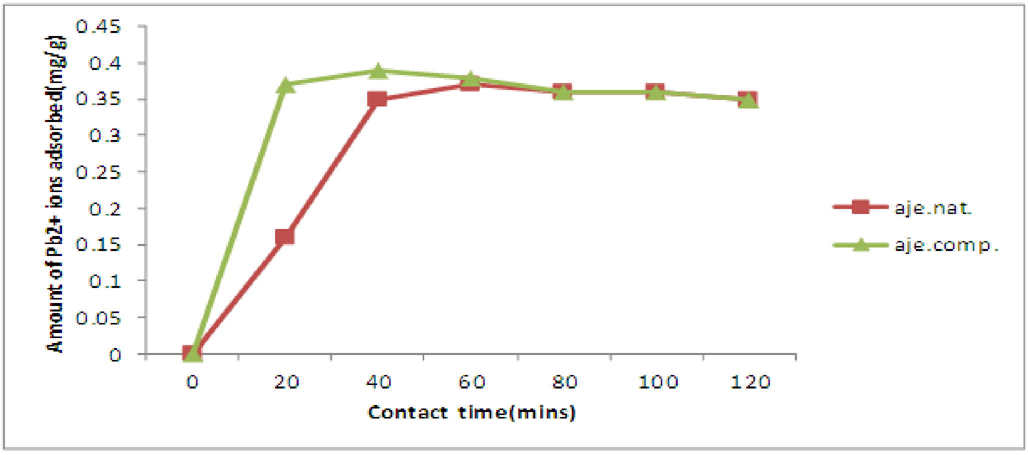

Fig. 5b: Effect of contact time on adsorption of Pb^{2+} onto Ajegunle natural and composite clay.

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 Ajegunle 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 Ajegunle natural and composite clay proceeded by a monolayer formation. Similar observation was made by Mistral and Patel (2009). The q_m (mgg^{-1}) parameter again suggested that Ajegunle natural clay exhibits great affinity for Pb(II) and Ni(II) and Ajegunle 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.

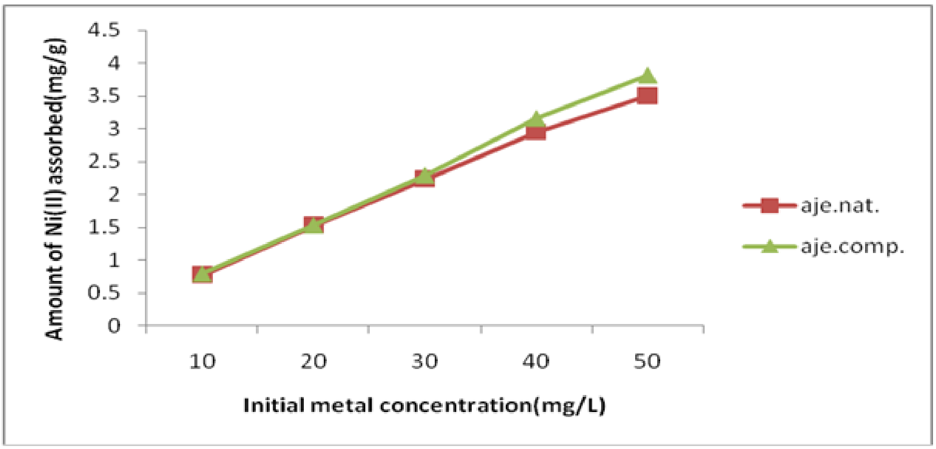

Fig. 6a: Effect of initial metal concentration on adsorption of Ni^{2+} onto Ajegunle natural and composite clay

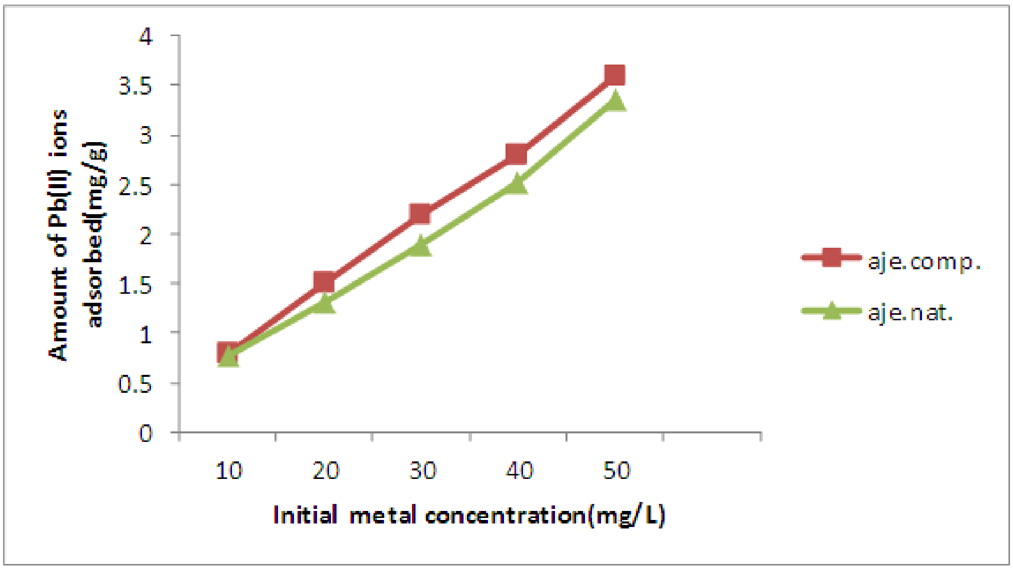

Fig. 6a: Effect of initial metal concentration on adsorption of Ni^{2+} onto Ajegunle natural and composite clay

