Adsorption behaviour of Lead in mangrove soils and their relationship with soil characteristics

R Renuka[1], S Sandeep[2], M P Sujatha[3]

[1,2,3] Soil Science Division, Kerala Forest Research Institute, Peechi, Thrissur, Kerala
Corresponding author: renukarajan09@gmail.com

***Abstract*: Adsorption studies were conducted in the mangrove soils collected from South Western coast of India to evaluate the potential of these soils to regulate Pb dynamics. Surface soils were collected (0-30cm) for the batch experiments. Results show that pH, cation exchange capacity (CEC), texture and organic carbon (OC) effect the sorption maxima of Pb in mangrove soils. The adsorption of Pb in the mangrove soils was best explained by Langmuir adsorption isotherm model. Thermodynamic analysis show that the Pb adsorption in these mangrove soils are non spontaneous and endothermic.**

***Keywords:* Mangroves, Soil, Lead, Batch experiment, Thermodynamics.**

I. INTRODUCTION

The most typical and pristine vegetation present in the coastal region is mangroves. They are halophytes seen worldwide between latitudes 25^0N and 25^0S. It provides major ecosystem services from offering nesting and breeding habitat for fishes and birds to providing a natural barrier against coastal erosion. It stores carbon approximately 2-4 times greater than tropical forests [1]. One of the major functions of mangrove systems is to trap sediments, heavy metals and other pollutants thereby preventing contamination of downstream water ways [2]. Among the different types of contaminants, heavy metals are potential pollutants due to their toxicity, bio concentration and persistence [3], [4], [5], [6].The subject field of heavy metal accumulation has been examined and reported in various nations, including India [7].

The mangrove systems along the Kerala coast suffers constant disturbances due to dumping of industrial and organic waste and washing in of agricultural inputs. Mangrove systems along the Kerala coast are highly susceptible to heavy metal contamination due to human interventions. Being a transition between the aquatic and terrestrial systems, heavy metal pollution in these ecosystems would have an unwanted effect on both the adjacent soil and water systems.

Lead (Pb) is one of the most dangerous heavy metals due to its toxicity even at low concentration. It is present in soil in both organic and inorganic forms and is usually derived from the combustion of alkyl Pb additives, cable coverings, batteries and its connected industries, plumbing ammunition, paints, caulking, sound and vibration absorbers [8],[9].Lead exposure mainly affect nervous and reproductive systems and its exposure may lead to nausea, anorexia, insomnia, inhibition of heme synthesis, mental retardation, birth defects, autism, psychosis, dyslexia, allergies, hyperactivity, shaky hands, weight loss, muscular weakness and paralysis [10],[11].

Heavy metals may change their form chemically or physically when it is sorbed or bound by natural substances like soil, which may decrease or increase their mobility [12] and they may react with various species in the soil, vary oxidation states and precipitate [9]. Heavy metal adsorption in soil depends on soil type, metal speciation, metal concentration, pH, soil: solution mass ratio and contact time [13],[14]. Soil pH is a major factor that determines the sorption behaviour of heavy metals [15], [16]. Earlier studies on the sorption behaviour of Pb using isotherm models [17], [18] show that the adsorption - desorption properties of Pb in soil could be effectively explained by Langmuir and Freundlich models. As the sorption of Pb and its subsequent bioavalability in soil is controlled by thermodynamic parameters, scrutiny of these the parameters like free energy change (ΔG0), entropy (ΔS0) and enthalpy (ΔH0) were considered an upright path to explain the adsorption and mobility processes of the metal [19],[20],[21], [22],[23]. The objective of the present work was to thermodynamically evaluate the adsorption pattern of Pb in the mangrove soils of Kerala.

