ADSORPTION OF LEAD ON SOME VARIABLE CHARGE SOILS IN CHINA: EFFECT OF INITIAL METAL CONCENTRATION.

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Abstract

Four soils with variable charges from China, locally referred to as Yellow brown soil (YBS), Latosol soil (LS), Red soil (RS) and Lateritic red soil (LRS) and classified as Alfisol, Oxisol, Ultisol, and Oxisol in American classification system respectively, were collected from Hubei, Hainan and Guanxi provinces of China. The adsorption of Pb^{2+} was studied as a function of metal ion concentration. Pb^{2+} showed stronger affinity to Yellow brown soil (YBS) at all concentrations. In all concentrations, except the highest concentration of 250 mg l-1, Pb^{2+} adsorption decreased in the order Yellow brown soil (YBS) > Latosol soil (LS) > Red soil (RS) > Lateritic red soil (LRS), with YBS soil having the highest sorption capacity for Pb2+ than the other soils. The adsorption process was favourable in the YBS. The experiment data were fitted by both the simple Langmuir and Freundlich models. However, the experiment data were best fitted by Freundlich models. The affinity of adsorbed Pb to the soils could be characterized by the Kd (distribution coefficient) values. The value was greater for the YBS than the other soils and increased in the order of Yellow brown soil (YBS) > Latosol soil (LS) > Red soil (RS) > Lateritic red soil (LRS), except in concentration of 250mg/L Pb.

Keywords: Adsorption of lead, variable charge soils, metal ion concentration, soil properties,

1. Introduction

Heavy metals such as Pb^{2+} are widespread in urban and industrial areas as a consequence of lead dispersion due to the production and recycling of lead batteries, metal mining, smelting and refining, gasoline processing, storage, distribution and production of painting materials and their use (Paff and Bosilovich, 1995).This heavy metal disperse beyond its sources to surrounding soils, surface, and ground waters, endangering the quality of water and plant used for human consumption (Fuge et al., 1993).

The most important chemical processes affecting heavy metal behaviour and bioavailability in soils are those concerned with the adsorption of metals from solution phase onto the solid phase (Alloway,1990).

Variable charge soils (Oxisols, Ultisols, Andisols and acid Alfisols) generally have low surface charge density with predominant pH-dependent charge, particularly at pH value of 4.0 – 5.0 (McBride, 1994) and heavy metals may become mobile in such soil under certain conditions (Naidu et al., 1994). Studies on heavy metals adsorption on soils and clay minerals (Qin et al., 2004 ; Adebowale et al., 2005) showed that soil type and metal ion concentration affected the adsorption of heavy metals onto soils and clay minerals. Pb^{2+} has been shown to exhibit the strongest affinity to clays, peats, Fe- oxides and usual soils (Bradl, 2004). The most important parameters controlling heavy metal adsorption and their distribution between soil and water are soil type, metal concentration, soil pH, and metal speciation (Bradl, 2004). The adverse effects of heavy metals are related to the soil ability to adsorb these elements. Such information is needed to predict the environmental impact of Pb^{2+} from anthropogenic sources, as well as to develop regulatory measures on the usage and disposal of Pb - containing materials on agricultural soils. Although, extensive research has been devoted to metal sorption in temperate soils, data on both sorption and desorption reactions in tropical and subtropical soils are limited (Naidu et al 1997). The process of adsorption, though widely

applied, is still only partially understood (Unuabonah et al., 2007).

The objectives of this study were to investigate the effect of metal ion concentration on adsorption of Pb^{2+} by variable charge soil and determine the adsorption capacity of these soils.

2   Materials and Methods
2.1   Soil sample

Four representative variable charge soils were used in this study : Yellow brown soil (YBS), Alfisol in American classification system, Red soil (RS), Ultisol in American classification system, Latosol soil (LS) and Lateritic red soil (LRS), Oxisol in American classification system from Hubei, Hainan, and Guanxi province in China（Hu et al., 2007）, respectively. These soils with contrasting properties were collected at 0 – 20 cm depth. Composite samples of the soils were air-dried, ground, sieved through 2-mm mesh prior to use.

