Sorption of lead on variable charged soils as affected by temperature and time in three Provinces of China

U.N. Nkwopara [1,2]*, and H. Hu[1]

[1]College of Resources and Environment, Key Laboratory of Subtropical Agricultural Resources and Environment, MOA,
Huazhong Agricultural University, Wuhan 430070, China
[2]Department of Soil Science and Technology, Federal university of Technology, Owerri, P.M.B 1526.
*Corresponding author:ugoiken2003@yahoo.com, ugochukwu.nkwopara@futo.edu.ng
Tel. number: +2348134150630

***Abstract*—*Effect of temperature and time on Lead (Pb) adsorption and affinity of the adsorbed Pb was evaluated in three acidic soils from China. The distribution coefficient increased slightly with increasing temperature up to 35 ^{0}C and then decreased at 45^{0}C.The increase of temperature was not favorable to sorption. The heat of reaction ($\triangle H$) was positive (endothermic) at lower temperatures, while it was negative (exothermic) at higher temperatures. It was observed that there was an increase in the percent adsorption of Pb^{2+} within the first 8 min of the reaction and a decrease within 20 min of the reaction. The equilibrium was reached after 40min with 95.8 %, 87.4 % and 83.8 % for the Yellow brown soil (YBS), Latosol soil (LS) and Lateritic red soil (LRS) respectively. The analysis of images obtained by scanning electron microscope (SEM) with adsorbed Pb showed coverage of the surface with white layer (molecular cloud).*

***Keywords*—** *sorption, lead; variable charge soils; time; temperature.*

I. INTRODUCTION

Lead is a common contaminant of soil and considered to be a risk to human health. Lead may contaminate soil through vehicle exhausts, sewage-sludge biosolids, mining, and smelting [16] [1]. Toxicity from Pb-contaminated soils primarily occurs from direct ingestion. Symptoms of lead poisoning in human beings include irritability, poor muscle coordination, nerve damage, increased blood pressure, developmental delays etc. [20].

Heavy metal concentration in soil solution is of great importance for all ecological consideration because the plants are likely to take up the available metals from soil solution. The transport of metals within the soil or even to groundwater depends on the metal concentration of the solution phase [5]. It was suggested that the fate and transport of toxic metal ions in the environment are generally controlled by adsorption reactions, complexation etc. [21]. Studies on Pb (II) adsorption were performed on soils, clay minerals and oxides [8] [17][21] [2]. These studies showed that soil type, ionic strength, ion type, contact time affected the adsorption of heavy metals onto soils and clay minerals. Other factors such as liquid: solid ratio [14], solution pH, ionic strength [12] and temperature also affect sorption process [4] [11].

It is well known, tropical and subtropical regions are distributed with large areas of variable charge soils. These soils usually carry both positive and negative charges on their surfaces, therefore can adsorbed both anions and cations [23].

It has been observed that increasing the contact time favor the adsorption of metal ions because the sorbed phase of metals changed from loosely bounded phase to strongly bounded phases with increasing contact time [9][15]. However, there are few studies and limited information on the effect of these operating variables on the adsorption and affinity of Pb onto variable charge soils .The process of adsorption, though widely applied, is still only partially understood [19].

This paper therefore investigated impact of reaction variables like contact time and temperature and on adsorption and affinity of Pb^{2+} onto three variable charge soils. The aim is to provide scientific information that will help in the management of lead contaminated soils.

II. MATERIALS AND METHODS

2.1 Soil samples and basic properties

Three representative variable charge soils were used in this study : Yellow brown soil (YBS), Alfisol in America Soil Taxonomy and Argosol in China Taxonomy; Latosol soil (LS) and Lateritic red soil, Oxisols in America Soil Taxonomy and Ferralosols in China Taxonomy，collected from Hubei, Hainan, and Guangxi provinces, respectively in China. These uncontaminated soils with contrasting properties were sampled at 0 – 20 cm depth. Composite samples of the soils were air-dried, ground, sieved through 2-mm mesh prior to use. Soil pH value was measured in de-ionized water at a soil: water ratio of 1:2.5. Cation exchange capacity (CEC) and organic matter content were determined by the methods described by Rhoades and Walkley – Black respectively [13]. Particle size distribution was determined using the pipette method. Amorphous iron (Fe) and aluminium (Al) oxides were determined by the oxalate extraction [10]. Crystalline Fe and Al oxides were determined by the oxalate – ascorbic acid extraction method of Shuman [18]. The mineralogical composition of the clay samples was determined with Cu-Ka radiation on X –ray diffractometer (D8 Bruker Advance X –ray diffractometer).