II. MATERIALS AND METHODS

A. Study area and soil sampling

Surface soil samples (0-30 cm) were collected from mangrove areas of Thrissur, TR_{SCL}($10^0$54'61.9"N, $76^0$06'42.5"S), Kannur, KA_{CL}($12^0$1'13.01''N $75^0$50.95''S) and Kollam, KO_{CL}($8^0$56'14.50°N ,$76^0$33'26.39''S) districts of Kerala by core method. Care was taken to select only natural mangrove systems and planted systems were avoided to minimize biases. The collected samples were air dried and sieved (2mm) for further analyses. About sixteen mangrove species were observed in the selected sites. The study sites experiences a tropical humid climate with an average rainfall of 2352.6 mm, 3351mm an 2468mm in Thrissur, Kannur and Kollam respectively, and mean yearly temperature of 27^OC.The collected soil was characterized for their physicochemical parameters and heavy metals using standard protocols [24]. Total heavy metals were examined by using acid digested soil samples and set by atomic absorption spectrophotometer.

B. Adsorption Studies

Batch experiments were used for the study. The batch adsorption studies were conducted by incubationg 1g of soil samples with different Pb concentrations viz. 0, 2.5, 5, 10, 20, 40, 60, 80, 100 and 120mgL^{-1}in 25ml centrifuge tubes at 25^0 C and 40 ^{0}C . The Pb solutions were prepared from stock solutions using $0.01MCaCl_2$ and adjusted to soil pH using $Ca(OH)_2$ or HCl. A 1:10: soil: solution ratio was maintained and this soil suspension was shaken for 3 hours at each temperature followed by centrifugation at 3000rpm for 15minutes.The separated supernatant was characterized for Pb contents in atomic absorption spectrophotometer (VARIAN AA240) and pH. The difference between the initial and final concentration of Pb (at equilibrium) in the solution was considered as Pb adsorbed to the soil particles.

C. Langmuir adsorption isotherm

The Langmuir adsorption isotherm was determined by following the formula

$$Q_{e=} Qmax*K*C_e/1+K*C_e \qquad (1)$$

WhereQe is the equilibrium adsorption capacity of Pb(mg g^{-1}), Ce is the equilibrium liquid phase concentration of Pb (mg L^{-1}), $Qmax$ is the maximum adsorption capacity, (mg g^{-1}) and K is adsorption equilibrium constant (L mg^{-1}). The adsorption isotherms were fitted by plotting Ce against Qe using R software version 3.5.1.

D. Thermodynamic Studies

Thermodynamic considerations of an adsorption process are required to resolve whether the process is spontaneous or not. The sorption data of Pb from two different temperatures were applied to define the thermodynamic reactions. The thermodynamic parameters of Gibb's free energy change, ΔG°, enthalpy change, ΔH°, and entropy change, ΔS°, for the adsorption processes were assessed using the following equations:

$$\Delta G^o = -RT \ln K \qquad (2)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (3)$$

Where$R$ is the universal gas constant and T is the absolute temperature in K

Enthalpy change (ΔH°) was calculated as

$$\Delta H = \ln\text{-}(K_1/K_2) * R\ (1/T_2 - 1/T_1) \qquad (4)$$

Where $K_1$and K_2 are the thermodynamic equilibrium constants at temperatures298 K and 313 K respectively. Entropy change ΔS° of adsorption was determined as

$$\Delta S = (\Delta H° - \Delta G^0)/T \qquad (5)$$

III. RESULTS AND DISCUSSIONS

A. Physico chemical characteristics of soil

The soils were alkaline in reaction. Electrical conductivity (EC) values ranged from 0.9 –2.8dS/m and organic carbon contents varied from 0.57–1.7%. Bulk density gives an indication of soil permeability and root growth suitability which varied in the order KO_{SL}< KA_{SL}<TR_{SCL}. Cation exchange capacity (CEC) ranged from 7.9 – 12.1 cmols (+) kg^{-1} soil. Sandy clay loam texture was found in TR_{SCL} where as sandy loam texture was found in KA_{SL} and KO_{SL} (Table I).

