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Hydrogeochemistry and sorption of heavy metals from contaminated onyeama mine waters using kaolinite clay

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Abstract
Clay minerals are good adsorbents due to its high surface area and abundant reactive sites. In this study the removal of heavy metals from the Onyeama mine water using a sourced kaolinite clay was investigated. Two water samples were collected from Onyeama mine audit and a nearby spring. These samples were analyzed for arsenic, chromium, cadmium and lead to determine their metal concentrations. The result of the analysis showed that arsenic is 40, lead is 8, cadmium is 230, and chromium is 18 times more than the maximum permissible limit indicated by World Health Organization. Adsorption mechanisms using the kaolinite clay was carried out as a function of time, pH and dosage. The quantity of metals removed remain constant irrespective of the amount of dosage added, however, after 90 minutes, approximately 98% Cr, 92% As, 45% Cd and 42% Pb were removed. At optimum pH of 6 and after 24 hrs, the uptake of Pb, As, Cd and Cr from the contaminated mine water were 100%. The present work contributes a new, efficient methods and cheap way for the removal of heavy metal ions from the mine.

Keywords: onyeama mine, heavy metal, acid mine drainage, sorption

Introduction

Oyeama coal mine was in active active production from 1916 to 2002 (Famboni, 1996; Ezemokwe et. al., 2016) [3]. However, the coal mining resulted to environmental damage including destruction of land, surface and groundwater as well as ecological system (Ezemokwe et. al., 2016) [3]. Coal mining among other mining activities is dominated with environmental degradation arising from pyrite oxidation and releasing of the heavy metal ions to the groundwater and surrounding environmental in the form of Acid Mine Drainage (AMD) (Greb, 2002; Koshal, 2002) [8, 19]. AMD of groundwater is a very severe form of environmental degradation to the area surrounding the mine (Egboka and Uma, 1985) [4]. Heavy metals are produced in Onyeama Mine as a result of Acid mine drainage (AMD), when sulfide minerals in the marine coal e.g., pyrite mine undergo the process of oxidation to generate a low pH (Egboka and Uma, 1985) [4]. The main problem of AMD are high acidity, high concentrated of sulphate containing a wide range of heavy metal ion such as Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+} (Weber *et al*., 2006; McCauley *et al*., 2009) [23, 14] that can be released to soil, water and ecological system. Therefore, remediation plans is necessary to avoid further damage to livestock and health.

Previous studies of the Onyeama mine and environs indicate that there are serious cases of pollution of the environment resulting from contaminated water from the mine audit, which enter the ground water and flows into the Ekulu river (Keating, 2001; Ozoko, 2015) [11, 16]. About 18.1 million litres of the mine water are pumped out of the coal mine into Ekulu river with heavy metal ion has serious potential for pollution (Ugwu, 1984) [21]. However, these researchers concentrate on determination of the extent of pollution and their effects without studying remediation strategies.

Remediation of abandoned and contaminated mine can be carried out using different techniques such as chemical precipitation, oxidation, hydrolysis, reverse osmosis, solvent extraction, neutralization, electrochemical remediation adsorption and biosorption (Eslami *et al* 2018; Feng, *et al*., 2018; Qasem et. al., 2021) [5, 7, 20]. Sorption is a popular and highly effective method for removal of heavy metals from waste water and AMD (Motsi *et al*, 2009; Ratat *et al*, 2018; Uddin, 2017; Hussain *et al*., 2021) [15, 18, 10]. The advantage of adsorption method include simplicity of operation, access to the adsorbent material, not recurring a chemical substance and little sludge production.

The aims of this research are firstly to evaluate the content of effluent from the audit of the Onyeama mine to the water from nearby Ekulu river. Secondly, to investigate the removal of heavy metal from the water obtained from Onyeama mine audit using locally sourced kaolinite clays from Nsukka, Nigeria.

Geology

The area falls within Anambra basin in is the Lower Benue Trough and comprises of Ajali and Mamu Formation (Figure 1). Ajali Formation consists of friable sandstone whereas the Mamu Formation is mainly made up of shale with intercalation of sand and siltstone, coal, sandstone, mudstone and sandy shale. The outcrop at Iva valley village near onyeama mine, consists mainly of fractured shale and coal. The coal seam in this section has a thickness of about 1.5m.

