Chemical Analysis of Rock and Water from dug Wells in a Residential Area in Lagos State, Nigeria

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Abstract

Samples of rock deposit dug out from wells at Alimosho local government in Lagos state, Nigeria were characterized for chemical composition and ultimate utilization. Fourier Transform Infrared Spectroscopy (FTIR), X-Ray diffraction (XRD) and Atomic Absorption Spectroscopy (AAS) were used to identify the rock as a mixed clay rock containing 35.04% Illite, 25.64% Illite plus Quartz, 22.20% Kaolinite and 17.09% Feldspar. This was corroborated by cation determination that showed the rock to be predominantly clayey rock.

The mean concentrations of lead and copper in water of the wells in the rock location are 0.004mg/L and 0.05mg/L respectively while cadmium is less than detectable limit. The well water in the area studied is therefore not contaminated by these heavy metals.

Heavy metals removal by the mixed clay from polluted underground water was studied using AAS. A general increase of sorption was observed with increase in the adsorbent dosage. 20g of the rock adsorbed a higher percentage of copper (80.23%) than lead and cadmium that were 70.25% and 65.83% respectively. The percentage of heavy metals adsorbed confirms the use of mixed clay minerals as a contaminants removal from the underground polluted water. The rock adsorbed copper readily than cadmium and lead. The maximum amount of lead removed from the contaminated underground water of the defunct battery site across the adsorbent dosage (5g, 10g, 15g and 20g) were 1.20mg/L, 3.19mg/L, 3.69mg/L and 4.09mg/L respectively indicating the effect of increase in adsorbent dosage in remediating the lead contaminated water. This data showed that the rock can be used to remove these heavy metals from contaminated water.

Keywords: clay rock, contaminants, remediation

1. Introduction

There are three main classes of clay rocks: Kaolinite, Micas (such as Illite) and Smectite (such as Montmorillonite). Of these three classes, Montmorillonite clay has the smallest crystals, largest surface area and large cation exchange capacity (CEC). Montmorillonite clay has been shown to have adsorption capacities five times that of Kaolinite (Schimdt and McDonald, 1979). Clay minerals have different adsorption capacities for metal ions depending on the conditions in which the adsorption reactions were carried out. Clay minerals could be modified like other adsorbents. Several methods have been employed to improve on the cation exchange capacity (CEC) of clay minerals. These include activation, pillaring or intercalation (Hung et al., 1997) and chemical modification of the surface using inorganic complex-forming ions or organic based complex forming ions. Montmorillonite clay was modified with hydroxyl aluminum and hydroxoaluminosilicate and kaolinite clay was modified with orthophosphate and tripolyphosphate (Erdem et al., 2004). It has also been reported that 2-mercaptobenzothiazole impregnated clay surface can be used for the removal of some heavy metal ions from water samples. The adsorption of metal ions onto mineral substrates is an important process not only in soil chemistry but also in hydrometallurgy and the treatment of industrial wastewaters. Diverse processes such as the uptake of nutrients by plants and the extraction of toxic heavy metal ions from industrial wastewaters depends often on adsorption to soil minerals.

The chemical analysis of rocks and minerals determines the concentrations of elements and certain components. Geological investigations, which are often an integral part of exploration for resources of raw materials in bedrocks, require increasingly detailed information on the chemical composition of rocks and minerals. Although

often covered, bedrock occurs everywhere on the globe. It is composed of different rocks which in turn are composed of minerals, most minerals of which over 2000 species are known are crystalline compounds. Majority are rare and thus unimportant as rock forming constituents.

Analysis of whole rocks for major and trace elements is often very important for understanding the conditions under which the rocks are formed, as well as their economic potential. This is particularly true of igneous and metamorphic rocks, but less so for sedimentary rocks. In all cases, bulk rock chemical analysis is a multi-step process, and the objectives have to be clear from the outset. Generally, any sample has two types of elements: majors and trace elements (Schimdt and McDonald, 1997).

Major elements are those whose oxides constitute more than 1% by weight (on average for a common, garden variety rock in the earth's crust). These elements are: silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K). Minor elements are those whose oxides constitute $0.1 - 1\%$ by weight of a common crustal rock, and include titanium (Ti), phosphorus (P), and manganese (Mn) ($\pm C \pm N$). Trace elements are all other elements in the periodic table and occur in concentrations of several parts per million (ppm) or parts per billion (ppb) of a typical rock.

Determination of chemical composition of both major and trace elements is very important in the study of different geological materials. For most of the analytical methods, the sample should be dissolved, which is the difficult part of the procedure, especially in the case of hardly soluble silicate rocks, as well as insoluble residues of carbonate rocks, bauxites and soils. Trace elements occupy corresponding sites in crystal lattices of silicate minerals. Their analyses are particularly useful in petro genetic studies of igneous rocks providing constrains for different magma types and their tectonic settings.