TABLE I: Physico chemical characteristics of mangrove soil (Mean ± SE)

Sampling location	pH	EC ds/m	OC %	BD g/cm^3	CEC cmols(+)kg^{-1} soil	Sand %	Clay %	Silt %
TR_{SCL}	6.9±0.23	0.9 ± 0.3	1.6 ±0.16	0.89±0.005	12.1 ± 0.18	61.4± 0.24	30.2±0.15	8±0.05
KA_{SL}	7.03±0.2	1.37± 0.74	1.7 ± 0.28	0.72± 0.01	10.43 ± 0.24	81.6± 0.14	16.0±0.05	1.9±0.05
KO_{SL}	8.03±0.6	2.8 ± 1.3	0.57±0.04	0.4± 0.01	7.9 ± 0.05	81.5± 0.34	15.9±0.1	1.9±0.05

B. Variation of Pb sorption at different temperatures

Table II: Adsorption and bonding energy coefficient of Pb in mangrove soils at 25^0 C and 40^0 C

Sampled sites	25^0 C		40^0 C	
	Q_{max} (mg Kg^{-1})	k (L mg^{-1})	$Q_{max}(10^3)$ (mg Kg^{-1})	K (10^{-3}) (L mg^{-1})
TR_{SCL}	22.59	-0.105	1.23	4.32
KA_{SL}	4.81	-0.149	0.08196	4530
KO_{SL}	16.24	-0.157	0.14928	30

The binding coefficient K derived from Langmuir isotherm is a measure of the shape of an isotherm, where higher k values indicate increasingly nonlinear isotherms. Curvature in the isotherm (high k) indicates sorption to high affinity sites at low Pb concentrations, and the decrease in slope observed at higher Pb concentrations may indicate progression to lower affinity chemical and physical adsorption sites. In TR_{SCL} soils had a higher Pb bonding energy ($4.32*10^{-3}$L mg^{-1}) followed by KA_{SL} (4.53 L mg^{-1}) and KO_{SL} soils (0.03 L mg^{-1}) (Table 2). In general, the k values of adsorption isotherms at 40^oC temperatures were found to be higher than that at 25^oC. At 40^0C, the maximum k value was observed in TR_{SCL} soil (0.00432 L mg^{-1}) and minimum in KO_{SL} soil (0.03 L mg^{-1}), reflecting the fact that adsorption isotherms were more nonlinear in the former and gets converted to more linear forms with rising temperature. The faster rates of adsorption with rising temperature could be attributed to the acceleration in the rate of aggregation [25] . Adsorption was maximum in soils with high clay content (TR_{SCL} having clay content of 30%). It shows that high amount of clay drive the sorption capacity by high density of edge and planar sites [26],[27] and depending on the type of clay will promote sorption to change from physisorption to chemisorption [28].Consequently type and quantity of clay colloids in these systems can be considered primarily responsible for Pb adsorption in these soils. However, adsorption with low bonding energies may pose threats when subjected to high degrees of contamination due to the inability of soils to strongly hold the metals and eventually leaching them to ground water.

In general, Qmax for Pb adsorption was found to be maximum in TR_{SCL} at 40^0C. The study indicated that the adsorption of Pb was endothermic and increased with rising temperature (Table 3 and Figures 1 a -3b). Organic matter decomposes under higher temperatures releasing organic moieties which help in the formation of stable soluble metal organic

ISSN 2348-313X (Print)
International Journal of Life Sciences Research ISSN 2348-3148 (online)
Vol. 7, Issue 1, pp: (140-146), Month: January - March 2019, Available at: www.researchpublish.com

complexes of Pb in the soil solution [29] . Alkaline soils favour the adsorption faster may be due to the precipitation of $PbCO_3$ as well as the formation of Pb (OH)C by competitive decrease between the HC and Pb [30], [31], [32]. Soon (33) show that at high pH, raising the adsorption of metal cations due to surface charge become more negative. Frost and Griffin [34] reported that soils dominant in 2: 1 type of clay such as montmorillonite accelerate the rate of adsorption of metal.

