

ADSORPTION OF LEAD (Pb) BY SOILS AND THEIR CLAY FRACTION

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Abstract

Adsorption of lead by three soils and their clay fraction were studied separately with three soil series viz., Ghior (high clay content), Ghatail (medium clay content) and Rajoir (organic soil). The maximum amount of lead was adsorbed by Ghior soil followed by the Ghatail soil while the minimum was adsorbed by the organic Rajoir soil. Variations in adsorption among the soils were attributed to the content and nature of the clay fraction, presence of organic matter, iron content and magnitude of CEC. Adsorption of lead by clay fraction of the corresponding soils showed a different trend to that of adsorption of lead by the whole soil. The order was Rajoir > Ghatail > Ghior soils. The extent of adsorption appeared to have varied with the variation of mineral types in the clay fraction of the soils.

Key words : Adsorption, lead, clay mineralogy

Introduction

Contamination of soil by lead is a major concern in many countries including Bangladesh. Soil is contaminated by lead from various sources. Lead particles are deposited in the soil from flaking lead paint, from incinerators (and similar sources), and from motor vehicles that use leaded gasoline (Imamul and Islam 1999). In recent years, much research has been conducted on lead pollution in soil from various anthropogenic sources such as industrial wastes (Ma and Rao 1997), mining activity (Xian 1989), urban city waste, sewage and industrial effluent irrigation (Sattar and Blume 1999), improper land filling (Singh 1999) etc. In the developed countries the discharged materials are treated to a safe level before their discharge into the natural ecosystems. But in developing countries like Bangladesh the indiscriminate disposal of these discharged materials (industrial waste, urban city waste, sewage sludge) on agricultural land is a major source of lead contamination in soils. Through rainwater and other sources, they move to the pond, rivers and the crop fields and create health and environmental problems (Sattar and Blume 1999). Pollution owing to lead released from various sources is a serious problem and a matter of great concern. The accumulation of lead in soil is

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primarily a function of the rate of deposition from the atmosphere. Lead accumulated in the vegetation reaches the soil and remains in the soil for longer periods due to its low mobility. It affects soil, water and air quality. In addition, it enters into the food chain through their accumulation in vegetables, fruits and cereal crops (Imamul *et al.*, 2000). Crops grown in such a lead rich soil take up and accumulate it and ultimately ending up in human and animal bodies causing various disorders like kidney damage, liver damage, genetic deformation, cancer and many other complications (Abhimanya and Bharadwaj 1999). Besides, lead concentration above toxic limit in plant affects the growth and productivity of many crops (Lee and Kim 1991). The fate of lead in soil is affected by the specific or exchange adsorption at mineral interfaces, the precipitation of sparingly soluble solid phases, and the formation of relatively stable organo-metal complexes or chelates with the organic matter in soil (EPA 1986).

It is obvious that remediation of lead should be undertaken for protecting our environment as well as human life. Unfortunately, the data available on the impact of Pb pollution, their remediation by chemical means on soils and crops and phyto-remediation practice are very rare in Bangladesh. To alleviate its entry into food chain and to protect human health in our country, it is important to initiate appropriate research program for remediation of Pb toxicity in soils by using different amendments, which may provide a basis for better management of Pb induced polluted soils for crop production as well as to create public awareness. Soils and the clay minerals might be good sources of soil ameliorators as these are omnipresent in nature. Moreover, these do not produce drastic changes in the physical, biological or chemical properties of the soils. Another important advantage is that the soil is not excavated and amendments could be applied on a large scale.

The aim of the present work was to investigate the adsorption of lead in a few selected soils of Bangladesh and the clay fraction thereof as potential binding agents.

Materials and Methods

Two mineral soils and one organic soil were used in the present research work. The soils were collected from three districts (Mymensingh, Madaripur and Gopalganj) of Bangladesh. The soils collected represent the Ghatail (Mymensingh), Ghior (Madaripur), and Rajoir (Gopalganj) series. After collection, the soils were air dried and ground to pass through a 2 mm sieve. The bulk sample was thoroughly mixed and stored. Particle size analysis (Table 1a) was performed by hydrometer method (Day 1965). The textural class (Table 1a) was determined by following Marshall's triangular co-ordinates USDA (1951). Soil pH (Table 1a) was measured by a combined electrode pH meter at a soil : water ratio

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Table 1. Some characteristics of the soils: (a) physico-chemical and (b) mineralogical properties.*

Soil series	pH	OM (%)	Sand (%)	Silt (%)	Clay (%)	Textural class	CEC (meq/kg)	Fe (%)	Pb (mg/kg)	
									Aqua regia extractable	Water soluble
Ghior	6.48	0.29	1.7	14.1	84.2	Clay	408.5	2.16	0.06	n.d.
Ghatail	6.33	0.5	4.5	39.9	55.6	Clay	322	2.8	n.d.	n.d.
Rajoir	4.81	19.75	71.7	10.9	17.4	Sandy loam	867.1	3.34	0.005	n.d.