2.2   Measurement of physicochemical and mineralogical properties.

Soil pH value was measured in de-ionized water at a soil : solution ratio of 1:1. Cation exchange capacity (CEC) was determined by the method described by Rhoades (1982). Organic matter content was determined by the Walkey – Black's procedure (Nelson and Sommers, 1982). Particle size distribution was determined using the pipette method. Amorphous Iron (Fe) and Aluminium (Al) oxides were determined by the oxalate extraction (McKeague and Day, 1966). Crystalline Fe and Al oxides were determined by the oxalate – ascorbic acid extraction method of Shuman (1982). The mineralogical composition of the clay samples was determined with the X –ray diffractometer (Cu alpha radiation).

2.3   Adsorption of Pb^{2+}

2.0 g of air dried soil were placed into 100 – ml polypropylene centrifuge tubes, and 50 ml of 0.01 mol L-1 KCl (pH 5.5±0.1) solution containing different levels of Pb^{2+} as Pb(N03)2 was added to each tube. The initial concentrations of added Pb^{2+} were 20, 50, 80, 100, 250 mg l-1. The suspensions were shaken at 230 rpm for 2h, at 25 0C ± 0.1 and then equilibrated in a dark incubator for additional 22 h, a time previously found to be sufficient for equilibration. At the end of the designated time, the suspensions were centrifuged at 5000 g relative centrifugal force for 10 min. and filtered. The filtrate were transfered into a 10-ml polypropylene centrifuge tube for measuring Pb^{2+} concentration using the AAS. Total amounts of adsorbed Pb^{2+}were calculated by the difference between the total applied Pb^{2+} and the amount of Pb^{2+} remaining in the equilibrium solution.

Two commonly used mathematical expressions for describing the adsorption equilibrium, namely, Langmuir and Freundlich isotherm models were tested with the experimental data (Table 2).

2.4   Statistical analysis

All experiments were replicated two times and only mean values were presented. All data were processed by Microsoft Excel.

3. Results and Discussion
3.1   Physicochemical and mineralogical properties

The results of the physicochemical properties showed that YBS has higher CEC and pH (27.42 cmol kg-1 and 4.79, respectively than the other soils while LS has higher organic carbon and crystalline Fe_2O_3 and Al_2O_3 (13.14 g kg-1, 84.03 g kg-1 and 5.20 g kg-1), respectively than the other soils (Table 1). The particle size analysis showed that LS was clay, The YBS was silt loam while RS and LRS were clay loam. Mineralogical composition showed that YBS consist mainly of illite, mica, vermiculite-illite and kaolinite, LS consist of goethite, gibbsite, mica, quartz, kaolinite and chlorite, RS consist of mica, kaolinite, hematite, illite and LRS consist of kaolinite, mica, goethite, gibbsite, quartz.

3.2   Adsorption studies

Adsorption isotherm of $Pb^{2+}$was constructed to

compare metal adsorption capacity between four tested soils. In all cases Pb^{2+} adsorption was greater in YBS than in other soils (Fig 1). At the lowest level of added Pb^{2+} (20 mg L-1), The YBS adsorbed 99.6 % of the applied Pb^{2+} as compared with 76.5 %, 65.4 %, and 59.4 % for LS, RS , LRS, respectively and at the highest level of added Pb2+ (250 mg L-1), YBS adsorbed 67.3 % of the applied Pb^{2+} as compared with 34.8 %, 35.6 % and 31.1 % for LS, RS, LRS, respectively (Fig. 2), probably due to its higher pH, CEC and the presence of vermiculite-illite minerals (Table 1). This observation was supported by reports of Jopony and Young (1994), Reddy and Patrick (1977), Coles and Yong (2002) and Yang et al., (2006) that soil pH and CEC were positively correlated with cadmium and lead retention indicating that lower soil pH can release more metals from soils. The lower pH of LRS soil compared to the other soils (Table 1) led to the lower adsorption capacity of Pb^{2+} than the other soils. The adsorption capacity of soils is likely related to pH (Table 1).This may be as a result of increased overall charge on the soil. Higher soil pH leads to higher net negative surface charge and thus increase soil's affinity for metal ions. The pH of the tested soils was in the order YBS > LS > RS > LRS, which agrees with the adsorption capacity. This is similar to previous work by Harter (1983) and Reddy and Patrick, (1977). It suggests that YBS soil is capable of receiving and holding more Pb^{2+} while LRS soil holds less Pb2+ compared to the other soils. Because YBS binds Pb^{2+} most strongly and LRS the least, it is likely that Pb^{2+} bound to LRS is released before the Pb2+ bound to YBS. LRS will be more polluted incase of any pollution of the various soils as more metals will be leached into the soil solution.

