

# Variation of Thermophysical Properties of Clay with Adsorption Optimization.

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## ABSTRACT

Clays have some properties which make them good adsorbents. The adsorption of heavy metal ions by clay usually affects its thermal properties and these properties have direct influence on seed germination and crop growth. In this study, the variation of thermophysical properties of clay with adsorption of some heavy metal ions at different concentrations was investigated. An Atomic Absorption Spectrophotometer (AAS) was used to determine the concentrations in the samples. A known mass of clay sample was mixed with certain volume of already prepared Pb (II), Cd (II), Cu (II), Ni (II), and Zn (II) solutions of different concentrations; after which some cylindrical pellets were made from the mixture of the clay sample with aqueous solutions of different concentrations and the thermal properties determined.

The transient measurement technique was used in this work to determine the thermal properties of doped clay. Results showed that Copper had the highest ion exchange in the clay, while Cadmium had the lowest ion exchange. The thermal conductivity of clay increases with increase in the concentration of heavy metal being adsorbed by the clay to a considerable level. The lowest thermal conductivity was found to be 9.5824W/mK (preliminary study) and the highest was found to be 10.5010 W/mK. Thermal diffusivity ranged from  $2.69674 \times 10^{-6} m^2/s$  to  $3.47991 \times 10^{-6} m^2/s$ . However, For all the samples, thermophysical properties increases as the concentration increases to a certain optimum level above which cation exchange is no longer possible.

From the results, it can be concluded that the concentration of heavy metals being adsorbed by clay affects its thermal properties. Increase in the rate of heat being conducted by clay usually leads

to poor seed germination, poor crop growth, rotting, etc. in agricultural sector.

(Keywords: heavy metals, clays, adsorption, thermophysical properties, transient method)

## INTRODUCTION

If two bodies of different temperatures are in contact, a transfer of heat occurs between them. Transfer of heat by conduction governs the thermal conditions within almost the entire crust of the earth, which is mostly formed by solid rock. Conduction is a significant process immediately at the Earth's surface but is not really significant above the surface since the atmosphere is composed of fluids. Heat conduction is a process whereby there is an exchange of heat within solid bodies by lattice interaction of molecules of two bodies in contact.

All kinds of materials have the ability to store heat and the capability of a body to store heat is expressed in terms of its specific heat. The process of change resulting from exposure of rocks to the influence of the atmosphere is known as weathering (Merill, 1967; Robert, 1967). Soil is the most common product of weathering on land. Formation of soil is brought about by the decomposition and disintegration of rocks and rock forming materials. Clay is a natural, earthy, fine grained material which develops plasticity when mixed with a limited amount of water, composed primarily of silica, alumina, etc. (McGraw-Hill Dictionary, 1989). Their mineralogical structure and small grain size (Emofurieta, *et al.*, 1994) result in specific properties that make them good adsorbents. Principally, they have a large specific surface area and their surfaces are negatively charged (Fetter, 1994). Clays also have some ion exchange properties and this is why ions from

solution are exchanged for similarly charged ions attached to the clay.

Clays also have cation exchange properties in that the negative charge on the clay surface is balanced by equal number of positive charges (or cations) in the solution in order to maintain electroneutrality. Clay soils play vital role as the medium on which plants grow. People depend on fertile soil to support plant growth and provide life-sustaining nutrients in food. However, clay may contain heavy metals depending on the prevailing geologic minerals. Heavy metals are a group of elements on the periodic table of elements, having specific gravities greater than 4.0 (Adriano, 1986). Heat flow in soils may be determined from the knowledge of thermal conductivity and temperature gradient. Fundamental information on how salts and water affect thermal conductivity of soil is also needed in modeling water and energy movement in systems containing salt-affected soils (Noborio and McInnes, 1993).

The thermo-physical properties of clay have a wide range of applications: determination of the best suitable soil for planting some crops (Sass, 1971; Schatz, 1972) and distribution of heat at the surface of the earth. Soil thermal properties are required in many areas of Engineering, Agronomy and Soil Science and this can find application in the distribution of heat at the surface of the earth. Soil thermal properties have direct influence on seed germination, seedling emergence and subsequent crop growth. (Ghuman and Lal, 1985). Knowledge of soil thermal properties is an important factor in understanding mass and energy exchange processes in the soil atmosphere system (Shabbir, *et al.*, 2000).

Although, Shabbir, *et al.*, 2000 are of the opinion that to understand the thermal structure of rocks, investigation of thermo- physical properties is very important, the effects of some other factors or properties such as texture of the soil and water content had also received more attention, but the effect of chemical composition on thermal properties had received little attention. Therefore, it is necessary to investigate the effects of adsorption of some heavy metal ions from solutions by clay on its thermal properties.

The aims of this work are: to determine the concentrations of some heavy metals in clay, to determine the thermo-physical properties of clay after adsorption and the variation of these properties with adsorption of some heavy metal

ions and the possibility of attaining saturation in cation exchange. Moreover, since heat distribution is very crucial in plant selection for various soil types, predominantly for application in the agricultural sector, the knowledge of the influence of soil thermal properties on seed germination, crops and plant growth and the distribution of heat at the surface of the earth is very important.