The flame atomic absorption spectrophotometer (FAAS) is a relatively quick method for determining the trace elements content in rocks. Various compositions of geological samples and refractory nature of their numerous parts make their analysis difficult and time-consuming (Moore and Reynolds, 1997). Although the development of analytical techniques has led to the expansion of new methods (Inductive Couple Plasma –Atomic Absorption Spectrophotometer, Inductive Couple Plasma –Mass Spectrophotometer etc.), which can also be widely applied in analytical chemistry, while Neutron Activation Analysis is still competitive in many areas. The indisputable advantage of the method is its sensitivity and accuracy especially in respect of some trace elements. The method is however of a multi element character. That is, it enables simultaneous determination of many elements without chemical separation.

Over the years, various techniques have been employed to remove metal ions from aqueous solutions. Conventional methods that have been used include ion-exchange, reverse osmosis, electrochemical treatment, evaporative recovery, and adsorption. These conventional techniques can reduce metal ions, but they do not appear to be highly effective due to limitations in the pH range as well as the high material and operational costs. However, adsorption has assumed a wide application because of its high efficiency and easy operation. Moreover, with adsorption process, there is no sludge formation that could add to the operational cost. In recent years various low cost adsorbents have been used in adsorption of various metal ions (Mitchell and Pedersen, 2000; Mulligan et al., 2001; Maturi and Reddy, 2006). They include Giridih coal and coconut shell, peat, Wollastonite ,waste tea, Turkish coffee, exhausted coffee, Nut shell and Walnut shell, Cypress leaves, Peanut hull carbon, China clay, Fly ash, Montmorillonite, Diorite, activated carbon from fertilizer waste and bagasse fly ash. Kaolinite clay has seldom been used because of its low cation exchange capacity (CEC, 3–15 meq/100 g) and small surface which is not more than $20 m^2 g^{-1}$ (Balan et al., 2010).

With the current awareness of heavy metals as very toxic contaminants, extensive effort has been devoted to investigation of their adsorption by solid surfaces as the most important mechanism for controlling metal content in soil solutions and natural waters (Mitchell et al., 2000; Khan et al., 2004). Heavy metals are dangerous environmental pollutants due to their toxicity and strong tendency to concentrate in the environment and in food chains (Appel and Ma, 2002; Algarra et al., 2004; Goloboca et al., 2004; Colombo et al., 2005; Davydova, 2005; Garrido et al., 2005)). One of the recent environmental applications of bentonites is connected with high-level nuclear waste disposal in underground repositories using a multi barrier system of two basic components, a host rock and an engineered barrier made of metallic containers filled with radioactive waste surrounded by bentonite blocks, as is documented by the results of large scale experiments (Randall, 2002).

The rock samples from Igando, Lagos state has been analyzed to determine their mineral and heavy metals content, ascertain the safety of the well water from where they were dug and to determine its beneficiation such as the remediation of polluted underground water in order to reduce the environmental pollution. Pipe borne water is a luxury in the area of rock studied and almost every home has to dig a well to have access to water for

their survival and the water is used as it is fetched without processing. Hence this study is in part to ascertain the level of the heavy metals present in it to be within the permissible limit.

2. Methodology

2.1 Rock Sample Location

The rock samples used for this study were collected from dug wells at Igando area in Alimosho local government of Lagos State. The site is located within latitude $6^0 34$'N and longitude $3^0 15$'E in south western part of Nigeria, and has accessible and well-connected roads and fast foot paths (Figure 1). Lagos metropolis is located within the Western Nigeria Coastal Zone, a zone of coastal creeks and lagoons (Jones and Hockey, 1964) developed by barrier beaches associated with sand deposition (Odewumi, 1995). Lagos is underlain by the Dahomey Basin with lithologic constituents that are mainly sands, clays and limestones (Jones and Hockey, 1964). The subsurface geology revealed two basic lithologies; clay and sand deposits. These deposits may be interbedded in places with sandy clay or clayey sand and occasionally with vegetable remains and peat (Ayolabi and Peters, 2005).

2.2 Underground Water Sample Location

The contaminated underground water was obtained from a defunct battery factory site which is located in east central part of Wofun village in Lagelu local government located north-east of Ibadan, southwestern Nigeria between Longitude $7^0 13$'39''N - $7^0 33$'39''N and Latitude $3^0 49$'56''E - $4^0 7$'58''E.