Increasing the initial metal ion concentration in aqueous solution from 20 – 250 mg L-1 resulted in an increase in the amount of Pb^{2+} adsorbed for all soils (Fig 1). This is due to increasing driving force of metal ion towards active sites on the soils .However the percentage of metal ion adsorbed decreased with increasing initial metal ion concentration (Fig 2). This indicates a decrease in active sites on soils as more metal ion is adsorbed. This is similar to results obtained by Unuabonah, et al., (2007) and Adebowale et al., (2006) on adsorption of Pb onto tripolyphosphate – impregnated kaolinite clay and kaolinite clay respectively..

The isotherms of Pb^{2+}adsorption in the soils can be well described by the simple Langmuir and Freundlich model (Table 2). The Freundlich model gave a relatively better representation of the experimental data based on fitting correlation coefficients (r2). The Freundlich parameters Kf and 1/n which, respectively, measure the capacity and intensity of adsorption (Bhattackaraya and Venkobachar, 1984), are listed in (Table 2). The Kf values of YBS (1.85) were greater than that of other soils, LS (1.67), RS (1.58), and LRS (1.50), which suggests that the YBS has a greater adsorptive capacity for Pb2+ than the other soils. The values of 1/n between 0 and 1, confirm the heterogeneity of the adsorbent (Mishra et al., 1998). The values of 1/n for YBS, LS, RS, and LRS soils were 0.44, 0.47, 0.56, and 0.61 respectively, which confirms the heterogeneity of soil mass. This would support the theory that Pb2+ is adsorbed to strong sites first (at low solution Pb^{2+}concentrations), and occupies weaker sites when additional Pb^{2+} is loaded into the system.

Langmuir equation was widely used because it had two constants with definite physical meaning. The monolayer maximum adsorption (Xm) value was 5000 mg g-1 for YBS soil, 3333mg g-1 for RS, and 2500 mg g-1 for LS, LRS soils. The b is a constant related to the binding energy and partly reflects adsorption energy level. If b is a positive value adsorptive reaction could spontaneously proceed at ordinary temperature. The larger the value of b, the stronger the degree of spontaneous reaction. The b values were 0.06, 0.03, 0.01, 0.01 for YBS, LS, RS, and LRS soils, respectively. The YBS soil had the strongest adsorptive intensity and the highest adsorptive capacity as indicated by the values of Xm and b (Table 2).

From the Langmuir constant, the dimensionless

separation factors KR can be calculated:

KR = (1 + Co .b)-1

Where Co = initial metal concentration (mg l-1), b = constant related to the binding energy and adsorption energy level.

KR is related to the nature of adsorbent/ adsorbate interaction and isotherm type. Unfavourable (KR > 1), Linear (KR = 1), Favourable (0 < KR < 1) or Irreversible (KR = 0).