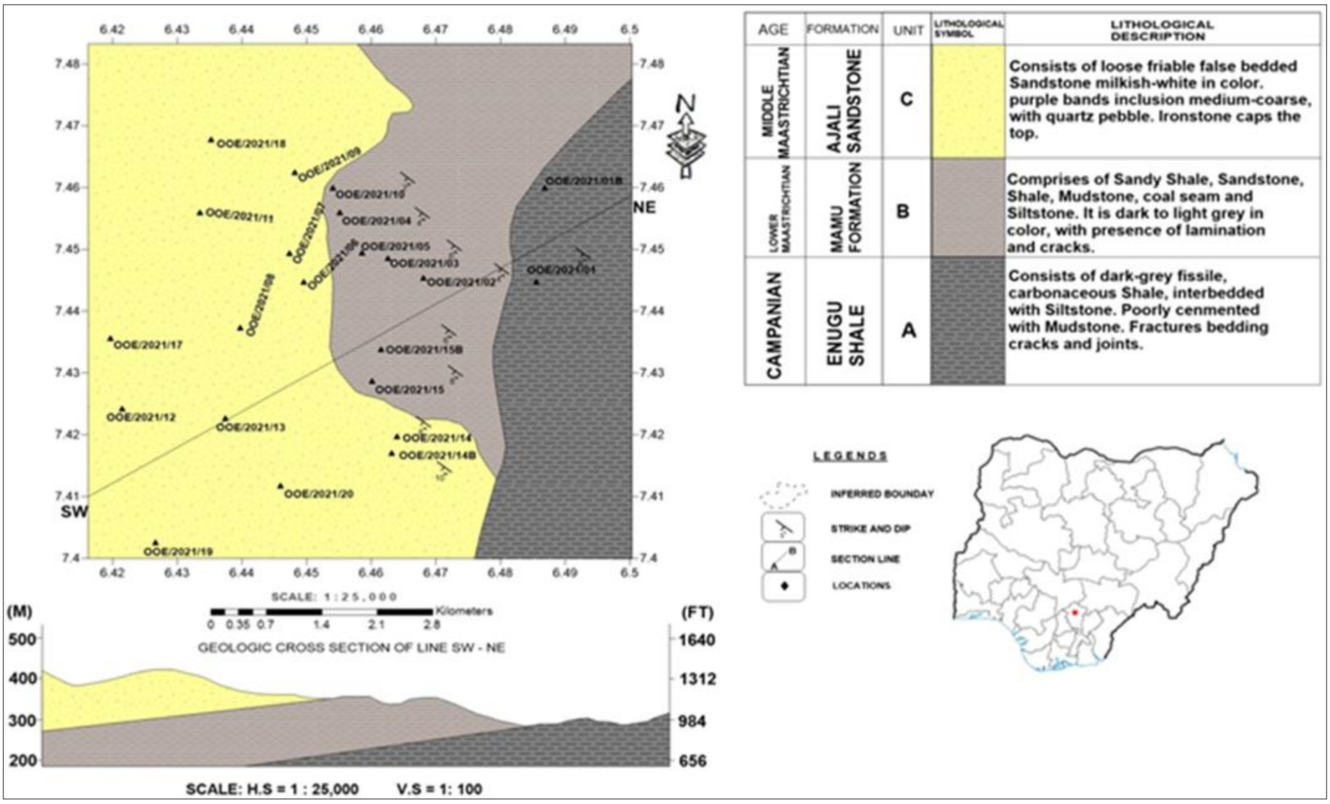

Fig 1: The geological map of the Ugwu Onyeama and environs

Materials characterization and method
Geochemical analysis of clay sample

A clay sample was collected from a clay unit at Edem Ani in Nsukka, Nigeria. The clay samples was collected from a fresh surface and stored in a transparent polythene bag. The concentration of minor and trace metals of the clay was determined using the Atomic Absorption Spectrophotometer (Pye. Unicam model Sp-9, 1984) and standard procedures laid out by the American Public Health Association (APHA, 2005) [1] at National Arbovirus and Vectors Research Centre (NAVRC), Enugu, Nigeria.