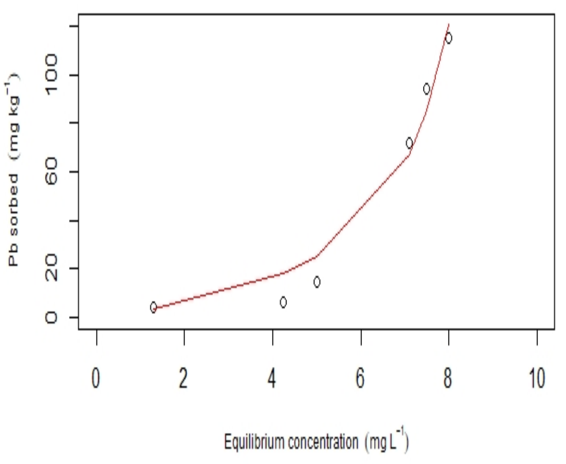

Fig. 1a. Langmuir adsorption isotherm TR_{SCL} at 25^0C

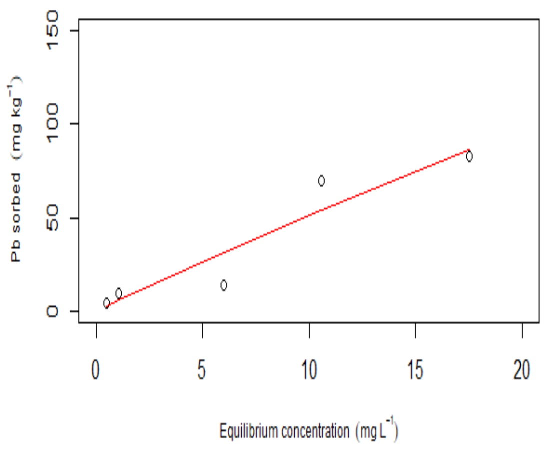

Fig. 1b. Langmuir adsorption isotherm TR_{SCL}at 40^0C

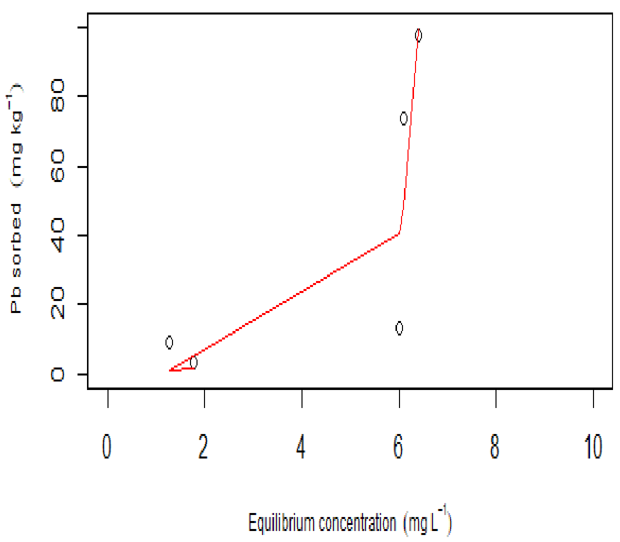

Fig . 2a. Langmuir adsorption KA_{SL} at 25^0C

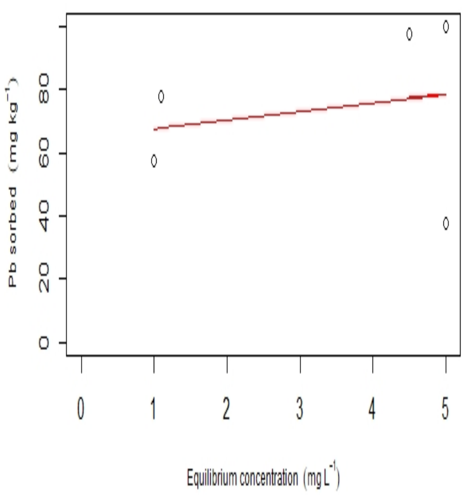

Fig.2b. Langmuir adsorption KA_{SL}at 40^0C

ISSN 2348-313X (Print)
International Journal of Life Sciences Research ISSN 2348-3148 (online)
Vol. 7, Issue 1, pp: (140-146), Month: January - March 2019, Available at: www.researchpublish.com