Soil series	Kt	Ill	Mont	Vt	Ct	Qz	Fd
**Ghior	20-40%	40-60%	5-20%	Trace	Trace	Trace	Trace
**Ghatail	20-40%	20-40%	Trace	5-20%	Trace	Trace	Trace
*Rajoir	20-30%	15-30%	Trace	Trace	Trace	Trace	Trace

* Brammer 1996, **SRDI Staff 1990, n.d. = not detected. Kt = kaolinite, Ill = illite, Mont = montmorillonite, Vt = vermiculite, Ct = chlorite, Qz = quartz, Fd = feldspar.

of 1 : 2.5 Jackson (1973). Cation exchange capacity (CEC) was determined (Table 1a) by using neutral 1N NH₄OAc saturation technique (Black 1965). The soil organic matter (Table 1a) was estimated by Walkley and Black's wet oxidation method as outlined by Jackson (1973). Moreover, the total content of Fe (Table 1a) in the soils was determined by using prescribed laboratory methods as outlined by Jackson (1973).

The total lead content was extracted by aqua regia (3 : 1, HCl : HNO₃). The samples were digested for approximately 4 - 5 hours, using a sand bath as a heating source and the water soluble Pb was extracted by shaking 10 g samples of soil with 50 ml distilled water at a 1 : 5 soil water ratio for 24 hours. After dissolution, samples were diluted to volume, mixed and filtered prior to analysis (Portman and Riley 1964). Then, the lead content in the extracts was estimated by Atomic Absorption Spectrophotometer following calibration of the equipment. With every set of digestion a blank and a spiked sample were included to ensure the QA/QC.

Soil clay fractions were separated by the method of Jackson (1975). The following two groups of potential adsorbent materials were selected for the lead adsorption test:

- (i) Soils (Ghatail, Ghior and Rajoir): On the basis of their clay content.
- (ii) Clays (Separated from the selected soils).

Solutions for batch tests with concentrations ranging between 0 and 15.0 mg/l lead (Pb) were prepared with de-ionized water from Pb(NO₃)₂. The pH of the soil suspensions was adjusted to 6.0 using 0.1M HCl or 0.1M NaOH. Adsorption tests were carried out by the process as described in Joardar *et al.* (2005). Lead concentrations in the supernatant were determined with a Varian Spectra-220 Atomic Absorption Spectrophotometer. All assays were carried out in triplicate and only mean values are presented (the variation coefficients were less than 5%). Adsorption by soil/clay (X) was calculated by deducting the value of Pb in the equilibrium solution (C) (supernatant) from the value of Pb (C₀) in the solution. The zero Pb treatment was used as background Pb for the experiment and these values were subtracted from the others to correct for the Pb that was released from the untreated soil. The following formula was used for the calculation:

$$X = \frac{V_0 C_0 - V_1 C_1}{W}$$

where,

X = amount of Pb adsorbed (mg/kg soil), V₀ = initial volume of Pb solution (ml), C₀ = initial concentration of Pb solution (mg/l), V₁ = total volume of equilibrating solution (ml), C₁ = final concentration of Pb in equilibrating solution (mg/l) and W = weight of soil taken.

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The following form of the Langmuir adsorption isotherm was tested to calculate the adsorption coefficients:

$$\frac{C}{X} = \frac{1}{kb} + \frac{C}{b}$$

where,

C = equilibrium concentration of Pb in solution (mg/l), X = amount of Pb adsorbed (mg/kg), b = adsorption maximum (mg/kg) and k = constant related to the bonding energy of Pb to the soil (mg/kg).

A plot of C/X versus C was made for each of the three soils. Values of adsorption maximum and bonding energy were calculated from slope ($1/b$) and intercept ($1/kb$) of the plot, respectively.

The following batch adsorption studies were carried out:

A comparative study of lead adsorption capacity by the different soils and their respective clays were carried out separately with the following conditions: Adsorbent dose: 1 g soil or 0.1 g clay in every 25 ml solution, shaking time 2 hours, pH 6.0, the initial lead concentration weres 0, 0.50, 1.0, 2.50, 5.0 and 15.0 mg/l (made from $\text{Pb}(\text{NO}_3)_2$).