Xray diffraction (XRD)

The clay sample was added in a standard circular holder and flattened using a glass slide. Mineralogical compositions were identified using X-ray diffractometer (Philips X-ray Analytical, Amsterdam, The Netherlands) with a graphite monochromatized copper Kα source operated at 40 kV and 40 mA. The spectra were acquired at a scan speed of 1 min-1 with a slit size of 1.0 degrees in the range of **2** to 70° 2ϴ, at step size of 0.02° at measurement temperature of 25°C. Mineral phases were identified using Origin Pro software. All the experiments were performed at National Arbovirus and Vectors Research Centre (NAVRC), Enugu, Nigeria.

Surface area pore volume and pore size data determination

The adsorption of nitrogen gas on the surface of clay sample was used to determine the equivalent nitrogen gas adsorbed to a single layer on the clay surface. This was carried out by using Quantachrome Nova Win at National Arbovirus and Vectors Research Centre (NAVRC), Enugu, Nigeria. Samples were analysed at outgas temp of 250°C, earth temp of 273 K using 0.15g of sample for 3 hours and equilibrium time of 60 seconds. For comparison, the surface area, pore volume and pore size data were obtained using different methods.

Hydrogeochemistry of the water samples

A total of two sample were collected from the mine and its environs. Sample A (collected at the mine audit) and sample B (collected at a spring at about 1Km away from the mine audit). These samples were analysed for cadmium (Cd), chromium (Cr), arsenic (As), lead (Pb) using the Atomic Absorption spectrophotometer (AAS). Water samples were also analysed for Total dissolve solid (TDS), Total solid (TS), Total suspended solid (TSS), Electrical conductivity (EC) and the pH and alkalinity.

Adsorption with kaolinitic clays

The clay was pounded in mortal for about 1hr 30 minutes to get a pulverized grain. For the adsorption studies, 0.5g of kaolinite clay were added to 14 different tubes and 20 ml of sample A obtained from the mine audit were added to each tube. The pH of the solution were adjusted to get pH range of 5 to 8 using few drops of 0.1 M HNO_3 and NaOH. The batch experiment were stirred constantly and allowed for 24 hours to equilibrate. For the sorbent dosage experiment, 1.0, 0.2, 0.3, 0.4, 0.6g of kaolinite clay were added to a container and 20 ml of water from the Onyeama mine audit were added. A 0.5 g of the clay samples were added to ten different tubes to determine the rate of adsorption (in relation to time). The pH were adjusted to 6, by adding 1 drop of 0.1M NaOH. The experiments were allowed for 1 hr at 25℃ and sampled every 30 minutes. At the end of the experiment, the supernatant were separated from the adsorbent (clay) after centrifuging for 5 minutes. The supernatant were analyzed using Atomic Absorption

Spectrophotometer (AAS) at National Arbovirus and Vectors Research Centre (NAVRC), Enugu, Nigeria.

The adsorption capacity at a particular time is called by the equation below The adsorption efficiency capacity, qt (mg/g) at a specified contact time t, was calculated using Eq. (1):

$$q_t = \frac{(C_o - C_t)V}{m} \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where C_o and C_t = the amounts of initial and retained metal ions in the solution at a particular time t (mg/L), respectively. V = solution volume (L) and m = mass of adsorbent (g).

Results

Geochemical analysis of clay sample

The results of the geochemical analysis for the clay sample obtained from Edem_Ani in Nsukka area (Table 1) reveal that the clay has very low amount of heavy metals. Heavy metals such as As and Cr are within the WHO limits for clays that can be used for remediation purposes. The low trace elements composition of Arsenic (As) and zero presence of Lead (Pb) satisfied the potential usage of these clays as ingredients for remediation. The clay does not contain Hafnium (Hf), Rubdium (Rb), and Zirconium (Zr) Samarium (Sm) Uranium (U), Thorium (Th), Lead (Pb), Lanthanum (La), Europium, Lutetium((Lu), Radium (Ra) and Yiterium (Yb). Bromine (Br), Cesium (Cs), Scandium (Sc) occur in lower concentrations in the kaolinitic clay.