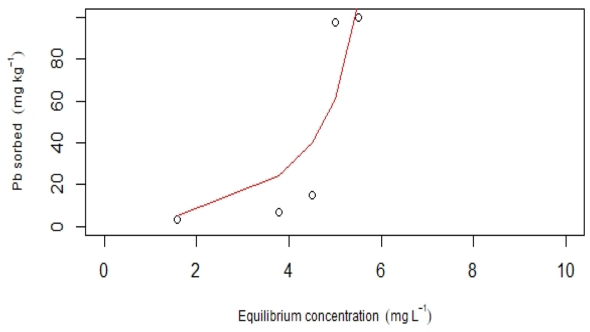

Fig. 3a Langmuir adsorptionKO$_{SL}$ at 25^{0}C

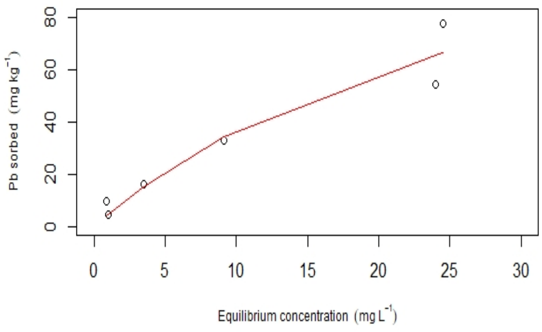

Fig 3b Langmuir adsorptionKO$_{SL}$ at 40^{0}C

C. Thermodynamic properties of Pb sorption

Table III : Thermodynamic behaviour for Pb sorption at two different temperatures

Sampling location	ΔG^0 (kJ mol^{-1})		ΔH^0 (10^6) (kJ mol^{-1})	ΔS^0 (J mol^{-1}K^{-1})	
	25^{0}C	40^{0}C		25^{0}C	40^{0}C
TR$_{SCL}$	5.58	14.17	4.27	-0.018	-0.045
KA$_{SL}$	4.71	-3.93	-4.5	-0.015	0.012
KO$_{SL}$	4.57	8.90	2.1	-0.015	-0.028

The thermodynamic parameters such as standard free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were computed at both 25^{0}C and 40^{0}C (Table III). The measured values of ΔG^0 were positive in all sampling sites at both temperatures except in KA$_{SL}$ at 40^{0}C (-3.93 kJ mol^{-1}). The positive values of ΔG° indicated that the Pb sorption process in the mangrove soils is possible only with an expenditure of energy or at higher temperatures. The process is not essentially spontaneous and adsorption preference of Pb by mangrove soil colloids is less. The same was confirmed in Langmuir sorption isotherm as well. For example in KA$_{SL}$, at 40^{0}C, ΔG^0 was negative indicating more Pb adsorption and spontaneity at high temperature. This is in agreement with the studies of Jurinak and Bauer [35] and Dutta et al. [36]. The ΔH^0 showed that the values were positive except KA$_{SL}$ at high temperature. This intimates that the reactions were endothermic in nature. Nevertheless, in KA$_{SL}$, at high temperature, ΔH^0 was negative and exothermic which may be owing to the various types of hydrated species of the metal ions [37].The positive standard entropy value (ΔS^0) observed in KA$_{SL}$ soils (0.012 kJ mol^{-1}) with rising temperature showed that during adsorption structural changes occur on the adsorbent, and randomness at the solid/liquid interface in the adsorption system. Conversely, this indicated that the degree of disorderness in adsorption processes were lower at rising temperature [23].

Table IV shows that sorption maxima was highly and negatively correlated with silt (-0.928**), clay (-0.754*), CEC (-0.754*) and BD (-0.771*).

Table IV: Correlation Coefficient of Soil parameters, Qmax and Thermodynamic properties

Soil characteristics	Qmax	ΔG^0	ΔS^0	ΔH^0
pH	0.866	-0.500	0.866	0.500
EC	0.500	-0.500	0.752	0.611
OC	0.429	0.541	-0.429	-0.071
BD	-0.771*	0.851	-0.776	0.366
CEC	-0.754*	0.871	-0.801	0.403
Sand	0.714	-0.991*	1**	-0.873
Clay	-0.771*	0.993*	-1**	0.866
Silt	-0.928**	0.992*	1**	0.871

*. Correlation is significant at the 0.05 level .**.Correlation is significant at the 0.01 level

ISSN 2348-313X (Print)
International Journal of Life Sciences Research ISSN 2348-3148 (online)
Vol. 7, Issue 1, pp: (140-146), Month: January - March 2019, Available at: www.researchpublish.com

IV. CONCLUSIONS

The study point out that Pb adsorption data can be explained satisfactorily by Langmuir isotherms. The soil properties such as silt, clay, pH, CEC and organic carbon can be considered as most key factors liable for the Pb adsorptive capacity of soils. Thermodynamic studies show that Pb sorption reaction in the mangrove soils are non spontaneous. The study elucided that the mangrove areas of Kerala would be vulnerable to Pb toxicity under higher releases of this metal to the environment as the Pb adsorption by these soils are non spontaneous and higher quantities could be retained only with the expenditure of energy.