2.3 Sample collection and Preparation

Rock samples were taken from 10 different well sites in the area of study and dried in an oven at 105^oC for four hours and cooled in a desiccator. It was then disaggregated with a stainless steel hammer, pulverized into powder that passed through a 40-mesh sieve and stored in a stopped bottle.

Water samples were collected from 10 wells where the rock samples were taken. The wells are between 8meters and 10meters deep. Polluted water samples from the defunct battery site were also collected with polythene sampling bottle attached to a telescope arm. It was filtered immediately and kept for analysis.

2.4 Loss on Ignition (LOI)

4 g of the powdered rock sample was weighed and oven dried at 105^oC for 10 hours after which 1 g of the dry sample was then transferred into a weighed platinum crucible. The crucible was placed in a muffle furnace and slowly heated and ignited to 900^oC for 3hours. The crucible was then transferred into a desiccator to cool down and then weighed. The difference in mass represented the loss on ignition

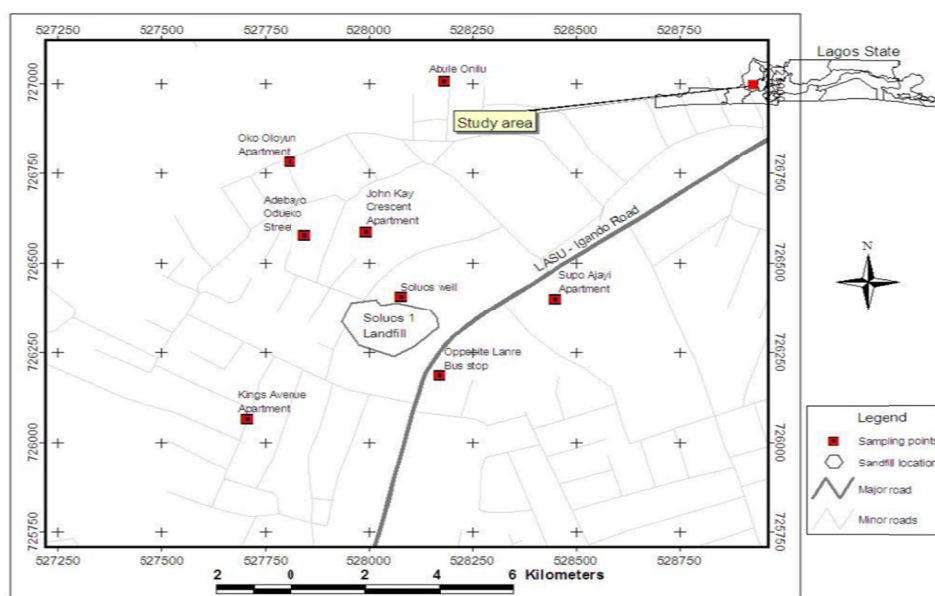$$LOI = \frac{Weight\ Loss \times 100}{Weight\ of\ sample\ used}$$

Figure 1. Map of the rock sample location

2.5 Cation Exchange Capacity (CEC) of Rock Sample

The method of Inglethorpe (1993) was used. 5 g of the rock sample was weighed into 250 ml polythene bottle with a magnetic stirrer. The bottle and its content were weighed (M_1). 100 mL of buffered barium chloride solution was added and the bottle was placed on a magnetic stirring plate and agitated for 1 hour. At the end of the period, the bottle was centrifuged at 1500rpm for 15 minutes and the supernatant was discarded after which 200 mL buffered barium chloride solution was added and the mixture was agitated on a magnetic stirring plate for another 1 hour. The bottle and its contents were left to settle down overnight. After 24 hours, the bottle and its contents were centrifuged at 1500 rpm for 15 minutes and the supernatant was discarded. 200 mL of distilled water was added and agitated for few minutes on the magnetic stirring plate. It was centrifuged for further 15 minutes and the supernatant discarded. The bottle and its contents were weighed (M_2). 100 mL of $MgSO_4$ solution was pipetted into the bottle, stirred properly and was left to stand for 2 hours with occasional agitation on the magnetic stirring plate. After 2 hours, the contents were centrifuged at 1500 rpm for 15 minutes and the supernatant decanted into the stoppered bottle.