Table 1: The result of the geochemical analysis for the clay sample obtained from Edem_Ani

S/N	Metals (ppm)	Concentration of clay (ppm)
1	Arsenic (As)	0.020
2	Barium (Ba)	0.092
3	Bromine (Br)	0.04
4	Cesium (Cs)	0.90
45	Cobalt (Co)	0.0
6	Europium (Eu)	0.0
7	Iron (Fe)	8.94
8	Hafnium Hf)	0.00
9	Mercury (Hg)	0.068
10	Lutetium ((Lu)	0.0
11	Rubdium (Rb)	0.0
12	Antimony (Sb)	0.038
13	Scandium (Sc)	0.60
14	Samarium (Sm)	0.000
15	Calcium (Ca)	4.798
16	Terbium (Tb)	0.063
17	Yiterium (Yb)	0.0
18	Zinc (Zn)	2.50
19	Zirconium (Zr)	0.0
20	Uranium (U)	0.0
21	Thorium (Th)	0.0
22	Radium (Ra)	0.0
23	Lead (Pb)	0.0
24	Potassium (K)	6.07
25	Chromium (Cr)	0.06
26	Lanthanum(La)	0.0

Xray diffraction (XRD)

The XRD pattern indicate that the major mineral is kaolinite with minor amount of quartz, orthoclase and ablite (Figure 2)

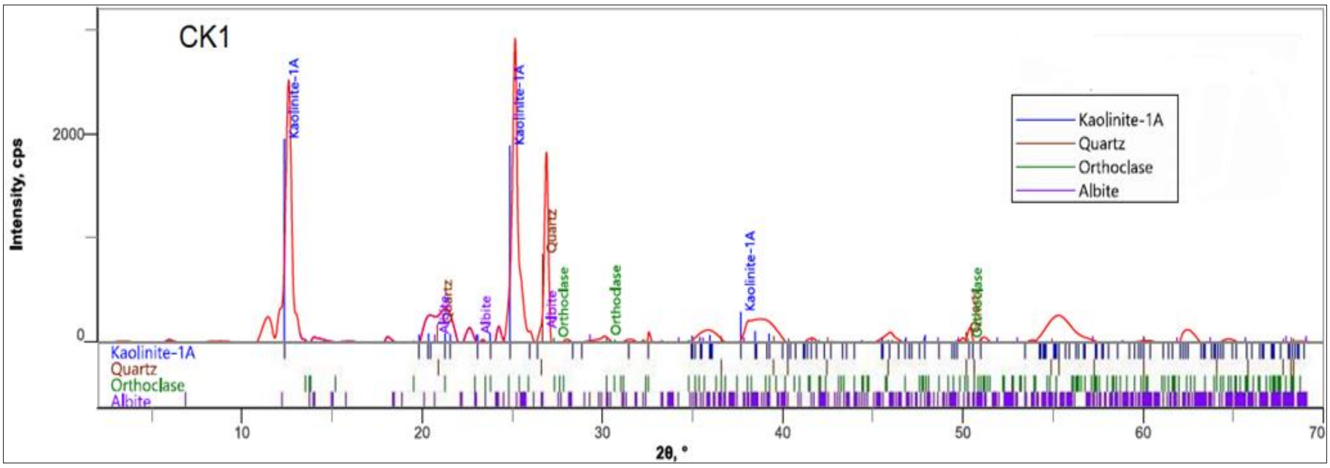

Fig 2: XRD spectra of clay sample showing presence of kaolinite, quartz, orthoclase and ablite

Surface area, pore volume and pore size data determination

The result of the surface area, ore volume and pore size data determination is summarised in Table 2 below. he BET surface are of the clay is 285 m^2/g. This is most higher for natural kaolinite with specific surface areas of 5 to 25 m^2 /g (Volzone *et al*. 1999) [22]. This indicates that the clay can be used for removing heavy metals from aqueous solution.