Adsorption Isotherms:

Langmuir Isotherm:

The experimental data obtained were fitted with the Langmuir adsorption Isotherm. The Langmuir adsorption Isotherm is given by (Langmuir,1916):

$$qe = \frac{qmKLCe}{1+KLCe} \text{---}(2)$$

And one of its linear forms is:

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{KLqm} \quad \underline{\hspace{8cm}}(3)$$

where q_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-b. 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 Ajegunle natural and composite clay. The correlation coefficient, (R^2) for Pb^{2+} -

Ajegunle natural clay adsorption and Pb^{2+}- Ajegunle composite clay was respectively 0.95 and 0.99. Adsorption of Pb^{2+} unto both Ajegunle natural and composite clay proceeded by a monolayer formation. Similar observation was made by Mistral and Patel (2009). The q_m (mgg^{-1}) parameter again suggested that Ajegunle natural clay exhibits great affinity for Pb(II) and Ni(II) and Ajegunle composite clay exhibits greater affinity for Pb (II) and Ni(II) than the natural clay, similar results were given by Njoku et. al., (2014), for heavy metal ion removal by Ezinachi Okigwe natural clay.

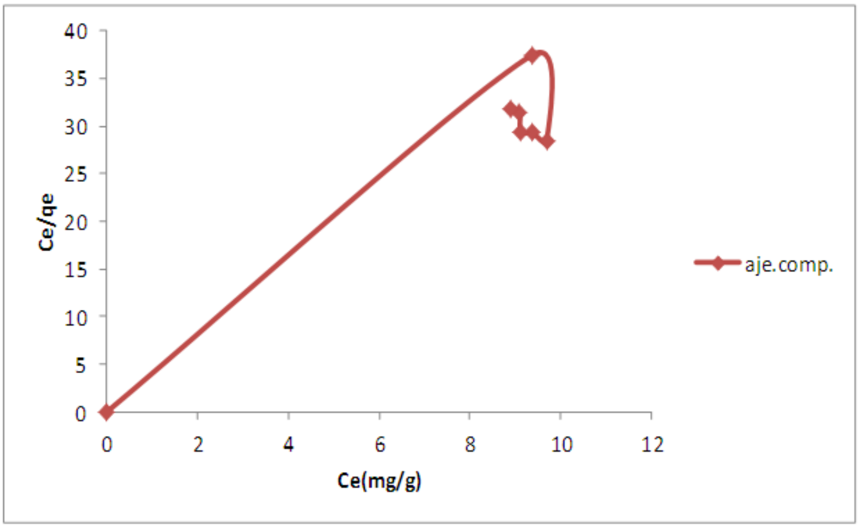

Fig.7a: Langmuir plot for adsorption of Ni(II) ions onto Ajegunle composite clay at 298K

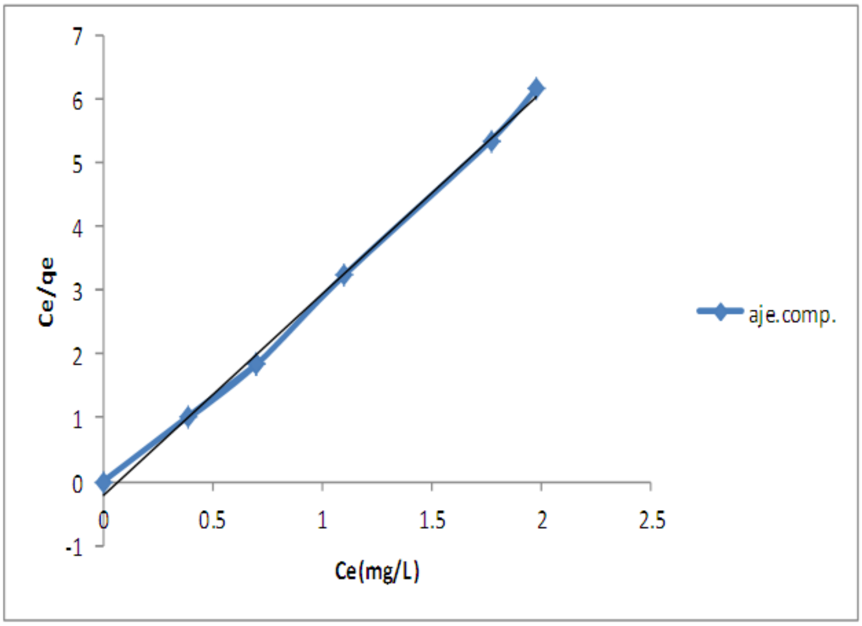

Fig.7b: Langmuir plot for adsorption of Pb(II) ions onto Ajegunle composite clay at 298K

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

ADSORBENT-ION	q_e(calc.)	q_e(expt.)	K_L	R^2	Error
Aje.nat-Ni(II)	0.2	0.2	0.88	0.8464	0.00
Aje.comp.-Ni(II)	0.3	0.34	15	0.9298	0.0016
Aje.nat.-Pb(II)	0.15	0.37	1.43	0.9526	0.048
Aje.comp.-Pb(II)	0.32	0.39	1.48	0.9962	0.0049

II. CONCLUSION :

The removal of Ni(II) and Pb(II) by Ajegunle 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 Ajegunle 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 0.85, 0.93, 0.95 and 0.99 for Ni(II) adsorption and Lead(II) adsorption onto Ajegunle 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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