## MATERIALS AND METHODS

The sample (clay) was collected from the clay pit at Ibadan Bricks and Clay Products Mining Industry site, Adesekun, Omi-Adio, along Abeokuta Road in Ido Local Government Area of Oyo State. The sample was collected at a depth of about 1.5m (approximately 5 feet). Enough quantity of the clay sample was collected and stored properly for the research work. The sample was washed with deionized water three times and decanted each time. This was done to remove all the water-soluble ions from the sample. It was then sun-dried for some days and thereafter was crushed and sieved with a 100  $\mu$  m mesh-size sieve.

The sieved clay sample was analyzed for its contents of Lead (Pb), Copper (Cu), Nickel (Ni), Cadmium (Cd), and Zinc (Zn). The sample was digested by the use of two methods: Complete digestion/Nitric acid extraction method and Baker and Amacher Method. Complete digestion/Nitric acid extraction method involves digestion of sample in a mixture of  $\text{HNO}_3 - \text{HF} - \text{HClO}_4$ , while Baker and Amacher Method involves digestion of sample in a mixture of  $\text{HF} - \text{HNO}_3 - \text{HClO}_4 - \text{H}_2\text{SO}_4$ . After using the two methods of digestion described above, the digested samples were analyzed for heavy metal concentration using AAS.

The concentrations of these heavy metals in the clay sample were given in *ppm or mg/L* and were converted to  $\mu$  g/g. Then, 2000ppm of Pb (II), Cd (II), Zn (II), Ni (II), and Cu (II) were prepared respectively as the stock solutions. The mass of salt that would contain 2g each of Pb, Cd, Zn, Ni, and Cu was calculated, weighed, and transferred quantitatively to a 1000ml (1L) standard flask and made up to mark with deionized water. From the 2000ppm stock solution, various concentrations each of Pb (II), Cd (II), Zn (II), Ni (II), and Cu (II) were prepared. This was done by diluting the

2000ppm stock solution down to the various concentrations. The following concentrations of Pb (II), Cd (II), Zn (II), Ni (II), and Cu (II) solutions were prepared: 50ppm, 100ppm, 200ppm, 400ppm, 800ppm, and 1600ppm. Each prepared solution was properly labeled as: Pb1 (50ppm), Pb2 (100ppm), Pb3 (200ppm), Pb4 (400ppm), Pb5 (800ppm), Pb6 (1600ppm), and Pb7 (2000ppm). Similar labeling was also done for other solutions too.

The sieved clay sample was then mixed with each concentration of metal prepared and cylindrical molds of known dimension were made from the pellets being formed by the mixture of the clay sample with the solutions of different metal concentrations. A preliminary work was carried out in order to know the volume of solution to be added to the clay sample to form paste which was later used to form pellets. This was done by weighing 5g of clay and adding deionized water to the clay drop by drop with the help of the calibrated burette until a thick paste was formed. The volume of deionized water used was noted. This was found to be approximately equal to 2ml.

The preliminary work was done in duplicates and the molds/pellets formed thereafter were labeled X and Y. After the preliminary work, 2ml each of the already prepared different concentrations of Pb (II), Cd (II), Zn (II), Ni (II), and Cu (II) solutions was added to the clay sample. The different concentrations added to the clay samples were: 50ppm, 100ppm, 200ppm, 400ppm, 800ppm, 1600ppm, and 2000ppm, respectively. Then, cylindrical molds/pellets were made from the paste being formed by the mixture. The molds that were being formed from the pastes were labeled: X, Y, Cu1, Cu2... Cu7; Pb1, Pb2, Pb3... Pb7; Zn1, Zn2,... Zn7; Ni1, Ni2, Ni3... Ni7; and Cd1, Cd2, Cd3,...Cd7, respectively.

All the samples were sun-dried for 2 days after which they were oven-dried. This was done to ensure that all the water content in the samples was removed. Then, temperature measurements were carried out on the different molds being formed from the mixture of the clay sample with solutions of different concentrations of Cu(II), Pb(II), Cd(II), Ni(II), and Zn(II). The temperature measurements were carried out in order to determine the thermal properties (i.e. thermal conductivity, specific heat capacity and thermal diffusivity) of the molded samples.

Given that the thermal conductivity,

$$K = \frac{Ivtx}{A\Delta\theta\Delta t} \quad (1)$$

Where,  $I$  = flowing current (A)  
 $v$  = voltage supplied in volts (V)  
 $t$  = time duration in (s)  
 $x$  = thickness of the slab/sample (m)  
 $A$  = area (m<sup>2</sup>)  
 $\Delta\theta$  = temperature gradient (K)

The specific heat capacity;

$$c = \frac{Ivt}{m\Delta\theta} \quad (2)$$

While thermal diffusivity,

$$\lambda = \frac{K}{\rho c} \quad (3)$$

$m$  is the mass of the sample and  $\rho$  is the density.