The calculated KR values for various initial Pb^{2+}concentrations were 0.0664 < KR <0.7937 (YBS), 0.1328 < KR > 1.5873 (LS), 0.3984 < KR > 4.7619 (RS and LRS). The adsorption process was favourable in the YBS. In LS adsorption process was favourable only at concentrations greater than 20 mg L-1 and in RS and LRS it was favourable only at concentrations greater than 80 mg L-1. The adsorption was more favourable for higher initial metal ion concentration with respect to lower concentrations. Similar trend has been observed by Unuabonah et al., (2007) and Adebowale et al., (2006) for adsorption of Pb^{2+}and Cd^{2+} on tripolyphosphate-impregnated kaolinite and kaolinite lcay respectively. Fig. 3 shows plot of separation factor (KR) against initial metal ion concentration. The highest Kd value of (713 mL/g) occurred in YBS while the lowest (11 mL/g) occurred in LRS (Fig.4). This indicates that there was greater attraction for Pb in YBS than the other soils and also less attraction in LRS than the other soils.

4.0   Conclusions

In view of the above, the YBS which is an Alfisol has the potential of holding Pb2+ from industrial wastewater more tightly, so that they are no longer available for plant uptake, reaction with the soil solution, or leaching loss to the environment .It will be less polluted in case of Pb^{2+} pollution in the soils. More Pb^{2+} was adsorbed onto YBS soils than the other soils due to higher soil pH and CEC. Generally, adsorption follows the soil pH. Other properties such as clay also affected adsorption of Pb^{2+} onto these soils. Data from adsorption of lead ion on soils showed satisfactory fits to Langmuir model and Freundlich model except for RS which showed poor fit to Langmuir model. However, from the correlation coefficient there is strong indication that the adsorption data obtained fits the Freundlich model better than the Langmuir model. It can be said that the adsorption of Pb^{2+} are on heterogeneous sites on the surface of these soils. The adsorption process was favourable in the YBS while it varies from unfavourable to favourable in the other soils.

The discrepancy in metal adsorption onto YBS, LS, RS and LRS soils showed that soil property had an important influence on adsorption. The factor studied in this study merit attention in the management of Pb polluted soils.

Finally, it should be realized that these data apply only for acid soil conditions, where adsorption is more important than precipitation processes in removing metal ions from solution. For near neutral and alkaline soils, solubility and complexation reactions may be superimposed on adsorption process, thereby complicating the prediction of relative retention of Pb^{2+}.

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Table 1: Basic properties of the tested soils

Items	YBS soil	LS soil	RS soil	LRS soil
Sample site	Hubei	Hainan	Hubei	Guangxi
Order	Alfisol	Oxisol	Ultisol	Oxisol
pH (H_2O)	4.79	4.46	4.16	4.12
O.M (g kg^{-1})	10.84	13.14	6.22	9.92
CEC (cmol kg^{-1})	27.42	15.89	20.91	21.87
sand (g kg^{-1})	64.8	270.7	304.4	279.2
silt (g kg^{-1})	678.7	313.4	405.7	359.6
clay (g kg^{-1})	256.5	415.9	359.6	361.2
Fe(g kg^{-1})				
crystal	15.98	84.03	21.29	20.98
amorphous	13.78	8.73	5.86	3.46
Al(g kg^{-1})				
crystal	1.29	5.2	2.28	2.06
amorphous	4.02	9.4	7.63	6.19
clay minerals	I, M,V-I K	GE,GI,M Q,K,CH	M,K,HE,I	K,M,GE, GI,Q