5 mL aliquot of this solution was pipetted into a 100 mL conical flask and 5 mL of ammonia buffer and 6 drops of indicator were added to it. This mixture was titrated with standard EDTA (titer A_1 mL). Another titration was done with a 5 mL of aliquot of 0.05 M $MgSO_4$ solution (titer B mL). The end point was indicated by a color change from blue to pink. Cation Exchange Capacity was calculated according to the method of Nelson and Sommers, 1996 as follows:

$$CEC = 8\{B - ([A_1 \times (100 + M_2 - M_1)] / 100)\} \text{ mg/100 g}$$

Where M_1= weight of bottle plus dry content (g)

M_2=weight of bottle plus wet content (g)

A_1 =titration end-point of sample (ml)

B=titration end-point of $MgSO_4$ solution (ml)

2.6 Digestion of Rock Sample

1g of the dry pulverized rock sample was weighed into a 250mL long necked digestion flask. 25ml of a mixture of nitric acid and hydrochloric acid (ratio 1:3) was added and heated for digestion to fully take place. It was allowed to cool and filtered. The digest was made up to 100mL in a standard flask with demineralized water. This was used for heavy metals analysis by AAS and determination of phosphorus, sulfate, chloride and nitrate content.

This procedure was used to digest all the ten rock samples.

2.7 Determination of Phosphorus in the Rock Sample

A calibration curve was drawn by measuring the color transmittances on the UV spectrophotometer at 420nm of standard solutions of potassium di-hydrogen phosphate in which color was developed by addition of 2mL solution of a mixture of vanadate and molybdivanadophosphoric acid.

5mL aliquot of the digested rock solution was pipetted into a 250mL volumetric flask and diluted to 10mL with demineralized water followed by addition of 2mL of phosphovanadiummolybdate. The transmittance of color developed was measured on the UV spectrophotometer at 420n while the µgram of phosphorus was read from the calibrated curve (ASTM D2974, 2000).

$$\% \text{ P in rock sample} = \frac{\text{µg P from curve} \times \text{dilution factor}}{10,000 \times \text{weight of rock sample (g)}}$$

This was carried out on all the ten rock samples.

2.8 Determination of Carbonate Content of the Rock Sample

25mL of standard 0.1M hydrochloric acid solution was measured into a 250mL standard flask and made up to mark with distilled water. 3.5g of rock sample was weighed out accurately into a stoppered weighing bottle. The rock was transferred quantitatively after mixing with small amount of water into a 250mL standard flask and made up to mark. The flask with the content was shaken vigorously. 25mL of this solution was measured with a pipette into a conical flask and titrated with the diluted hydrochloric acid solution using methyl orange as indicator. The mean of 5 titers with good precision were taken and the amount of carbonate in the rock was determined.

The above procedure was used for all the rock samples.

2.9 Determination of Sulfate Content

Standard sulfate solution was prepared by dissolving 0.543g of K_2SO_4 in 100mL distilled water to give 50mg/L SO_4^{2-}. Other standard solutions of potassium sulfate containing 1, 2, 3 and 4mg/L of sulfate ion were also prepared. 2mL $BaCl_2$ solution was added and diluted to 50mL with distilled water. 25mL of the digested rock solution was measured into 50mL standard flask followed by addition of 20mL of demineralized water and 2mL $BaCl_2$ solution. The resulting solution was made up to 50mL mark and allowed to stand for 30mins. The absorbance of the standard solutions and that of the samples were read from PerkinElmer22-10-079710 UV spectrophotometer at 400nm and the sulfate concentration was evaluated from the calibration graph.

2.10 Determination of Nitrate Content

Standard solutions of potassium nitrate was prepared. 2mL aliquot of the standard solution was transferred into a 250mL volumetric flask and 2mL of brucine reagent was added followed by rapid addition of 10mL of concentrated H_2SO_4. This was mixed for about 30seconds and allowed to stand for 5minutes for the color to develop. The flask was set in cold water for about 5minutes. The absorbance was measured at 470nm. This was repeated using 4, 6, 8 and 10mL aliquot of the standard solution. A calibration curve was then plotted for the rock sample and the absorbance was also measured at 420nm. Nitrate concentration in the rock sample was evaluated from the calibration graph.

2.11 Determination of Chloride Content

0.1M standard solution of silver nitrate was prepared. Powdered rock was dried at 110^0C for one hour and cooled in a desiccator. 1g of the dry powdered rock was weighed into a 250mL Erlenmeyer flask and 100mL of demineralized water was added. Small quantity of sodium hydrogen carbonate was added until effervescence ceased. 2mL of potassium chromate was added. The resulting solution was titrated against silver nitrate to the first appearance of red silver chromate. The mass and the percentage of the Cl- in the rock sample were then calculated.

2.12 Rock pH

The pH of the rock was determined with a pH meter model HI 2212 according to the method of Mclean, [E. O. Mclean, 1996].

2.13 Measurement of Exchangeable Acidity

The exchangeable acidity was determined by titrimetric technique with sodium hydroxide solution and phenolphthalein indicator to permanent pink end point.