The experiment was carried out by rapidly exposing the top surface of the clay sample that is insulated on all other surfaces to the heat source and measuring the temperature at the base of the clay sample at an interval of 30s up to 300s after the introduction of heat. The 300-s measurement duration is generally ample to obtain linear behavior in a sample approximately 1.0cm thick (Middleton, 1993). The actual temperatures were obtained by subtracting the initial ambient temperature,  $\theta_i$  (effectively making the measurements relative to zero) from the final temperature,  $\theta_f$ . The temperatures on the surface of the clay samples were taken at an interval of 30s up to 300s. Then, the actual temperatures were plotted against time and straight line graphs were obtained.

## RESULTS AND DISCUSSION

Table 1 shows the concentrations of heavy metals as determined in the clay sample in duplicates for the two methods and the averages were taken and these are presented in the Table 1 below:

**Table 1:** Concentrations of Heavy Metals in Clay ( $\mu\text{g/g}$ )

Metals	Complete Digestion Method ( $\mu\text{g/g}$ )	Baker and Amacher Method ( $\mu\text{g/g}$ )
Zn	82.875	79.750
Cu	110.375	117.500
Cd	0.975	1.088
Pb	27.038	23.950
Ni	60.225	50.238

The results obtained from the Atomic Absorption Spectrophotometer after the two methods of digestion were employed to analyze for the

concentrations of heavy metals in the clay sample showed that Copper (Cu) had the highest concentration in the clay sample followed by Zinc (Zn). Nickel (Ni) was next to Zinc followed by Lead (Pb) and the least was Cadmium (Cd).

The results obtained for the masses,  $m(\text{kg})$  for all the samples; the radius,  $r (m)$ ; the area,  $A (m^2)$ ; the thickness,  $x (m)$  and volume,  $V (m^3)$  for all the samples are presented in Table 2. Samples X and Y were used for preliminary studies i.e. the control experiment. Their masses ( $\text{kg}$ ), radius ( $m$ ), area ( $m^2$ ), thickness ( $m$ ) and volume ( $m^3$ ) are also presented in Table 2.