Results and Discussion

Lead adsorption on soils: Equilibrium solution lead concentrations (C) and amounts of lead adsorbed (X) at various initial lead solution concentrations (C_0) are graphically shown in Fig.1.

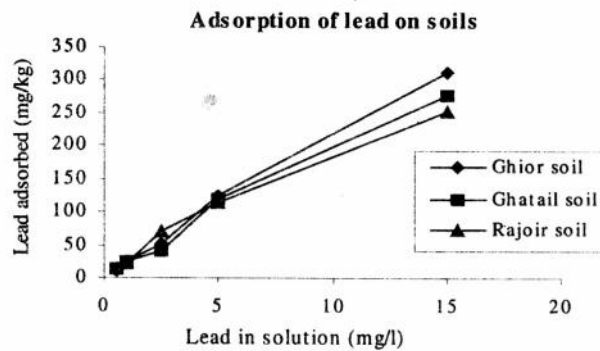


Fig. 1. Lead adsorption isotherms for soils.

The adsorption of lead varied amongst the soils as well as with the initial solution concentrations, which ranged from 0 to 15 mg/l. Both the minimum value, 10.98 mg/kg soil (at 0.5 mg/l) and the maximum value, 312.86 mg/kg soil for adsorption were

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observed for Ghior soil. It was thus, observed that Ghior soil adsorbed the maximum amount of lead amongst the soils of two other series. For all soils, lead adsorption increased with increasing rate of lead addition. The fit of the lead adsorption data to the Langmuir adsorption model was tested (Fig. 2).

The *b* values (adsorption maximum) for the soils studied as presented in Table 2 followed the order: Ghior > Ghatail > Rajoir. The values of adsorption maximum increased with the increased clay content and with decreased organic matter and Fe content in the soils (Fig. 3). Schnitzer and Kerndorff (1981) also found that there was a positive relationship between the adsorption of lead and clay content of the soil and a negative relationship with the presence of organic matter.

Rule and Martin (1999) stated that the high proportion of lead in biosolids was due to the binding on to the inorganic (clay) fraction of the biosolid materials. Considering the *b* parameter of the Langmuir equation, it was observed that the soils with the greatest cation exchange capacity showed the lowest adsorption capacity for lead (Table 2). The bonding energies for lead represented by *k* (Table 2) were different for the soils. In soils, where the lead adsorption was high, the bonding energy was high; this corroborates the findings of Rule and Martin (1999). Adsorption of lead varied from soil to soil depending on certain dominant properties. In general, the absolute values of adsorption maximum were different. However, the observed wide variations in the adsorption maximum and bonding energy of Pb between soils are attributable to the content and nature of clay fraction, organic matter content and Fe content.

Table 2. Correlation between C/X and C, and Langmuir coefficients for soils/clays.

Lead source	Soil series	b (mg/kg)		k (mg/kg)		r	
		Soil	Clay	Soil	Clay	Soil	Clay
Lead nitrate [Pb(NO ₃) ₂]	Ghior	319.21	1263.68	10.18	0.88	0.43	0.98**
	Ghatail	302.38	1370.29	4.16	1.84	0.94*	0.999***
	Rajoir	295.26	1864.68	2.77	3.72	0.56	0.999***

*, **, *** indicate significance at 5, 1 and 0.1 per cent confidence level, respectively.

Lead adsorption on clays: Adsorption varied among the soil clay materials separated from the three soils as well as with the initial solution concentrations, which ranged from 0 to 15 mg/l. The minimum value of 108.62 mg/kg clay was observed for Ghior soil clay at 0.5 mg/l and the maximum adsorption of 1829.15 mg/kg clay was observed for Rajoir soil clay. Unlike the adsorption by the whole soils, it was thus