Table 2: Summary of the surface area, pore volume data and pore size of clay

Single Point BET	**195 m^2/g**
MultiPoint BET	285 m^2/g
Langmuir Surface Area	945 m^2/g
DJH Method cumulatibe adsorption surface area	350 m^2/g
DG method cumulative adsorption surface area	374 m^2/g
t-method external surface area	385 m^2/g
DR method micropore area	327 m^2/g
DFT cumulative surface area	77.2 m^2/g
Pore Volume Data	
BJH method cumulative adsoprption pore volume	17.1cc/g
DH method cumulative adsorption pore volume	17.6 cc/g
DR method pore volume	11.6 cc/g
HK method pore volume	528 cc/g
SF method pore volume	142 cc/g
DFT method pore volume	917 cc/g
Pore size data	
BJH method pore Diameter (Mode Dv (d))	21.38nm
DH method pore Diameter (Mode Dv (d))	21.38nm
DA method micropore Pore Width	5.83 nm
DR method pore Diameter (Mode)	2.84 nm
HK method pore Diameter (Mode)	36.7nm
SF method pore Diameter (Mode)	45.3 nm
DFT method pore Diameter (Mode)	2.64 nm

Hydrogeochemistry of the water samples

The results of the water analyses show that the concentrations of the heavy metal follows the order of Cr > As > Pb > Cd (Table 3). The mean value of Cr, As, Pb, Cd are 0.831, 0.406, 0.086, 0.6923 mg/l, respectively exceed the Maximum Contaminant Limits. Trace metal of this, level are very toxic, unsupportive to aquatic life, and causes environmental problem and degradation to our environment (Huttan, 1987). Some of metal concentration decreases away from the mine audit. For example, the concentration of chromium decreases from 0.939 (sample A) to 0.723 mg/l (sample B). The average value of Cr is 0.831mg/L and this is above the WHO limit of 0.05mg/l. High amount of Cr can cause cancer and other form of neuro diseases after prolong consumption (WHO, 2011). Arsenic have an average concentration of 0.406 mg/l which is more than 40 times the maximum permissible limit of 0.01mg/l indicated by WHO (2022). This high level has an adverse effect on the liver and causes cirrhosis and liver cancer (Huttan, 1987). Lead has mean concentration of 0.086 mg/l which above the standard limit WHO 2022)) of 0.01mg/l by eight times. This can cause cancer, death, mental health issue and serious effect on the nervous system (WHO, 2022). Finally, cadmium has averages concentration of 0.6923 mg/l, which is 230 times higher than the permissible limit of 0.003 mg/l. In addition, the water analysis results of the water samples from Onyeama mine audit and a spring about 1 km from the mine reveal that the Total dissolve solid (TDS) ranges from 120-520 mg/l. The maximum permissible limit of TDS using WHO standard is 500mg/l. The average pH is 5.4 indicating low acidity. This indicates that the water is not suitable for drinking, agricultural and domestic purposes.

Table 3: Hydrogeochemical analysis of the waters from Onyeama Mine and environs in mg/L

Sample Identification	pH	EC	Temp	Pb	Cr	Cd	As	TS	TSS	TDS
Onyemine audit (A)	5.6	20	32	0.0740	0.939	0.0680	0.679	100	80	120
Spring water (B), 1 Km away from mine	6.0	190	30	0.0980	0.723	0.0705	0.133	480	400	520
WHO limits (2007)	6.5-8.5	1000	-	0.01	0.05	0.003	0.01	-	-	500

Adsorption with kaolinitic clays

Influence of pH

The results for the adsorption experiment indicate that at pH 5 – 8, the adsorption of Pb (II), As (II), Cd (II) and Cr (II) from the contaminated mine water containing 0.0740 Pb mg/L, 0.939 mg/L As, 0.0680 mg/L Cd, 0.679 mg/L Cr were 100% (Fig. 3). In the range of pH studied, uptake of both charged and uncharged metal species exist. The pH of solution largely controls the amount of metal to remove in any aqueous solution due to metal speciation. The surface area and surface charge of the clay materials play important role during sorption process (Kumari and Mohan 2021) [13]. The adsorption of cations on clay minerals increases as pH increases (Rao and Kashifuddin, 2016) [17], thereby causing the surface of the clay to become negatively charged, and reducing the repulsive force.