**Table 2:** Values of the Dimensions of Samples used for Experiment.

Samples	Masses (kg)	Radius, $r (m)$	Area, $A (m^2)$	Thickness, $x (m)$	Volume, $V (m^3)$
X	0.00380	0.00910	$2.602 \times 10^{-4}$	0.00930	$2.4199 \times 10^{-6}$
Y	0.00350	0.00885	$2.461 \times 10^{-4}$	0.00950	$2.3380 \times 10^{-6}$
Cu <sub>1</sub> (50ppm)	0.00420	0.00930	$2.717 \times 10^{-4}$	0.01010	$2.744 \times 10^{-6}$
Cu <sub>2</sub> (100ppm)	0.00430	0.00905	$2.573 \times 10^{-4}$	0.01020	$2.624 \times 10^{-6}$
Cu <sub>3</sub> (200ppm)	0.00420	0.00925	$2.688 \times 10^{-4}$	0.00970	$2.607 \times 10^{-6}$
Cu <sub>4</sub> (400ppm)	0.00420	0.00905	$2.573 \times 10^{-4}$	0.01000	$2.573 \times 10^{-6}$
Cu <sub>5</sub> (800ppm)	0.00430	0.00930	$2.717 \times 10^{-4}$	0.00970	$2.635 \times 10^{-6}$
Cu <sub>6</sub> (1600ppm)	0.00430	0.00935	$2.746 \times 10^{-4}$	0.00960	$2.636 \times 10^{-6}$
Cu <sub>7</sub> (2000ppm)	0.00420	0.00945	$2.806 \times 10^{-4}$	0.00960	$2.694 \times 10^{-6}$
Cd <sub>1</sub> (50ppm)	0.00420	0.00925	$2.688 \times 10^{-4}$	0.00950	$2.554 \times 10^{-6}$
Cd <sub>2</sub> (100ppm)	0.00410	0.00925	$2.688 \times 10^{-4}$	0.00980	$2.634 \times 10^{-6}$
Cd <sub>3</sub> (200ppm)	0.00420	0.00930	$2.717 \times 10^{-4}$	0.00980	$2.663 \times 10^{-6}$
Cd <sub>4</sub> (400ppm)	0.00430	0.00940	$2.776 \times 10^{-4}$	0.01010	$2.804 \times 10^{-6}$
Cd <sub>5</sub> (800ppm)	0.00440	0.00925	$2.688 \times 10^{-4}$	0.01010	$2.715 \times 10^{-6}$
Cd <sub>6</sub> (1600ppm)	0.00420	0.00930	$2.717 \times 10^{-4}$	0.00950	$2.581 \times 10^{-6}$
Cd <sub>7</sub> (2000ppm)	0.00440	0.00925	$2.688 \times 10^{-4}$	0.00990	$2.661 \times 10^{-6}$
Zn <sub>1</sub> (50ppm)	0.00420	0.00930	$2.717 \times 10^{-4}$	0.00940	$2.554 \times 10^{-6}$
Zn <sub>2</sub> (100ppm)	0.00430	0.00945	$2.806 \times 10^{-4}$	0.00960	$2.694 \times 10^{-6}$
Zn <sub>3</sub> (200ppm)	0.00440	0.00930	$2.717 \times 10^{-4}$	0.01000	$2.717 \times 10^{-6}$
Zn <sub>4</sub> (400ppm)	0.00420	0.00910	$2.602 \times 10^{-4}$	0.00980	$2.549 \times 10^{-6}$
Zn <sub>5</sub> (800ppm)	0.00440	0.00910	$2.602 \times 10^{-4}$	0.01040	$2.706 \times 10^{-6}$
Zn <sub>6</sub> (1600ppm)	0.00400	0.00910	$2.602 \times 10^{-4}$	0.00970	$2.524 \times 10^{-6}$
Zn <sub>7</sub> (2000ppm)	0.00440	0.00940	$2.776 \times 10^{-4}$	0.00960	$2.665 \times 10^{-6}$
Pb <sub>1</sub> (50ppm)	0.00420	0.00933	$2.735 \times 10^{-4}$	0.00960	$2.626 \times 10^{-6}$
Pb <sub>2</sub> (100ppm)	0.00430	0.00923	$2.676 \times 10^{-4}$	0.01010	$2.703 \times 10^{-6}$
Pb <sub>3</sub> (200ppm)	0.00445	0.00918	$2.647 \times 10^{-4}$	0.01000	$2.648 \times 10^{-6}$
Pb <sub>4</sub> (400ppm)	0.00450	0.00920	$2.659 \times 10^{-4}$	0.01010	$2.686 \times 10^{-6}$
Pb <sub>5</sub> (800ppm)	0.00420	0.00910	$2.602 \times 10^{-4}$	0.00995	$2.589 \times 10^{-6}$
Pb <sub>6</sub> (1600ppm)	0.00450	0.00935	$2.746 \times 10^{-4}$	0.01025	$2.815 \times 10^{-6}$
Pb <sub>7</sub> (2000ppm)	0.00410	0.00918	$2.647 \times 10^{-4}$	0.00975	$2.581 \times 10^{-6}$
Ni <sub>1</sub> (50ppm)	0.00440	0.00935	$2.746 \times 10^{-4}$	0.01000	$2.746 \times 10^{-6}$
Ni <sub>2</sub> (100ppm)	0.00440	0.00920	$2.659 \times 10^{-4}$	0.01030	$2.739 \times 10^{-6}$
Ni <sub>3</sub> (200ppm)	0.00420	0.00930	$2.717 \times 10^{-4}$	0.00980	$2.663 \times 10^{-6}$
Ni <sub>4</sub> (400ppm)	0.00420	0.00930	$2.717 \times 10^{-4}$	0.01010	$2.744 \times 10^{-6}$
Ni <sub>5</sub> (800ppm)	0.00430	0.00930	$2.717 \times 10^{-4}$	0.00960	$2.608 \times 10^{-6}$
Ni <sub>6</sub> (1600ppm)	0.00420	0.00910	$2.602 \times 10^{-4}$	0.01000	$2.602 \times 10^{-6}$
Ni <sub>7</sub> (2000ppm)	0.00440	0.00915	$2.630 \times 10^{-4}$	0.01020	$2.683 \times 10^{-6}$

The results for the thermal conductivity,  $K$  ; specific heat capacity,  $c$  ; density,  $\rho$ ; and thermal diffusivity,  $\lambda$  summarized in Table 3 showed that samples X and Y used for the preliminary studies had the lowest values of thermal conductivity (9.6653W/mK for X and 9.5824W/mK for Y). This shows that samples X and Y conduct heat at a lower rate because solutions of different concentrations of Cu (II), Pb (II), Cd (II), Ni (II), and Zn (II) had not been added or mixed with the samples.

concentrations of some heavy metals ions in the samples. The low values X and Y are followed by samples (Cd1-Cd7) containing different concentrations of Cd (II) solution having the thermal conductivity ranging from 9.9183W/mK – 10.0106W/mK while highest range of values of thermal conductivity and diffusivity were discovered in clay samples (Pb1-Pb7) containing different concentrations of Pb (II) solution, the range of values of thermal conductivity for Pb1-Pb7 is 9.6870 W/mk – 10.5010 W/mk.

The low values of the thermal conductivity and diffusivity of X and Y are due to low