2.2. Effect of temperature on sorption

Weight of 1 g of soil samples were placed in 50 mL polyethylene bottles. Twenty-five mL of 0.01 KCl solution containing 100 mg L^{-1} Pb^{2+} was added. The solutions were adjusted to pH 5.5±0.1 with either 0.1 M NaOH or HCl. These were agitated at 230 rpm at different temperatures within the range of 5 – 45 ^{0}C, after which they were centrifuged and the supernatant solution taken for metal ion analysis using AAS. The amount adsorbed was calculated by the difference between the total applied Pb^{2+} and the amount of Pb^{2+} remaining in the equilibrium solution. The heat of reaction (△H) was determined using the formulae:

Heat of reaction = q/1000÷ Moles [3]

Where q= mass x specific heat capacity x change in temperature.

2.3. Effect of time on sorption

Weight of 1 g of soil samples were placed in 50 mL polyethylene bottles. 25 mL of 0.01 KCl solution containing 100 mg L^{-1} Pb^{2+} was added. The solutions pH were adjusted to 5.5±0.1 with either 0.1 M NaOH or HCl. These were agitated at 230 rpm at different times within the range of 5 – 80 min, after which they were centrifuged and the supernatant solution taken for metal ion analysis using AAS. The amount of metal ions adsorbed was calculated as above.

2.4. Scanning electron microscopy

After adsorption, the soil residues were air-dried for 7 days and gold coated under vacuum in a JFC – 1600 sputter coater (JEOL, Japan) for 20 min. The SEM images obtained by a JSM 6390 scanning electron microscope (JEOL, Japan)

2.5. Statistical analysis

All experiments were carried out in duplicate and only mean values are presented. All data were processed by Microsoft Excel, SAS and sigmaplot10.

III. RESULTS AND DISCUSSION

3.1. Physicochemical and mineralogical properties of soils

The results of the physicochemical properties showed that YBS had higher CEC and pH (27.4 cmol kg^{-1} and 5.2) respectively than the other soils, while LS had higher organic carbon and crystalline Fe_2O_3 and Al_2O_3 (13.1 g kg^{-1}, 84.0 g kg^{-1} and 5.2 g kg^{-1}) respectively than the other soils (Table 1). The particle size analysis showed that LS was clay, YBS was silt loam and LRS was clay loam. Mineralogical composition showed that LRS mainly consisted of kaolinite 60 %, and illite 40 % characterized by diffraction peaks at 0.719nm and 1nm, respectively. The LS consisted of kaolinite 75 %, hydroxyinterlayed vermiculite 15 % and goethite characterized by diffraction peaks at 0.71nm, 0.48nm and 0.27nm, respectively. Yellow brown soil consisted of illite 45 %, vermiculite 25 % and kaolinite 30 % characterized by diffraction peaks at 1nm, 1.396nm and 0.717nm, respectively (Fig.1). The YBS has higher adsorption capacity probably due to its higher CEC, pH and illite content (Table 1). This result is in agreement with previous reports suggesting that adsorption capacity of Pb^{2+} by soil has a significant relationship with CEC of soils [6][22]. Other properties that are associated with metal adsorption e.g. clay content and organic matter may also influence metal retention through their relation to CEC [22]. The result of particle size analysis agrees with [7] that oxisols with high Fe oxide content are rich in clay; however, the soils exhibit moisture characteristics of sands.

Table.1: Properties of the soils studied

soil	pH (H_2O)	O.M g kg^{-1}	CEC g kg^{-1}	Clay (<0.002mm) g kg^{-1}	Clay minerals	Crystal Fe g kg^{-1}	Crystal Al g kg^{-1}
YBS	5.2	10.8	27.4	256.5	I (45),V(25), K (30)	16.0	1.3
LS	4.5	13.1	15. 9	415.9	K(75), HIV(15), GE	84.0	5.2
LRS	4.1	9.9	21.9	361.2	K(80),GE(20)	21.0	2.1

I = illite, V = vermiculite, K = kaolinite, HIV =hydroxyinterlayed vermiculite, GE= goethite. Data in the parentheses are the contents (%) of the corresponding minerals.