2.14 Determination of Organic Carbon and Total Organic Matter

The organic carbon and total organic matter was determined by the wet oxidation method of Walkey and Black (1984). 2g of the powdered rock sample was weighed into a conical flask followed by pipetting 10ml of 1N $K_2Cr_2O_7$ solution into it. 10ml of concentrated H_2SO_4 was added to prevent interference of chloride ions. The mixture was shaken vigorously and allowed to remain for 30mins with occasional swirling. Another 10ml of distilled water was added. The excess potassium dichromate was determined by titrating the resulting solution against ferrous sulfate solution using 4 drops of ferroin indicator until the color change to maroon. A blank titration was carried out without the rock sample.

Percentage organic carbon was obtained as follows:

$$\% \text{ organic carbon} = [(M_e\ K_2Cr_2O_7 - M_e\ FeSO_4) \times 0.003 \times 100 \times F] / \text{mass of sample}$$

Where Me = Normality of solution x volume of solution used.

F is the correction factor = 1.33

% organic matter in the rock = % organic carbon x 1.729

2.15 X-ray Diffraction

The powdered rock sample was sieved to 0.074mm and then pelletized. The sample was later taken in an aluminum alloy grid (35mm x 50mm) on a flat glass plate and covered with a paper followed by compacting it by gently pressing with hand. The sample was run through the Rigaku D/max-IIIc X-ray diffractometer which produced diffractions at scanning rate of 2°/min from 2° (2θ) to 50° (2θ) at room temperature with a Cu kα radiation set at 45Kv and 25Ma.

2.16 Fourier Transform Infra-red Spectrometer (FTIR)

The sample was prepared by applying the disc techniques (mixing 1mg rock sample with 200mg KBr) and was

placed in a mold. These intimate mixtures were then pressed at very high pressure (10 tons per cm^2) to obtain the transparent disc which were placed in the sample compartment. The spectra were recorded over the range of 4000 to 350cm^{-1}.

2.17 Elemental Analysis

The major and trace metals in the rock samples were determined using Buck Scientific 210/211 VGP model Atomic Absorption Spectrophotometer (AAS).

2.18 Remediation Study

Stock solutions (10mg/L) of Pb^{2+}, Cd^{2+} and Cu^{2+} were prepared from analytical grade of lead nitrate, hydrated copper sulfate and cadmium nitrate respectively. The concentration of each stock solution was ascertained by using AAS.

5g of the dry powdered rock sample was added to 100mL of the stock solution of each of the heavy metals and shaken at interval for two weeks. This was repeated by using 10g, 15g and 20g of the rock sample. The heavy metals concentrations were determined using AAS. The amount adsorbed by the rock sample was determined. The percentage adsorbed was calculated as:

$$\% \text{ adsorbed} = \frac{(C_0 - C_e) \times 100}{C_0}$$

Where C_0 (mg/L) is the initial concentration of a particular heavy metal in the solution and C_e (mg/L) is the final concentration of the heavy metal in the solution after adsorption.

The initial concentration of lead, cadmium and copper in 100ml of the polluted water samples from the battery factory was measured with AAS. 100mL each of the polluted water was treated with 5g, 10g, 15g and 20g of the dry powdered rock for two weeks in a similar manner with the stock solutions. The heavy metals concentrations were determined at the end of the second week using AAS. The percentage of heavy metals adsorbed was also calculated.

2.19 Determination of Heavy Metals in the Well Water

The concentration of the heavy metals in water samples from ten different wells at the location where the rock samples were obtained was determined using AAS.

2.20 Quality Assurance and Quality Control

Every glassware used were properly cleaned and dried in the oven. All the instruments were calibrated before use (AOAC, 1996).

3. Results and Discussion

Table 1. Physicochemical parameters of the rock samples

Well	pH	Cation Exchange Capacity (mg/100g)	Loss on Ignition (%)	Exchangeable acidity (mg/L)	Total Organic carbon (%)	Total Organic Matter (%)
1	6.9	32.3	17.33	0.40	0.50	0.86
2	7.0	33.5	18.00	0.45	0.60	1.04
3	6.8	34.1	17.70	0.50	0.55	0.95
4	7.2	35.1	17.60	0.56	0.67	1.16
5	7.5	34.6	19.01	0.60	0.72	1.24
6	7.2	34.7	18.90	0.59	0.57	0.99
7	6.7	32.9	17.90	0.62	0.69	1.19
8	7.6	35.6	18.63	0.55	0.59	1.02
9	6.6	36.2	19.30	0.48	0.63	1.09
10	7.4	33.7	18.40	0.63	0.70	1.21

The anions determination showed that the sulfate (SO_4^{2-}), nitrate (NO_3^-) and chloride (Cl^-) in the rock sample were 0.61, 0.01 and 0.003% by weight respectively. The carbonate content of the rock was 30.85%. This implies that the rock contains little or no phosphate, sulfate, nitrate and chloride but rich in carbonate. A typical clay rock contains 0.0.15% chloride (Krauskopd, 1979; Howard, 1996). The results of the physicochemical parameters of the rock sample are presented in Table 1. The total organic carbon (TOC) and total organic matter (TOM) were low suggesting that this characterized rock that does not contain plant residue.