YBS: Yellow brown soil, LS: Latosol soil

RS: Red soil, LRS: Lateritic red soil

O.M: Organic matter,CEC: Cation exchange

capacity,I: illite, M: mica,K: kaolinite

V-I: vermiculite-illite, GE:geothite, GI: gibbsite,

Q: quartz, CH: chlorite, HE: hematite

Table 2: Isothermal characteristics of Pb^{2+} in tested soils

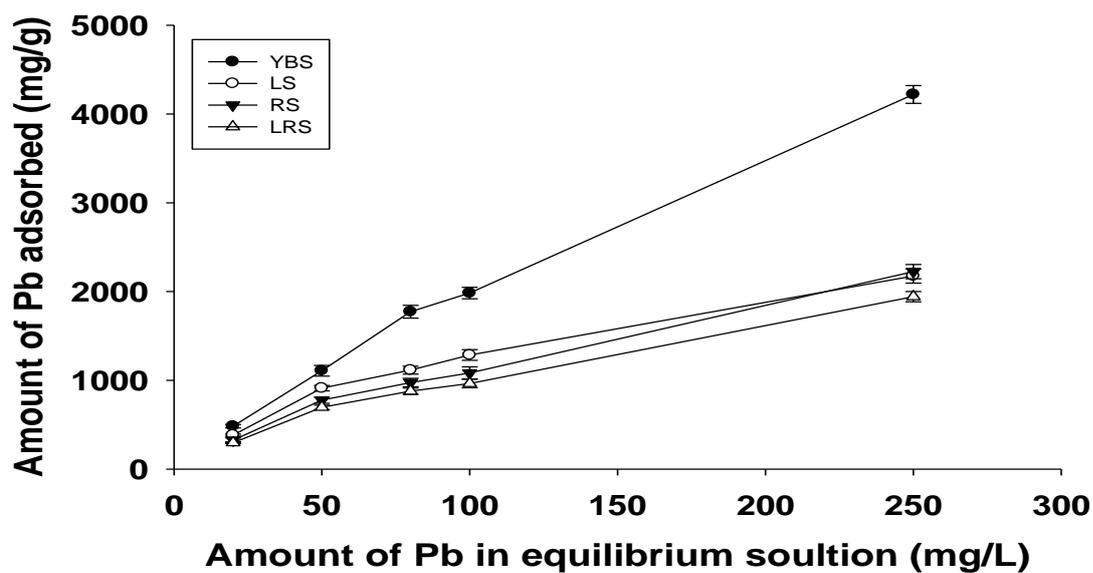| Soils	Langmuir equation			Freundlich equation		
	Xm(mg kg^{-1})	b	r2	Kf(L mg g^{-1})	1/n	r2
YBS	5000	0.06	0.95	1.85	0.44	0.98
LS	2500	0.03	0.94	1.67	0.47	0.95
RS	3333	0.01	0.88	1.58	0.56	0.96
LRS	2500	0.01	0.94	1.50	0.61	0.99

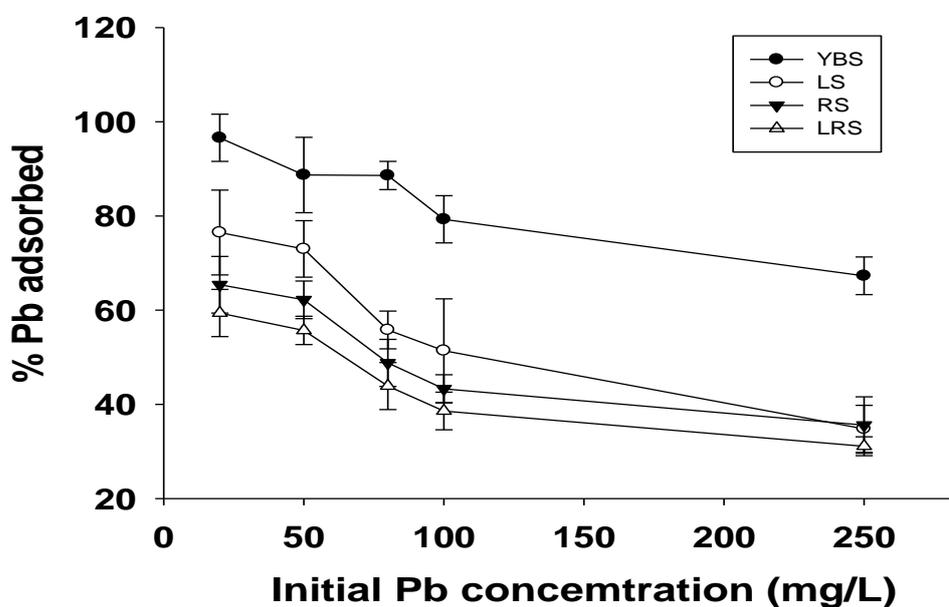Fig 1: Adsorption isotherm for the adsorption of Pb^{2+} onto soils