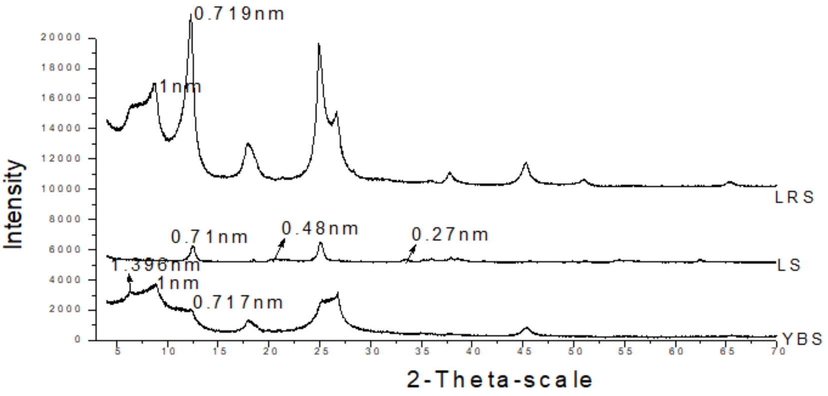

Fig.1: X-ray diffraction patterns of three soils, a. LRS; b. LS; c. YBS

3.2. Effect of temperature on sorption

In a series of adsorption experiments at temperature between 5 ^{0}C and 45 ^{0}C, the distribution coefficient (K_d) increased slightly with increasing temperature up to 35 ^{0}C and then decreased at 45 ^{0}C. The maximum increase of 365 mL/g was observed in YBS, while the maximum reduction of 608 mL/g was observed in LS (Fig.2). The heat of reaction (△H) was positive at lower temperature and negative at higher temperatures. At 5 ^{0}C, 15 ^{0}C and 25 ^{0}C, △H was 962 kJ mol^{-1},544 kJ mol^{-1}, and 126 kJ mol^{-1} respectively. At 35 ^{0}C, and 45 ^{0}C, △H was – 293 kJ mol^{-1} and -711 kJ mol^{-1} respectively (Table 2). To the best of our knowledge, this result has not been reported. The attraction of Pb^{2+} to soils increased slightly with increasing temperature up to 35 ^{0}C and then reduced at 45 ^{0}C. This could be because at (25 -35 ^{0}C) the temperature is warm and the environmental condition is conducive for rapid decomposition and mineralization or release of simple inorganic products such as sulfates, nitrates etc. which may lead to increase adsorption of Pb^{2+} onto soils, while at high temperature of 45 ^{0}C there was damage of active binding sites in the soils. The negative value for △H indicates that desorption is favoured as temperature increase [24] The distribution coefficient (K_d) of YBS is greater than other soils, indicating that Pb^{2+} has a greater affinity for YBS than other soils.

Table.2: Enthalpy change at different temperatures during Pb adsorption.

Temperature °C	Enthalpy change △H (kJ mol^{-1})
5	962
15	544
25	126
35	-293
45	-711

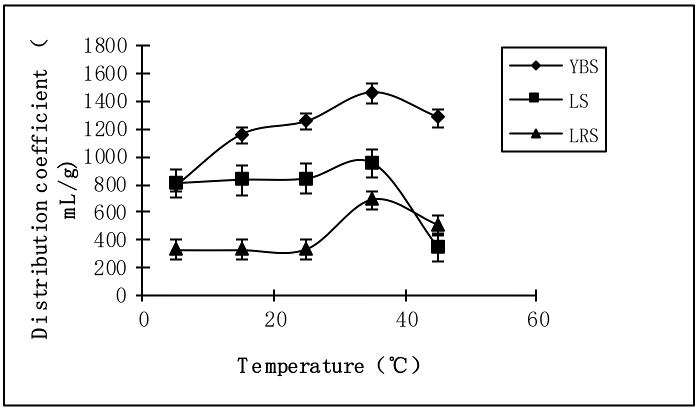

Fig.2: Distribution coefficient of Pb^{2+} at different temperatures

3.3. Effect of time on sorption

From Fig.3, it was observed that there was an increase in the percent adsorption of Pb^{2+} within the first 8 min of the reaction and a decrease within 20 min of the reaction. The equilibrium was reached after 40min with 95.8 %, 87.4 % and 83.8 % for the YBS, LS and LRS, respectively. In the experiments, 24 h was selected to achieve the adsorption equilibrium. The effect of time on adsorption of Pb ion is contrary to previous observation by [2] that adsorption of Pb^{2+} onto kaolinite clay increased with time and reaches equilibrium after 8 min and 20 min for P-modified and unmodified kaolinite respectively. The reason for this trend is not understood. Further investigation is warranted to explain this behavior, presumably associated with the interaction between Pb^{2+} and soils.