This is not surprising since the dug wells are within 8m to 10m deep. The mean pH of the rock samples is 6.9 which is approximately neutral. The total nitrogen content was 0.07%, the exchangeable acidity with sodium hydroxide and cation exchange capacity were 0.40mg/100g and 22.3mg/100g characterize the sample as clay rock rich in illite mineral (Abdallah et al., 1999; MacFarlane, 1969).

The CEC of a typical illite rock is 20 – 30mg/100g (Abadallah et al., 1999). The mean value obtained for the rock samples is 32.3mg/100g which is in close agreement with the literature value. The CEC of clay soil in general, depends on the type of clay. CEC can be affected by cations in the presence of Ca^{2+} and Mg^{2+} present in the rock since they may also compete for adsorption sites with metal ions to be adsorbed. This can reduce metal adsorption.

The loss on ignition carried out on the rock samples to determine the percentage of volatile components is 17.33%. This accounts for the volatiles like carbon dioxide, fluorine, chlorine, sulfur and loss of water of hydration. This is in agreement with literature value for clay rock with LOI 20% (Abdallah et al., 1999).

The elemental analyses of the rock sample (Table 2) showed that there is no significant difference within each group of the parameter. Mean value of the percentage concentration of potassium (K), calcium (Ca) and silicon (Si) were higher than those of other elements such as sodium and magnesium. This characterized the clay rock as a double salt rock and made it possible for the mixed clay to be used as a coagulant in the remediation of polluted water.

Table 2. Mean value of the percentage concentration of the elements in the rock samples

Well	K	Ca	Na	Si	Mg	Pb	Cu	Zn	Fe	P
1	8.57	1.56	0.33	28.9	0.12	0.040	0.020	0.230	0.57	0.150
2	8.26	1.60	0.40	30.2	0.10	0.036	0.025	0.233	0.60	0.147
3	7.89	1.70	0.31	28.0	0.14	0.042	0.023	0.240	0.63	0.155
4	8.00	1.42	0.35	29.3	0.17	0.044	0.022	0.231	0.62	0.145
5	8.30	1.50	0.42	29.7	0.13	0.041	0.026	0.242	0.59	0.153
6	8.50	1.48	0.37	28.5	0.15	0.043	0.027	0.249	0.54	0.148
7	7.95	1.65	0.34	28.3	0.16	0.045	0.024	0.234	0.53	0.154
8	8.40	1.58	0.29	29.3	0.11	0.039	0.021	0.238	0.61	0.146
9	8.45	1.40	0.36	28.7	0.17	0.037	0.023	0.235	0.65	0.156
10	8.20	1.62	0.32	28.5	0.14	0.036	0.028	0.236	0.55	0.152

The mean value of percentage concentrations of trace metals (Pb, Zn, Cu, and Fe) in the rock sample were very low (0.02-0.57%) as shown in Table 2. This is similar to what was reported earlier (MacFarlane, 1969).

The combination of Fourier Transform Infra-red spectrometer and X-ray diffraction results provided a better identification of the clay mineralogy for Igando mixed clay. X-ray diffraction spectrum of the rock sample showed that the rock sample was mixed clay which comprises of different clay mineral (Illite, Smectite, Kaolinite, Quartz and Feldspar) with highest percentage of illite mineral which was 35.04%. Kaolinite, Illite + Quartz and Feldspar were respectively 22.20%, 25.64% and 17.09% as shown in Figure 2 and Table 3. The angle of absorption, $2\theta^o$ for illite, kaolinite are respectively at 8° and 18°, 12° and 24° while quartz absorbed at 20°. These are close to the literature values (Moore and Reynolds, 1997).