REFERENCES

[1] USDA. Mangroves among the most carbon-rich forests in the tropics; Coastal trees key to lowering greenhouse gases. USDA Forest Service, Pacific Southwest Research Station; 2011.

[2] Verma R, Dwivedi P. Heavy metal water pollution- A case study. *Rec. Res. Sci. Technol*. 2013; 5(5): 98-2p.

[3] MacFarlane GR, Burchett MD. Toxicity, growth and accumulation relationships of copper, lead and zinc in the grey mangrove Avicennia marina (Forsk.) Vierh. *Marine Environ Research*. 2002; 54: 19p.

[4] Lindsey DT, Hillger DW, Grasso L, et al. Climatology and Analysis of Thunderstorms with Enhanced 3.9-μ m Reflectivity. *Monthly Weather R*, 2006; 134: 2342-12p .

[5] Vane CH, Jones DG, Lister TR. Mercury contamination in surface sediments and sediment cores of the Mersey Estuary, UK. *Marine Pollut Bull*. 2009; 58(6): 940-6p.

[6] Lal Shah, S. Hematological changes in Tinca tinca after exposure to lethal and sublethal doses of Mercury, Cadmium and Lead. *Iran J fish sci.* 2010; 9(3): 434-9p.

[7] Dudani NS, Lakhmapurkar J, Gavali D, Patel T. Heavy Metal Accumulation in the Mangrove Ecosystem of South Gujarat Coast, India. *Turk J Fish. and Aquat. Sci.* 2017; 17: 755-11p.

[8] Hardy DH, Myers J, Stokes C. Heavy Metals in North Carolina Soils: Occurrence and Significance. NC Department of Agriculture, Consumer Services, 2008; 1-2p.

[9] Al Hagibi HA, Al-Selwi KM, Nagi HM , Al-Shwafi NA. Study of Heavy Metals contamination in Mangrove Sediments of the Red Sea Coast of Yemen from Al-Salif to Bab-el-Mandeb Strait. *J Ecol & Nat Resour*. 2018: 2(1): 121-18p.

[10] Mataka LM, Henry EMT, Masamba WRL, Sajidu SMI . Lead remediation of contaminated water using Moringa stenopetala and Moringa oleifera seed powder. *Int. J. Environ. Sci. Technol*. 2006 3(2): 131-8p.

[11] Nigeria BA, Adelekan, Abegunde KD. Heavy metals contamination of soil and groundwater at automobile mechanic villages in Ibadan.*In J Physical Sci*. 2011; 6(5): 1045-13p.

[12] Dube A, Zbytniewski R, Kowalkowski T, et al. Adsorption and Migration of Heavy Metals in Soil. *Pol J Environ Stud.* 2001; 10(1) : 1-10p.

[13] Nazir R,Khan M,Masabi M, et al.Accumulation of Heavy Metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physico-chemical parameters of soil and water Collected from Tanda Dam kohat. *J. Pharm. Sci. & Res*. 2015; 7(3): 89-8p.

[14] Kent DB, Abrams RH, Davis JA, Coston LeBlanc DR Modeling the transport of zinc under variable chemical conditions in a contaminated aquifer using semiempirical surface complexation models. 2000; *Water Resour. Res*., 36: 3411 – 16p.

[15] Anderson PR, Christensen TH. Distribution coefficients of Cd, Co, Ni, and Zn in soils. J. Soil Sci. 1988; 39: 15-7p.

[16] Tahervand S, Jalali M. Sorption, desorption, and speciation of Cd, Ni, and Fe by four calcareous soils as affected by pH. *Environ Monit Assess*. 2016; 188-134p.