**Table 3:** Calculated Values of Thermophysical Parameters.

Samples	Thermal Conductivity, K (W/mk)	Specific Heat Capacity, c (J/kgK)	Density, $\rho$ (kgm <sup>-3</sup> )	Thermal Diffusivity, $\lambda$ (m <sup>2</sup> /s)
X	9.6653	2186.235	1570.313	2.81535 x 10 <sup>-6</sup>
Y	9.5824	2373.626	1497.006	2.69674 x 10 <sup>-6</sup>
Cu <sub>1</sub> (50ppm)	10.0630	1978.022	1530.61	3.32378 x 10 <sup>-6</sup>
Cu <sub>2</sub> (100ppm)	10.0675	1932.021	1638.72	3.17984 x 10 <sup>-6</sup>
Cu <sub>3</sub> (200ppm)	10.0683	1976.212	1611.05	3.16238 x 10 <sup>-6</sup>
Cu <sub>4</sub> (400ppm)	10.1041	1978.022	1632.34	3.12936 x 10 <sup>-6</sup>
Cu <sub>5</sub> (800ppm)	10.1068	1932.021	1631.88	3.20563 x 10 <sup>-6</sup>
Cu <sub>6</sub> (1600ppm)	10.1078	1932.021	1631.26	3.20717 x 10 <sup>-6</sup>
Cu <sub>7</sub> (2000ppm)	10.1053	1978.022	1559.02	3.27692 x 10 <sup>-6</sup>
Cd <sub>1</sub> (50ppm)	9.9183	1974.406	1644.48	3.05473 x 10 <sup>-6</sup>
Cd <sub>2</sub> (100ppm)	9.9543	2024.413	1556.57	3.15895 x 10 <sup>-6</sup>
Cd <sub>3</sub> (200ppm)	9.9679	1978.022	1577.17	3.19517 x 10 <sup>-6</sup>
Cd <sub>4</sub> (400ppm)	9.9679	1932.021	1533.52	3.36436 x 10 <sup>-6</sup>
Cd <sub>5</sub> (800ppm)	9.9869	1888.112	1620.63	3.26377 x 10 <sup>-6</sup>
Cd <sub>6</sub> (1600ppm)	10.0051	1978.022	1627.28	3.10834 x 10 <sup>-6</sup>
Cd <sub>7</sub> 2000ppm)	10.0106	1888.112	1653.51	3.20646 x 10 <sup>-6</sup>
Zn <sub>1</sub> (50ppm)	10.0208	1978.022	1644.48	3.08065 x 10 <sup>-6</sup>
Zn <sub>2</sub> (100ppm)	10.0354	1932.021	1596.14	3.25426 x 10 <sup>-6</sup>
Zn <sub>3</sub> (200ppm)	10.0381	1888.112	1619.43	3.28293 x 10 <sup>-6</sup>
Zn <sub>4</sub> (400ppm)	10.0436	1978.022	1647.70	3.08163 x 10 <sup>-6</sup>
Zn <sub>5</sub> (800ppm)	10.0436	1888.112	1626.02	3.27142 x 10 <sup>-6</sup>
Zn <sub>6</sub> 1600ppm)	10.0436	2075.023	1584.79	3.05418 x 10 <sup>-6</sup>
Zn <sub>7</sub> 2000ppm)	10.0421	1888.112	1651.03	3.22138 x 10 <sup>-6</sup>
Pb <sub>1</sub> (50ppm)	9.6870	1978.022	1599.63	3.06153 x 10 <sup>-6</sup>
Pb <sub>2</sub> (100ppm)	10.3996	1932.021	1590.94	3.38338 x 10 <sup>-6</sup>
Pb <sub>3</sub> (200ppm)	10.4046	1866.820	1680.83	3.31588 x 10 <sup>-6</sup>
Pb <sub>4</sub> (400ppm)	10.4415	1846.154	1675.60	3.37539 x 10 <sup>-6</sup>
Pb <sub>5</sub> (800ppm)	10.5010	1976.126	1622.25	3.27566 x 10 <sup>-6</sup>
Pb <sub>6</sub> (1600ppm)	10.2711	1846.154	1598.75	3.47991 x 10 <sup>-6</sup>
Pb <sub>7</sub> 2000ppm)	10.1510	2026.266	1588.66	3.15342 x 10 <sup>-6</sup>
Ni <sub>1</sub> (50ppm)	10.2614	1866.384	1602.33	3.39488 x 10 <sup>-6</sup>
Ni <sub>2</sub> (100ppm)	10.2661	1888.112	1606.43	3.38467 x 10 <sup>-6</sup>
Ni <sub>3</sub> (200ppm)	10.2670	1976.212	1577.17	3.29406 x 10 <sup>-6</sup>
Ni <sub>4</sub> (400ppm)	10.2745	1976.212	1530.61	3.39674 x 10 <sup>-6</sup>
Ni <sub>5</sub> (800ppm)	10.2754	1932.021	1648.77	3.22572 x 10 <sup>-6</sup>
Ni <sub>6</sub> 1600ppm)	10.2885	1978.022	1614.14	3.22240 x 10 <sup>-6</sup>
Ni <sub>7</sub> 2000ppm)	10.2811	1888.112	1639.96	3.32031 x 10 <sup>-6</sup>

The Specific Heat Capacity,  $c$  ( $J/kgK$ ) ranged from 1846.154  $J/kgK$  (Samples Pb4 and Pb6) - 2373.626  $J/kgK$  (sample Y). The Density,  $\rho$  ( $kgm^{-3}$ ) also ranged from 1497.006  $kgm^{-3}$  (sample Y) to 1680.83  $kgm^{-3}$  (sample Pb3). The values of thermal diffusivity,  $\lambda$  ( $m^2/s$ ) ranged from  $2.69674 \times 10^{-6} m^2/s$  (sample Y) -  $3.47991 \times 10^{-6} m^2/s$  (sample Pb6).