Table 3. Percentage mineral composition of analyzed rock sample

Component	% composition
Illite	35.04
Kaolinite	22.2
Illite + quartz	25.64
Feldspar	17.09
Total	100

FTIR studies of the rock sample helped in the identification of various forms of the minerals present in the clay samples. Coupled vibrations are appreciable due to the availability of various constituents and observed bands (in the range 3696-352 cm^{-1}) have been assigned as shown in Figure 3.
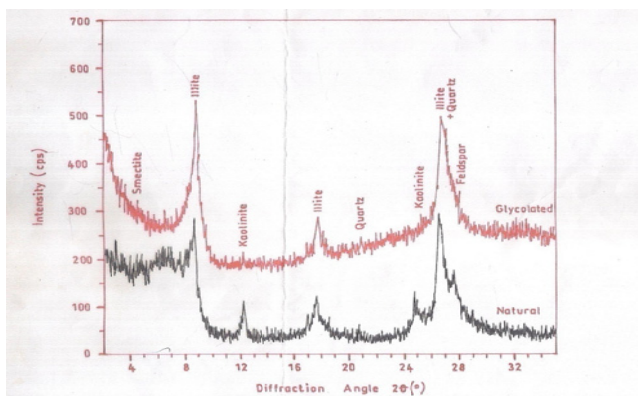
Figure 2. x-ray diffraction spectrum of the rock sample

In the IR studies of the clay, the Si-O stretching vibrations were observed at 469.99 cm^{-1}, 536.20 cm^{-1}, 693.95 cm^{1}, 752.70 cm^{-1}, and 793.50 cm^{-1} showing the presence of Quartz for the clay sample. The appearance of v (Si-O-Si) and δ (Si-O) bands also support the presence of quartz, a strong band at 3696.60 cm^{-1}, 3668.38 cm^{-1}, 3621.07 cm^{-1}, 3654.37 cm^{-1}, 3468.73 cm^{-1}, and 3436.3 cm^{-1} indicate the possibility of the hydroxyl linkage. However, broad band at 3436.3 cm^{-1}, 3468.73 cm^{-1}, and band at 1634.66 cm^{-1} in the spectrum of clay suggests the possibility of water of hydration in the samples. Most of the bands such as 3668.38cm^{-1}, 3654.37 cm^{-1}, 3696.60 cm^{-1}, 3621.07 cm^{-1}, 3468.73 cm^{-1}, 3436.3 cm^{-1}, 1115.39 cm^{-1}, 1031.55 cm^{-1}, 1007.27 cm^{-1}, 793.50 cm^{-1}, 752.70 cm^{-1}, 536.20 cm^{-1} and 469.99 cm^{-1} show the presence of illite. The vibrations observed at 536.62 cm^{-1}, 352.13 cm-1, and 469.99 cm^{-1} indicate the possibility of the presence of Smectite (Farmer, 2000). The presence of bands at 3436.3 cm^{-1}, 1115.39cm^{-1}1031.55 cm^{-1}, 1007.27 cm^{-1}, 793.50 cm^{-1}, 752.70 cm-1, 536.20 cm^{-1} and 469.99 cm^{-1} indicate the possibility of the presence of Kaolinite. These results are similar to those observed in kaoline and dicite (Farmer, 2000).
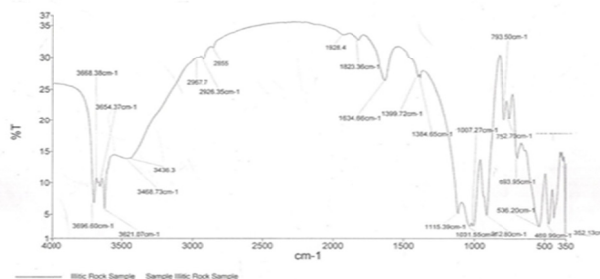

Figure 3. FTIR spectrum of the rock sample

The results of the AAS measurement of the heavy metals concentration in the in the well water (Table 4) show no significant difference in the mean values for each metal. The mean amount of copper and lead obtained were 0.05mg/L and 0.003mg/L respectively which are less than the permissible level by World Health Organization (1.0mg/L and 0.010mg/L respectively). Cadmium content is less than detectable limit. This implies that the heavy metals in these wells are less than the permissible limit as set by WHO.

Table 4. Mean Concentration of heavy metals in the well water

Well	Copper (mg/L)	Cadmium (mg/L)	Lead (mg/L)
1	0.050	LTDL	0.003
2	0.045	LTDL	0.004
3	0.055	LTDL	0.003
4	0.047	LTDL	0.004
5	0.049	LTDL	0.005
6.	0.051	LTDL	0.006
7	0.048	LTDL	0.006
8	0.052	LTDL	0.005
9	0.053	LTDL	0.003
10	0.054	LTDL	0.006

LTDL means less than detectable limit

The influence of several operational parameters such as initial metal ion concentration and amount of adsorbent

for the effective removal of Pb^{2+}, Cd^{2+} and Cu^{2+} from solution by adsorption onto the rock sample as an adsorbent were studied. Table 5 showed adsorption capacities of the rock sample for cadmium, copper and lead. It could be noted that the percentage of cadmium, copper and lead adsorbed at varying adsorbent dosage indicated that higher Cu removal was achieved at given amount of adsorbent dosage for the stock solution. This is also presented in Table 6 and illustrated in Figure 4.