[17] Peters RW, Shem L. Adsorption/Desorption characteristics of lead on various types of soil. *Environ Progr.*1992; 11(3): 234–7p.

[18] Yang JY, Yang XE, He ZL.et al. Adsorptiondesorption characteristics of lead in variable charge soils Part A. J. environ. sci. Health. 2004; 39: 1949–18p .

[19] Sperotto R, Ricachenevsky F, Williams L, Vasconcelos M, Menguer P . From soil to seed: micronutrient movement into and within the plant. *Front Plant Sci* . 2014; 5: 438-4p.

[20] Kaewtubtim P, Meeinkuirt W, Seepom S, Pichtel J. Heavy metal phytoremediation potential of plant species in a mangrove ecosystem in Pattani Bay, Thailand. *Appl Ecol Environ Res.* 2016; 14(1): 367-15p.

[21] Harbison P. Mangrove muds - A sink and asource for trace metals. *Mar Pollut Bull* . 1986 ; 17(6): 246-5p.

[22] MacFarlane GR, Koller C, Blomberg S. Accumulation and partitioning of heavy metals in mangroves: A synthesis of field-based studies. *Chemosphere*. 2007; 69(9): 1454-10p.

[23] Adhikari T, Singh MV. Sorption characteristics of lead and cadmium in some soils of India. *Geoderma*. 2003; 114: 81-12p.

[24] Jackson ML. Soil chemical analysis by Prentice Hall of India Pvt. Ltd. Newdelhi, 1957

[25] Karak T, Paul RK, Das DK et al. Thermodynamics of Cadmium Sorption on Different Soils of West Bengal, India.The Scientific World Journal.2014; 11p.

[26] Dolcater DL, Jackson ML, Syers JK.Cation exchange selectivity in mica and vermiculite. *The Amer.Minera.* 1972;57: 1823-8p.

[27] Inskeep WP, Baham J. Adsorption of Cd(II) and Cu(II)by Na-montmorillonite at low surface coverage. *Soil Sci Soci Amer*. 1983; 47(4): 660–5p.

[28] Sparks DL. *Environmental Soil Chemistry*, Academic Press,New York, NY, USA, 1995.

[29] Bolan NS, Adriano DC, Duraisamy P, Mani A. Immobilization and phyto availability of cadmium in variable charge soils. III. Effect of biosolid compost addition," *Plant and Soil*. 2003; 256(1): 231–241.

[30] Garcia-Miragaya J, Page AL. Sorption of trace quanities of cadmium by soil with different chemical and minerlogical composition. 1978; Water, Air and Soil Pollut. 9: 289-10p.

[31] McBride MB, Tyler LD, Hovde DA. Cadmium Adsorption by Soils and Uptake by Plants as Affected by Soil Chemical Properties. 1981; *Soil Sci. Soci. Am. J.* 45: 739-6p.

[32] Esfandbod M , Forghani,A , Adhami E , Rashti, MR. Cadmium adsorption behavior of some soils from northern of Iran.19th World Congress of Soil Science, Soil Solutions for a Changing World., Brisbane, Australia. 1 – 6 August 2010.

[33] Soon YK. Solubility and sorption of cadmium in soils amended with sewage sludge. *J. Soil Sci*. 1981; 32: 85–10p.

[34] Frost RR, Griffin, RA. Effect of pH on Adsorption of Arsenic and Selenium from Landfill Leachate by Clay Minerals. *Soil Sci. Soc. Am. J*, 1977, 41(1): 53-4p.

[35] Jurinak JJ, Bauer N . Thermodynamics of zinc adsorption on calcite, dolomite and magnesite type minerals. *Proc Soil Sci Soci of Amer*. 1956; 20 :466-6p.

[36] Dutta SK, Singh D, Sood A. Effect of soil chemical and physical properties on sorption and desorption behavior of lead in different soils of India. *Soil Sedi. Contaminant In J.* 2011; 20p.

[37] Adhikari T, Singh MV. Sorption of cadmium in some soils of India. In: Yadav, J.S.P. (Ed.), *International Conference on Managing Natural Resources for Sustainable Agricultural Production for 20th Century*. ICAR, New Delh; 2000. 143 – 2p.