Table 4 shows the results obtained for the variation of thermal conductivity with various concentrations of heavy metal ions being adsorbed by clay. It showed that the thermal conductivity of clay increases with increase in the concentration of heavy metal ions being adsorbed by the clay to a considerable level. For all the samples, the thermal conductivity increases as the concentration increases to a certain level above which (optimum), cation exchange is no longer possible.

From Table 1, the samples containing solutions of Cu (II), Ni (II) and Zn (II) ions of various concentrations in the clay sample had values of thermal conductivities increasing up to the concentration of 1600ppm before the values dropped at 2000ppm concentration. This is brought about because beyond 1600ppm, the samples had reached their saturation levels and could no longer adsorb the heavy metal ions from the solutions and so beyond 1600ppm, there is decrease in thermal conductivity because of the decrease in concentration of heavy metal ions being adsorbed by the clay.

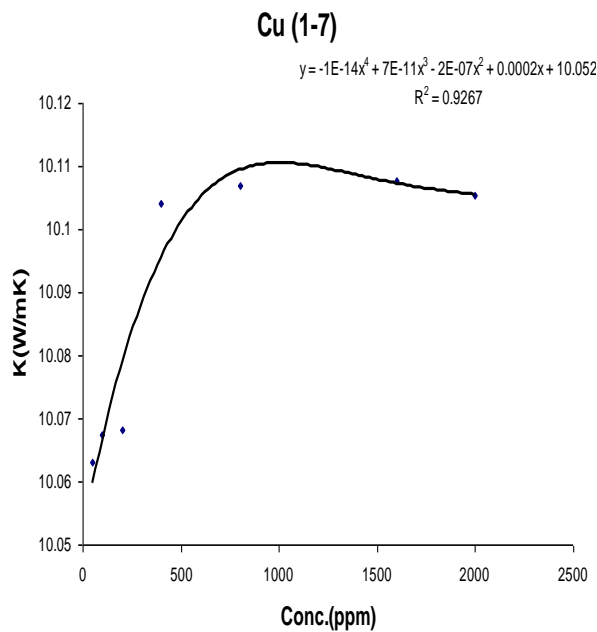
Although saturation is supposed to keep the graphs constant rather than falling, but the fall is as a result of the inability of the samples to adsorb beyond 1600ppm and beyond this concentration, cation exchange is no longer possible, thermal conductivity decreases and there is a fall in the graph because heavy metal ions from solution only accumulate at the surface of the clay sample grains and they can be removed (desorbed) under reverse conditions of temperature and pressure. This is referred to as desorption. Figures 1-5 are graphs of thermal conductivity,  $K$  ( $W/mk$ ) against concentration (ppm) for the samples.

From these graphs, thermal conductivity increases with increase in concentrations up to 1600ppm before reducing for samples with Cu, Ni and Zn ions, while for samples with Cd ions, the thermal conductivity continues to increase even up to 2000ppm.

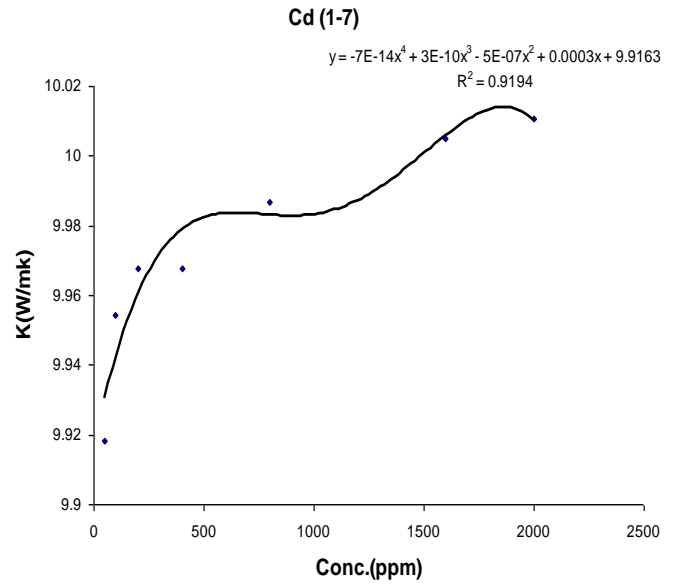
It can be inferred from Figure 3 that the samples (i.e. Cd1 – Cd7) containing solutions of different concentrations of Cd (II) ions continue to adsorb the Cd (II) ions from the solution without reaching the saturation level even up to the 2000ppm concentration. Initially, the concentration of Cd in the clay sample was 0.975  $\mu g/g$  for the Complete Digestion method and 1.088  $\mu g/g$  for the Baker and Amacher method and due to the initial low concentration of Cd in the clay sample, the samples continue to adsorb more and more Cd (II) ions from the solutions with various concentrations without being saturated even up to the concentration of 2000ppm.

Table 4: Variation of thermal conductivity with various concentrations of heavy metals in clay.