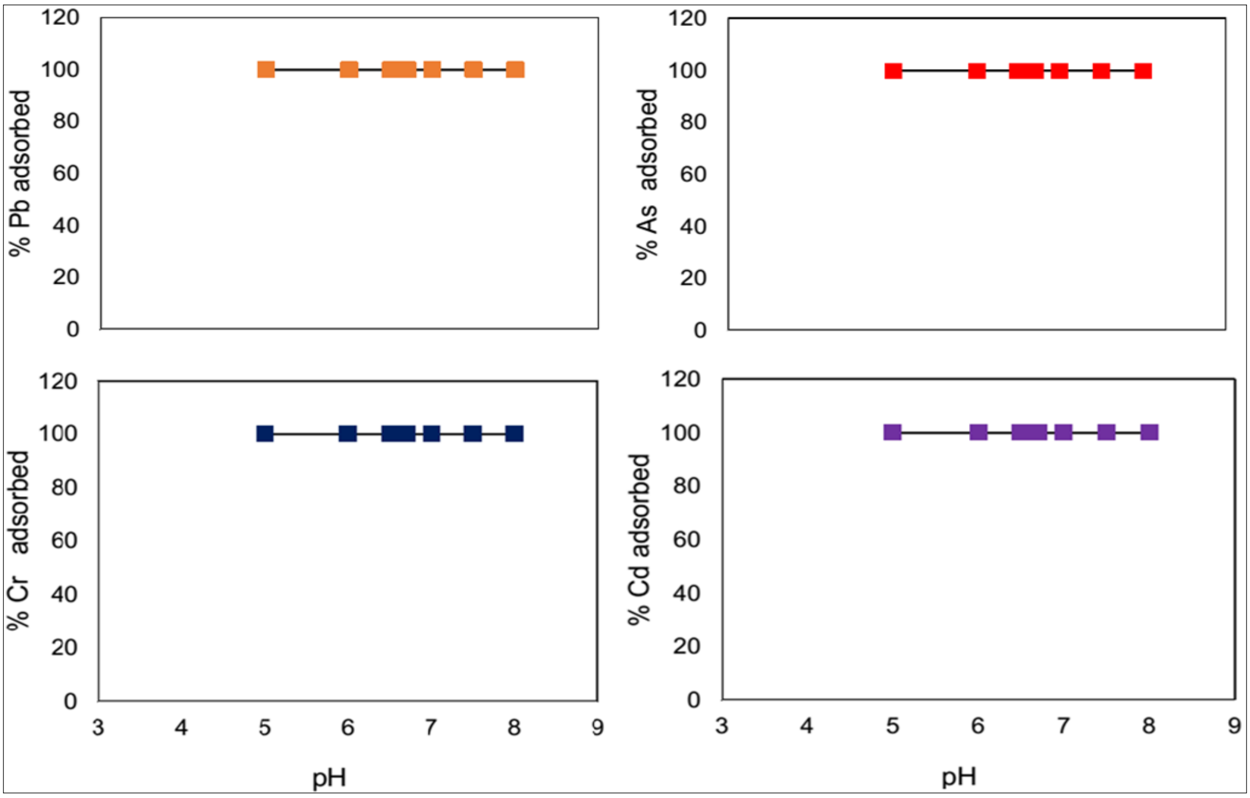

Fig 3: Adsorption of heavy metals from Onyeama mine audit water using kaolinite from Nsukka Formation as a function of pH.

Effect of dosage

The adsorbent dosage can influences the amount of the metal uptake from the solution. The amount of heavy metals removed remains constant irrespective of the amount of dosage of kaolinite added (Fig. 4). The increase in the percentage of metal ion adsorbed with increase in the weight of the adsorbent may be attributed to increase in the number of available binding sites and decrease in the electrostatic potential near the solid surface which favours sorbent–solute interaction (Rao and Kashifuddin, 2016) [17]. For the concentration of the metals present in the mine water, 0.2g of adsorbent has the ability to achieve the adsorption ability of 1g clay as the adsorbent.