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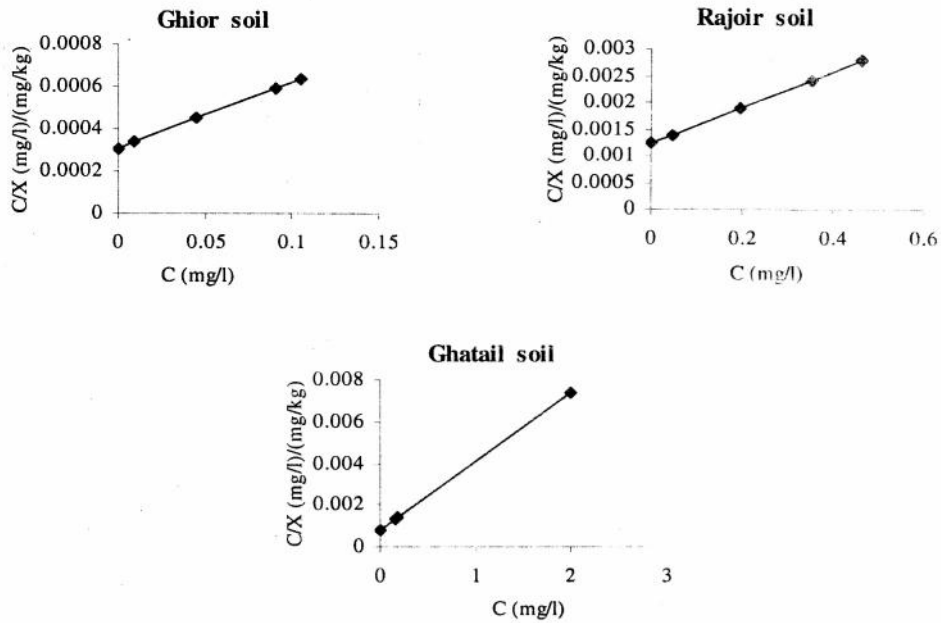


Fig. 2 Langmuir adsorption plots for soils.

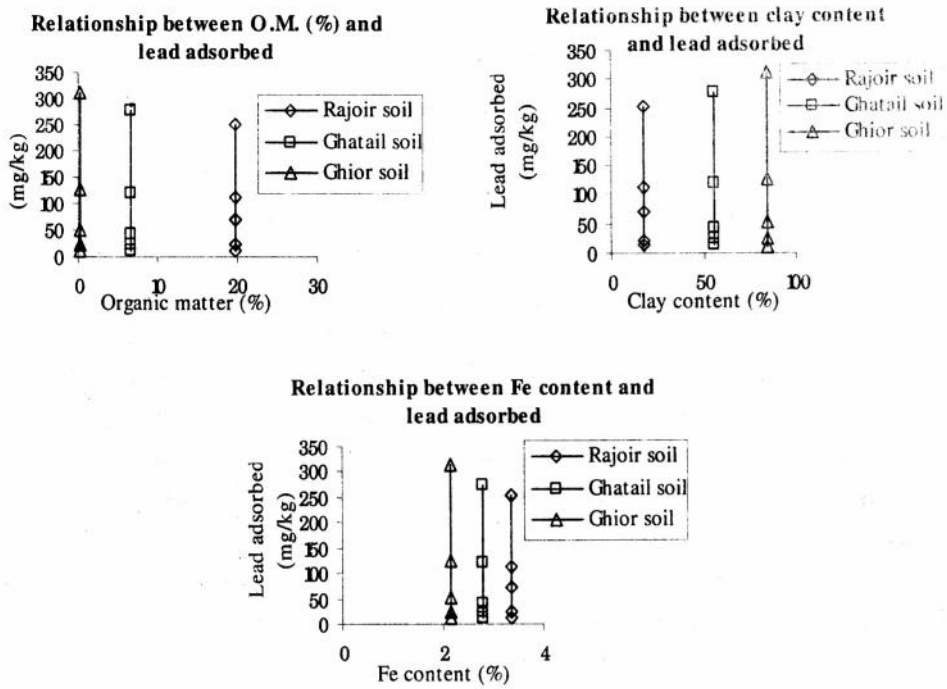


Fig. 3. Relationship between clay content, organic matter and Fe-content with adsorption of lead.

observed that Rajoir soil clay adsorbed the maximum amount of lead amongst the soil clays studied. The difference in adsorption by clays at the same initial concentration was probably due to the mineralogy of the clay fraction (Table 1b) as they contained variable proportions of clay minerals having different surface characteristics and charges. So, the mineral composition of the clays might have played a role in the sorption process. Table 1b shows the semi-quantitative mineral composition of the selected soil clays.

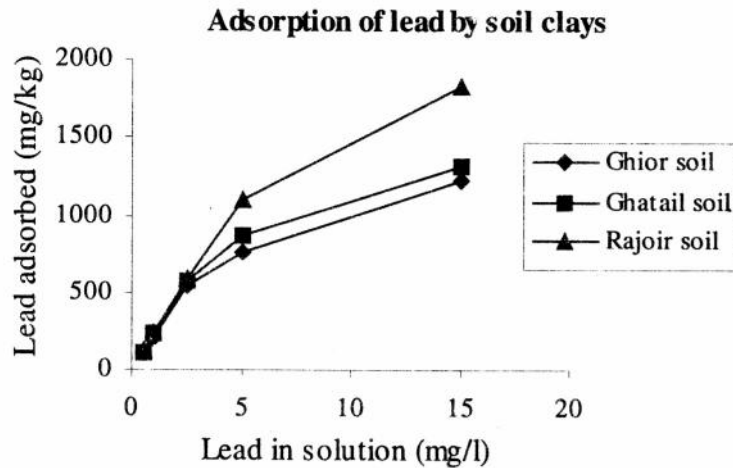


Fig. 4. Lead adsorption isotherms for clays.