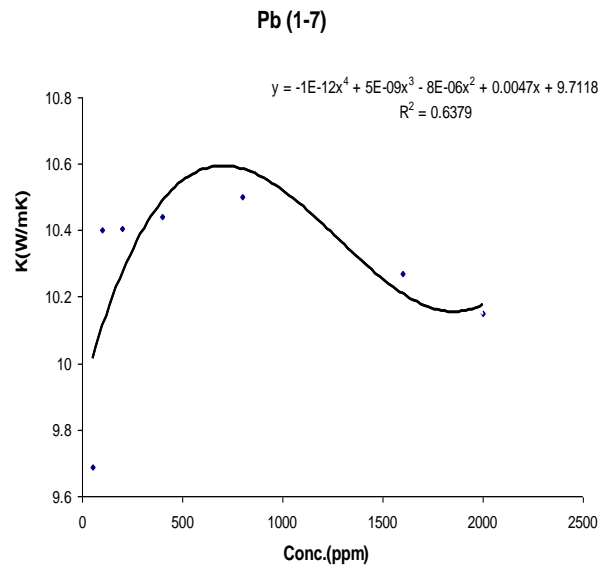
Concentration (ppm)	Thermal Conductivities, K (W/mK)				
	Cu	Pb	Cd	Ni	Zn
50	10.0630	9.6870	9.9183	10.2614	10.0208
100	10.0675	10.3996	9.9543	10.2661	10.0354
200	10.0683	10.4046	9.9679	10.2670	10.0381
400	10.1041	10.4415	9.9679	10.2745	10.0436
800	10.1068	10.5010	9.9869	10.2754	10.0436
1600	10.1078	10.2711	10.0051	10.2885	10.0436
2000	10.1053	10.1510	10.0106	10.2811	10.0421



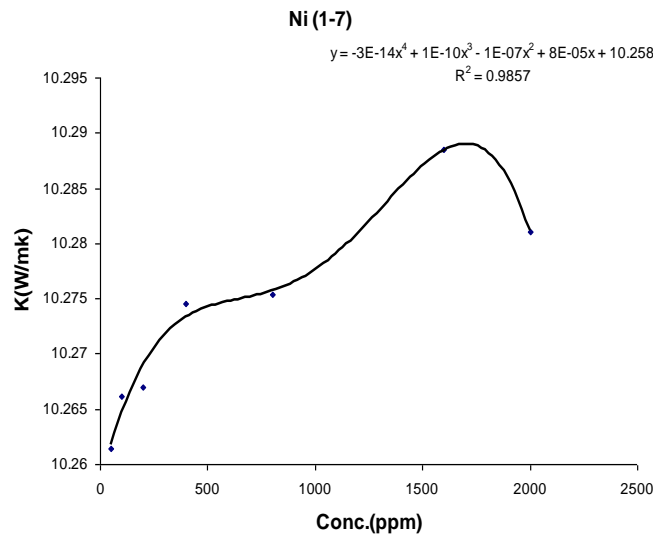
**Figure 1:** Graph of Thermal Conductivity, K (W/mK) against Concentration (ppm) for Samples Cu1-Cu7.



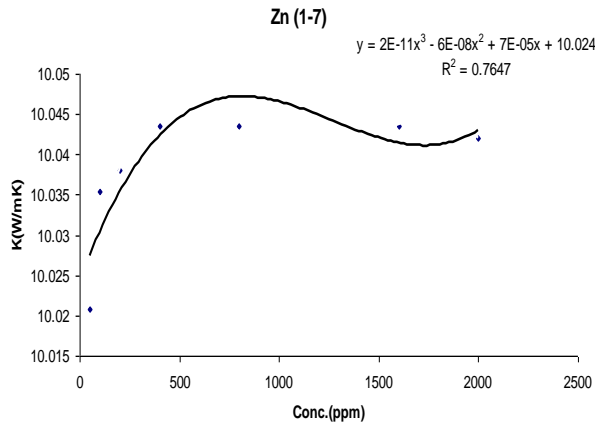
**Figure 3:** Graph of Thermal Conductivity, K (W/mK) against Concentration (ppm) for Samples Cd1-Cd7.



**Figure 2:** Graph of Thermal Conductivity, K (W/mK) against Concentration (ppm) for Samples Pb1-Pb7.



**Figure 4:** Graph of Thermal Conductivity, K (W/mK) against Concentration (ppm) for Samples Ni1-Ni7.



**Figure 5:** Graph of Thermal Conductivity, K (W/mK) against Concentration (ppm) for Samples Zn1-Zn7.

Also, Table 4 showed that, for samples containing Zn (II) ions solutions, at 400ppm – 1600ppm, the values of Thermal conductivity were constant indicating that the samples were becoming saturated before the value of thermal conductivity dropped. However, the concentration of Nitrate solutions at saturation generally varies with ions.