Table 5. Mean concentration of unadsorbed heavy metal in the stock solution

Amount of rock sample (g)	Cu (mg/l)	Cd (mg/l)	Pb (mg/l)
0.0	1.000	1.000	1.000
0.5	0.725	0.744	0.816
1.0	0.463	0.584	0.604
1.5	0.246	0.452	0.493
2.0	0.197	0.285	0.342

Table 6. Effect of the mixed clay rock dosage on a given stock solution of the metals

Amount of rock added (g)	% of metal adsorbed		
	Cu	Cd	Pb
0.5	27.5	25.6	18.4
1.0	53.7	41.63	36.6
1.5	75.4	54.8	50.67
2.0	80.3	71.5	65.8

The remediation studies of polluted underground water using the rock sample as a coagulant in the treatment of the polluted water were performed. The results of the concentration of heavy metals in the polluted water using AAS showed that the polluted water sample did not contain detectable level of Cd and Cu but contained 5.75mg/L of lead. The rock sample removed lead from the contaminated water sample at every amount added but at higher dosage of 20g, the lead reduced from 5.75mg/L to 1.66mg/L (Table 7). Similar results have being reported in the literature (Hung et al., 1997; Ran et al., 2000). This implies that the rock sample removed 80% of the lead present in the contaminated water.
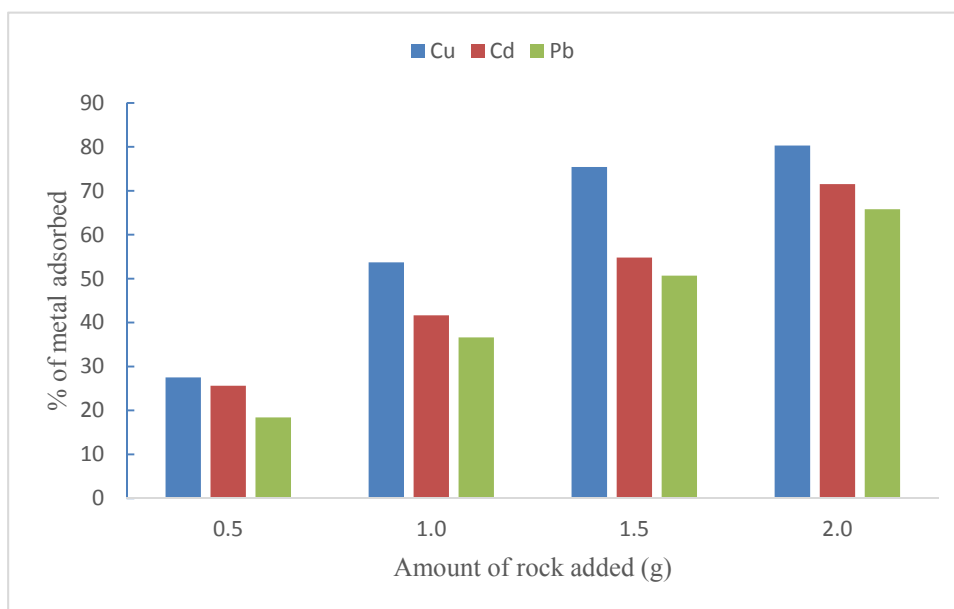

Figure 4. Percent of metal absorbed as a function of the quantity of the rock sample added

Table 7. Atomic absorption spectrophotometer result for contaminants removal

Amount of rock	Amount of heavy metal left (mg/L)		
added (g)	Cu	Cd	Pb
0	0.05	LTDL	5.75
5	0.02	LTDL	4.55
10	LTDL	LTDL	2.56
15	LTDL	LTDL	2.06
20	LTDL	LTDL	1.66

4. Conclusion

The work has demonstrated the successful application of Igando mixed clay for heavy metals removal as a cheap and environmentally friendly method. The removal of Pb^{2+} from the contaminated underground water and the reduction in concentration of Cu^{2+} and Cd^{2+} cations in stock solution by the mixed clay does not require any addition of a base or acid because at a pH of about 7, removal of about 80% of the metals was obtained at higher adsorbent dosage. Efficient removal of heavy metal ions by this mixed clay could possibly lead to new commercial markets for it as well as serving as a solution to potential environmental pollution problems.

The concentrations of heavy metals in well water in the area where the rock was dug are below the permissible level. Hence the well water is not contaminated by heavy metals.

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