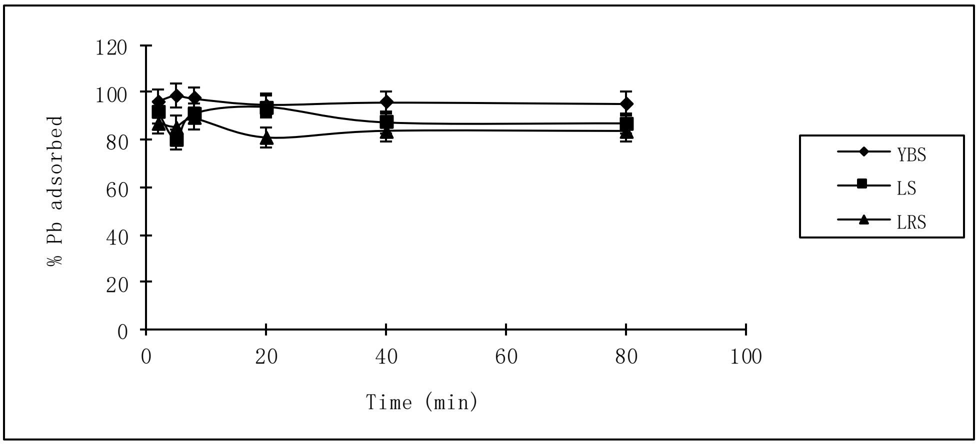

Fig.3: Percent Pb^{2+} adsorbed at different time intervals

3.4. Scanning electron microscopy analysis

The morphology of the soils with Pb^{2+} ion showed some important observations. Typical SEM photographs are shown in Fig.4 (a–f). Coverage of the surface of the soil due to adsorption of Pb^{2+} ion presumably leading to formation of layer of lead molecules over the soil surface. It is evident from the formation of white layer (molecular cloud). There was higher surface coverage of lead in YBS and LRS than LS. It is noticed that soils have bigger pore structures, 1 – 5µm and after adsorption, the pore size have been reduced to 0.4 – 0.6 µm where the lead has attached to it due to its surface chemistry. There was spherical like structures attached in bundles. This could be due to adsorption of Pb^{2+} ion on soils. We see beautiful surface adsorbed spherical shaped Pb particles on the soils.

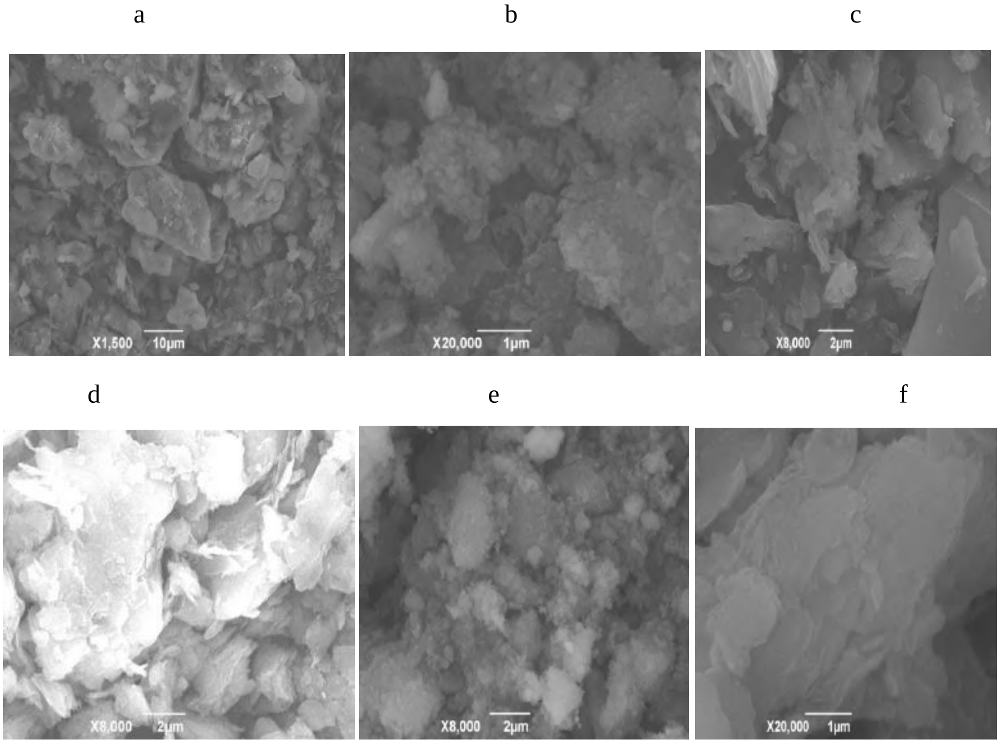

Fig.4: Scanning electron microscopy of soils without and with Pb a. LRS, b. LS, c YBS without Pb, d. LRS, e. LS, f. YBS with Pb

IV. CONCLUSIONS

At warm temperature the distribution coefficient (K_d) was highest in all the soils. Sorption of Pb^{2+} decreased with the increase in temperature. The Pb^{2+} has a greater affinity for YBS than other soils. Lead ion adsorption decreased with time in all the soils and decreased pore structures in studied soils.

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