Comparative study of the lead adsorption tests of the different types of soil clays selected permits the classification of the soil clays in the following order according to their lead adsorption capacity (from maximum to minimum) Rajoir > Ghatail > Ghior. The equilibrium solution lead concentrations (C) and amounts of lead adsorbed (X) by the clays are graphically presented in Fig. 4. For all clays, lead adsorption increased with increasing rate of lead addition. The b values (adsorption maximum) for clays as presented in Table 2 followed the order: Rajoir > Ghatail > Ghior. The bonding energies for lead adsorption represented by k (Table 2) were different for the clays. Lead adsorption data for the clay fraction conformed to the Langmuir adsorption isotherm because the fit is excellent (Fig. 5). The results obtained here showed that the fit of Pb adsorption data by clays to the Langmuir isotherm was better than for the whole soils. This is also evident from the significant r values obtained for C/X versus C values (Table 2). The observed variation in the adsorptive capacity and bonding energy for lead on soil clays indicated the influence of the mineralogy of the clays.

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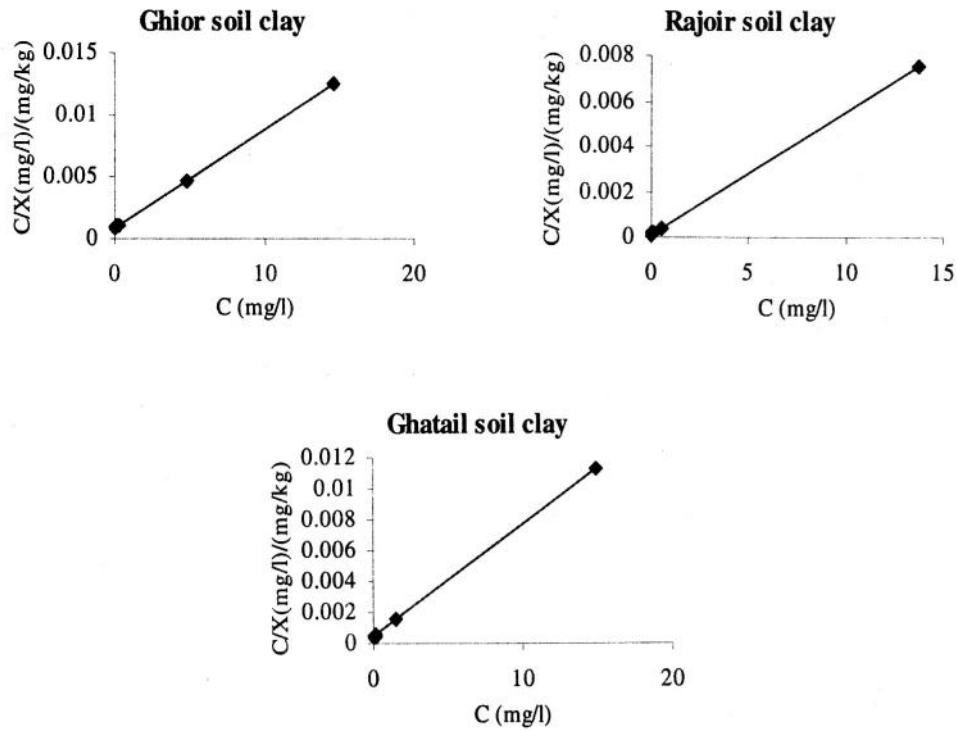


Fig. 5. Langmuir adsorption plots for clays.

The values of adsorption maximum increased with decreased proportion of illite and montmorillonite minerals in the soil clays. This is evident by the fact that clay of Rajoir soil, containing less amounts of illite and montmorillonite, has b values of 1864.68 as compared to the values of 1370.29 and 1263.68 observed for clays of Ghatail and Ghior soils which contained higher amount of illite and montmorillonite respectively. The clay content and the nature of minerals present should be considered when predicting the lead adsorptive capacity of a soil and clarifying interaction of lead and soil.

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(Revised manuscript received on 25 May, 2005)