Fig 2: Percent of Pb^{2+} adsorbed at different metal ion concentration.
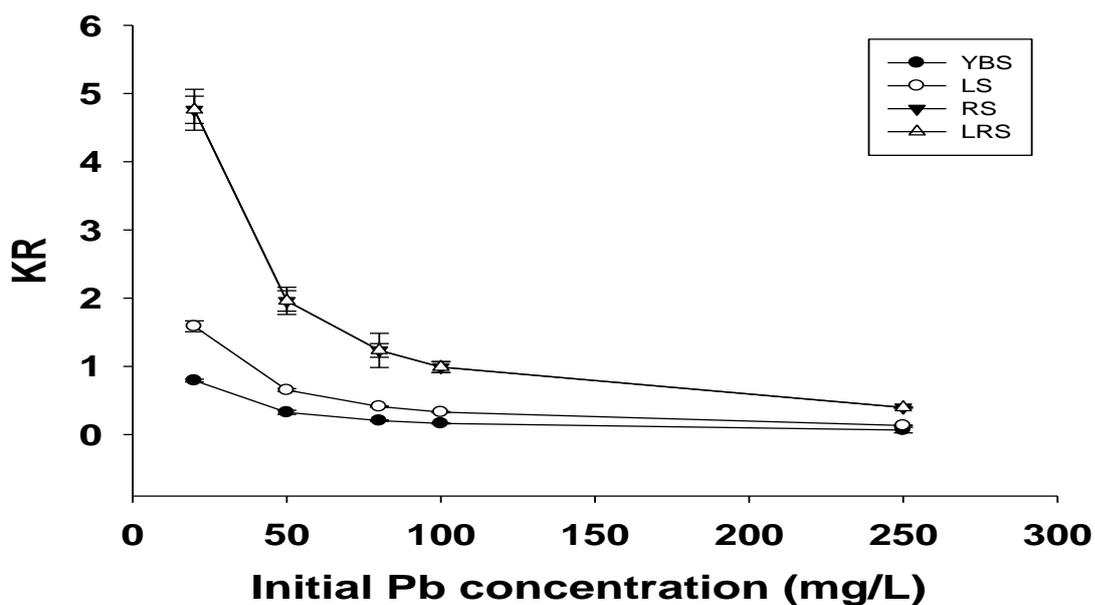
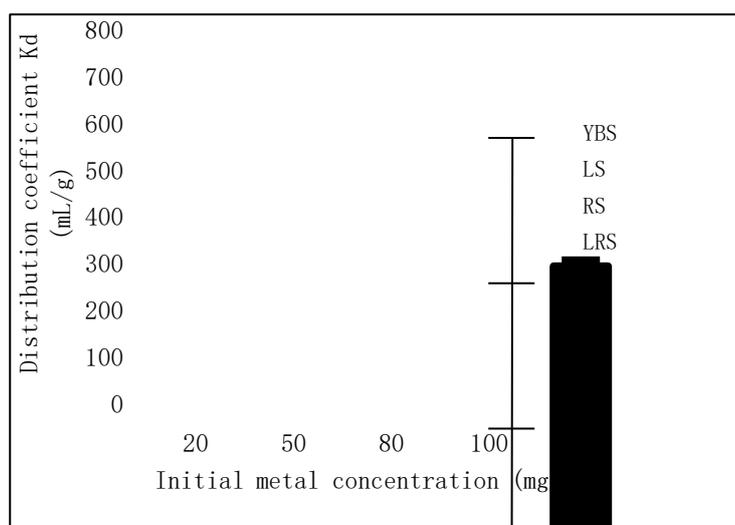Fig 3: Values of the separation factor, K_R for the adsorption of Pb2+ on soils. Temperature 298K.

Fig.4: Distribution coefficient of Pb^{2+} at different metal ion concentrations