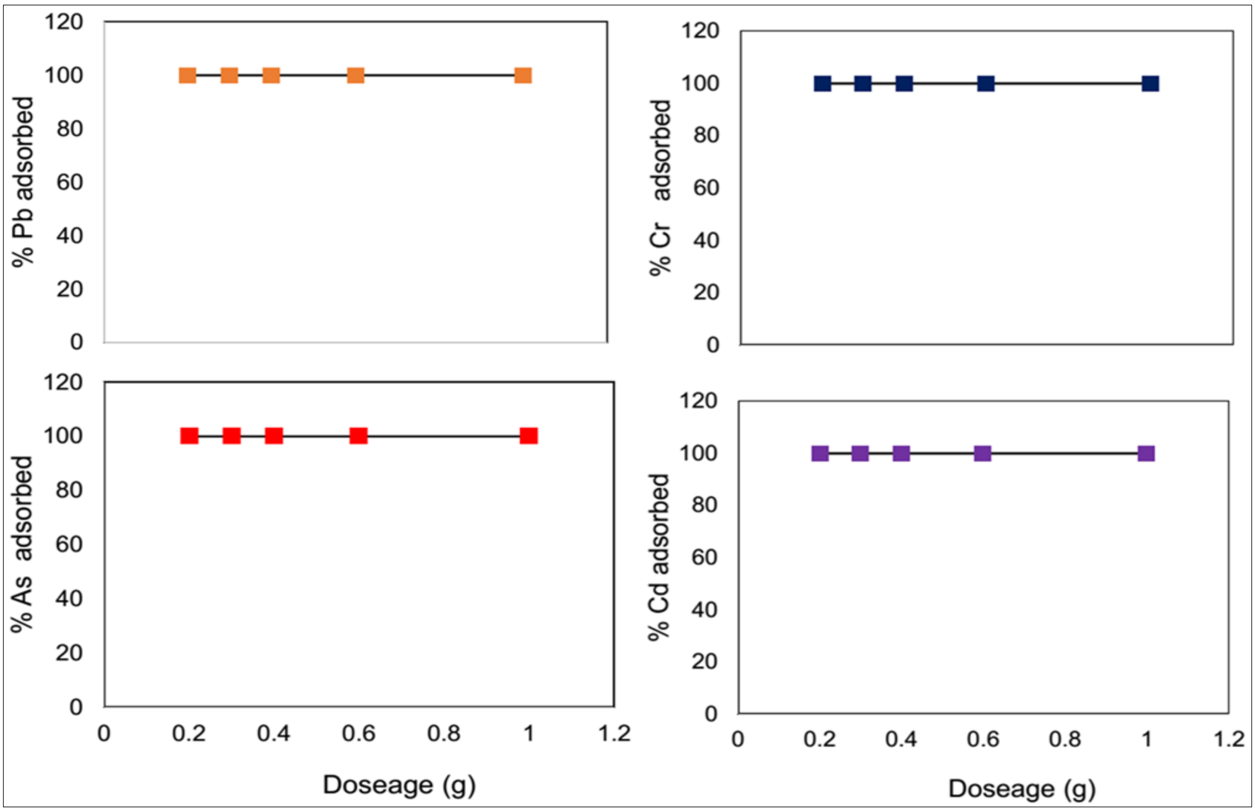

Fig 4: Adsorption of heavy metals from Onyeama mine audit water using kaolinite from Nsukka Formation as a function of sorbent dosage (g)

Effect of time

For the sorption of metals on kaolinite clay, the overall kinetic rate of differs from each ion. The initial sorption rate is highest for As compared to other ions (Fig. 5). The adsorption of Pb, Cr and Cd is fairly linear suggesting a steady increase in adsorption over time. However, the adsorption of As revealed two critical paths; fast metal adsorption process up to 100 min and a slow adsorption until the equilibrium was attained. The fast rate adsorption is consistent with the adsorption of Cu, Pb, Ni and Co described by Bhattacharyya and Gupta, 2009.