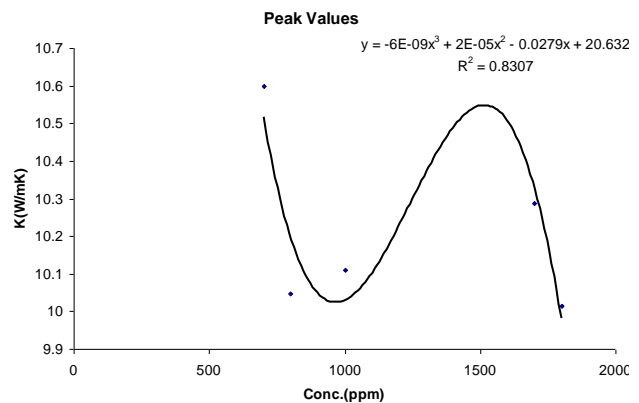
For the samples containing solution of Pb(II) ions of various concentrations in the clay sample, the values of the thermal conductivity increased up to the concentration of 800ppm before the values started dropping after the 800ppm concentration. At 800ppm, the samples had reached their saturation levels and could no longer adsorb the heavy metal ions from solutions beyond 800ppm and so beyond 800ppm, cation exchange is no longer possible and since there is decrease in the amount of heavy metal ions being adsorbed by the clay, electroneutrality will not be maintained (i.e., the clay surface negative charge will not be balanced by equal number of positive charges (or cations) from the solution and heavy metal ions that are being held at the surface without being adsorbed are being removed (desorbed) under reverse conditions of temperature and pressure since adsorption is reversible).

This may have led to the decrease in the values of thermal conductivity beyond 800ppm. Consequently, this showed that samples containing Pb(II) ions being adsorbed by the clay from solutions of different concentrations reached saturation level (at 800ppm) compared to samples containing solutions of various concentrations of Cu (II) ions, Ni (II) ions, and Zn (II) ions that reached saturation levels at 1600ppm each.

Table 5 showed the peak values of the values of thermal conductivity, K(W/mK) obtained from the samples and their various concentrations at these values. The peak values of the thermal conductivity, K(W/mK) were plotted against the various concentrations (ppm) and the graph plotted is also shown in Figure 6.

**Table 5:** Peak Values of Thermal Conductivity and Concentrations (ppm) for all the Samples.

Samples	Thermal Conductivity, K	Concentration (ppm)
Cu1-Cu7	10.1110	1000
Ni1-Ni7	10.2890	1700
Cd1-Cd7	10.0140	1800
Pb1-Pb7	10.6000	700
Zn1-Zn7	10.0475	800



**Figure 6:** Graph of Peak Values of Thermal Conductivity, K(W/mK) against Concentration (ppm).

From the graph, samples (i.e. Pb1-Pb7) containing solutions of different concentrations of Pb (II) ions being adsorbed by the clay had the highest peak value of 10.6000 W/mK at the concentration of 700ppm. This highest peak value was followed by samples (Ni1-Ni7) having the peak value of 10.2890 W/mK at the 1700ppm concentration. Next to samples Ni1-Ni7 are samples Cu1-Cu7 having the peak value of 10.1110 W/mK at 1000ppm and this peak value is followed by samples Zn1-Zn7 having the peak value of 10.0475 W/mK at 800ppm and samples Cd1-Cd7 had the least peak value of thermal conductivity of 10.0140 W/mK at 1800ppm.



Samples Pb1-Pb7 were the first to reach saturation and the peak value of thermal conductivity was at 700 ppm, while Samples Cd1-Cd7 had the peak value at 1800ppm. Samples Cd1-Cd7 continued to adsorb more Cd(II) ions from the solutions containing different concentrations of Cd(II). And as more Cd(II) ions are being adsorbed, cation exchange continues and electroneutrality is maintained. The negative charges on the clay surfaces are being balanced by the positive charges from the solution being adsorbed by the clay, therefore adsorption continues without a reversible process of desorption.

Also, the peak values of thermal conductivity decreases as the Atomic Number of each metal increases except for Lead, Pb. The peak value of thermal conductivity of samples containing Ni(II) ions was 10.2890W/mK while the atomic number of Ni is 28. For samples containing Cu(II) ions, the peak value was 10.1110W/mK while the atomic number of Cu is 29. Also, the peak value for samples containing Zn(II) ions was 10.0475 W/mK and the atomic number of Zn is 30. The atomic number of Cd is 48 while the peak value was 10.0140 W/mK.

Lead (Pb) was an exception because the atomic number of Pb is 82 while the peak value was 10.6000W/mK which was the highest peak value.

## CONCLUSION

From the research presented in this paper, the determination of the thermal properties of the clay as presented in Table 3 showed that the concentration of heavy metal ions being adsorbed affects these properties. The conduction of heat by each sample depends on the concentration of heavy metal ions being adsorbed by the sample and the ability of their constituent minerals to conduct heat.

The thermophysical properties of the clay increases as the adsorption of heavy metal ions from solutions of different concentrations increases to a considerable level. Therefore, as the concentration of these heavy metals in soils (especially clay soils) increases thereby leading to increase in temperature, an increase in the rate of heat conduction by the soil and the heat being distributed at the surface of the earth are brought about. In Soil Science, this can lead to poor seed

germination and retarded or stunted growth in crops.

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