The fast initial part is as a result of the presence of a large number of vacant sites available, however, after 100 min, the removal rates reduced due to the rapid filling of active sites of the adsorbents by the ions.

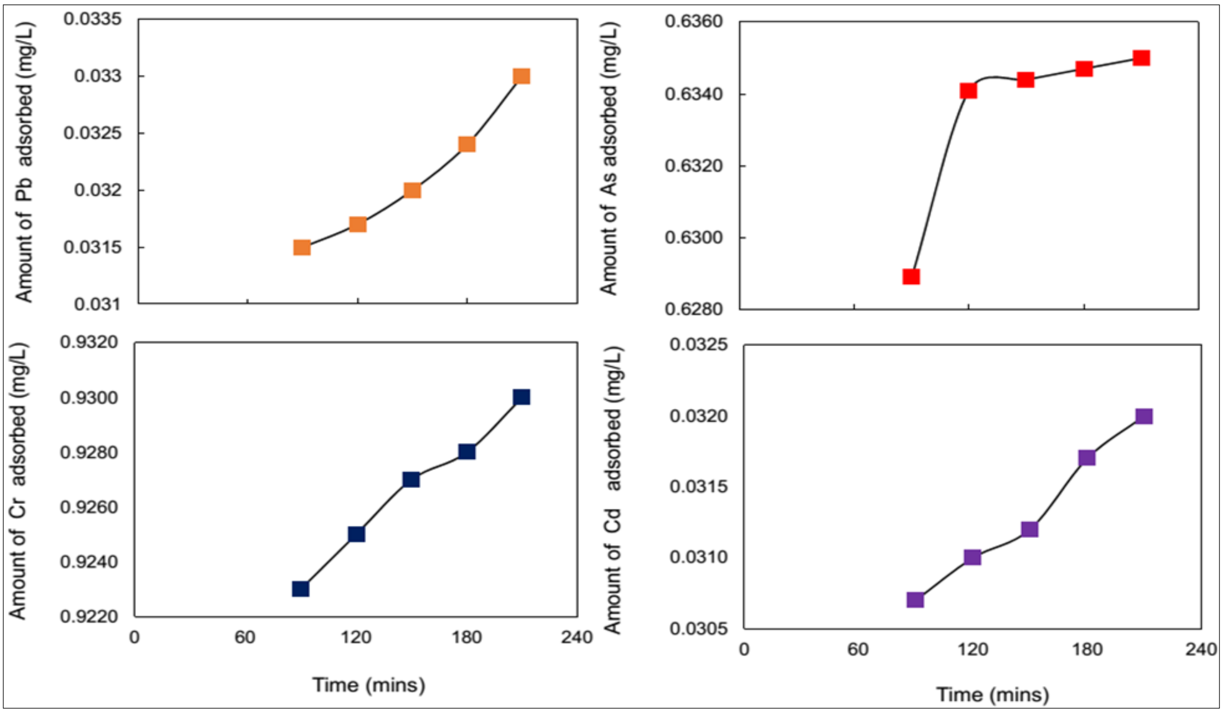

Fig 5: Adsorption of heavy metals from Onyeama mine audit water using kaolinite from Nsukka Formation as a function of time.

Conclusion

The water quality of the spring near the mine as well as the water from the mine audit revealed presence of heavy metals with contaminant level above the Maximium Contaminant Levels of WHO. The detected heavy metal pollutant have being continuously discharging into the Ekulu river, and has a negative impact on the ground water around the mine and surface water condition of the studied area and the people of Trans Ekulu, Enugu Metropolis. The kaolinite clay obtained from Nsukka Formation in Enugu state, Nigeria is successfully used for the remediation of polluted water from Onyeama mine. The adsorption mechanism were studies as a function of contact time, pH and sorbent dosage. Kaolinite clay was able to remove the contaminant in 24hrs. The present work contributes to efficient methods and cheap way for the removal of heavy metal ions from the Onyeama mine. We recommend that the government should provide funds for the remediation of the water from the abandoned mine.

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