Original Research Paper

Adsorption-Desorption Studies of Cadmium in Three Different Soil Orders

Asha Sahu*,†, S.K. Singh*, Nisha Sahu**, Bali Ram*** and M.C. Manna****
*Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi-221 005, India
**National Bureau of Soil Survey & Land Use Planning (ICAR), Amravati Road, Nagpur-440 033, India
***Department of Chemistry, Faculty of Sciences, Banaras Hindu University, Varanasi-221 005, India
****Division of Soil Biology, Indian Institute of Soil Science, Nabibagh, Berasia Road, Bhopal-462 038, India
†Present Address: Div. of Soil Biology, Indian Institute of Soil Science, Nabibagh, Berasia Road, Bhopal-462 038, India
Corresponding author: Asha Sahu

ABSTRACT

Sorption isotherms have been widely used to assess the heavy metals retention characteristics of soil particles. Adsorption behaviour of cadmium (Cd) in soils is an important process which exerts a major influence on its uptake by plant roots. Desorption behaviour of the retained metals, however, usually differ from that of adsorption, leading to a lack of coincidence in the experimentally obtained adsorption and desorption isotherms. Three soils differing in physico-chemical properties (pH 5.7 to 8.2) and varied taxonomy (Typic Ustochrepts, Typic Rhodustalfs and Entic Chromusterts), were subjected to Cd treatment at various concentrations (0, 2, 4, 8, 15, 30, 45, 75 mg Cd/L). The Cd adsorbed by each soil was calculated as the difference between the amount of Cd present in the solution initially and that remaining after equilibration. Immediately after adsorption, desorption took place using successive dilution method with five consecutive desorption steps. Both, Cd adsorption and desorption data were described by Freundlich equation. The adsorption and desorption reactions, however, did not provide the same isotherms, indicating that hysteresis occurred in Cd adsorption-desorption process. Results indicated that the adsorption capacity of the soils for Cd increased with an increase in the pH or alkalinity of the soils. The rate of adsorption was, however, found to decrease with increased pH. But no specific trend was observed in case of desorption. All the three soils used in this study followed Freundlich adsorption isotherms. The adsorption data, in general, indicated that Cd was in a fixed form at higher pH levels. The Cd adsorption was in the order of Entic Chromusterts > Typic Ustochrepts > Typic Rhodustalfs.

INTRODUCTION

Heavy metal pollution of soil is one of the major environmental issues worldwide (Kabata-Pendias 1995, Nriagu & Pacyna 1988, Yanai et al. 2005). These metals being sufficient in distribution and abundance are biologically toxic substances (Lester 1987). Among heavy metals, cadmium (Cd) is considered to be an important soil pollutant because it is potentially biotoxic in nature that is readily absorbed by plants and has the potential to enter the human food chain. Excessive accumulation of Cd in man causes bronchitis (Lewis et al. 1969), hypertension (Schroeder 1965), cardiovascular (Page & Bingham 1973) and "ouch-ouch" (Tsuchiya 1969) diseases. It may accumulate in agricultural soils through the application of soil additives, such as phosphatic fertilizers and sewage sludges which contain 7.3-170 mg/kg (Lisk 1972) and <1- 3410 mg/kg (Alloway 1990) cadmium, respectively. The phytoavailability and, hence, potential toxicity of Cd in soils is controlled by adsorption and desorption properties of the soil (Swift & McLaren 1991). If adsorption isotherms do not follow their corresponding desorption isotherms, this phenomenon i.e., non-unique relationship of solution concentration and sorbed amount of a chemical when equilibrium is reached from forward or reverse directions, is called adsorption-desorption hysteresis. Sorption characteristics of various soil particles and minerals have been frequently studied through sorption isotherm experiments. A sorption isotherm represents the quantity of an ion sorbed by a solid as a function of the equilibrium concentration of that ion in solution, at a constant temperature. Desorption of the sorbed ions from the solid phase controls the availability and leachability of those ions in soils. Thus, estimation of sorptive capacity of soils provides valuable information relating to the vulnerability of a soil after the incorporation of a given load of heavy metal (Jain & Ram 1997). Hodgson (1970) also found that cadmium content in plants depends primarily on soil adsorption capacity which, in turn, is governed by the physico-

chemical characteristics of the soils concerned. Therefore, the present investigation was undertaken to study cadmium adsorption by three taxonomically different soil orders.

MATERIALS AND METHODS

Soil sampling and analyses: Bulk composite surface (0-15 cm) soil samples *viz.,* fine loamy, mixed hyperthermic, Typic Ustochrepts (Alluvial soil), fine loamy, mixed hyperthermic, Typic Rhodustalfs (Red soil) and fine loamy, mixed hyperthermic, Entic Chromusterts (Karail soil) were collected from Agricultural Research Farm, Banaras Hindu University, Varanasi (25°18' N latitude and 83°03'E longitude), Rajiv Gandhi South Campus, Barkachha, Mirzapur (25°10' N latitude and 83°37' E longitude) and Shahanshahpur, Varanasi (25°08' N latitude and 83°52' E), respectively. The samples were processed, passed through a 2 mm sieve and analysed for pH, EC, organic carbon, clay and $CaCO_3$ using standard analytical methods (Sparks 1996). Cation exchange capacity (CEC) was determined by using 1N sodium acetate solution as proposed by Hesse (1971). Concentration of available Cd in soil samples was determined using DTPA extraction method (Lindsay & Norvell 1978).

Adsorption Studies (Adhikari & Singh 2003): For determination of equilibration time, 2 g soil was taken in a series of centrifuge tubes and 20 mL 0.01 M $CaSO_4.2H_2O$ solution containing graded levels of heavy metal i.e., 0, 2, 4, 8, 15, 30, 45 and 75 mg Cd/L as $CdSO_4.8H_2O$ was added and shaken on a horizontal shaker for different time intervals (2, 4, 6, 8, 10, 12 h). The equilibration time was found to be 8 h which was used in adsorption studies.

Aqueous solutions of different concentrations of Cd *viz.,* 0, 2, 4, 8, 15, 30, 45 and 75 mg/L were prepared in $CaSO_4.2H_2O$ solution. Two gram soil was taken in triplicate in centrifuge tubes and 20 mL aqueous Cd solution was added. A blank with 20 mL 0.01 M $CaSO_4.2H_2O$ was run side by side. The contents were shaken on horizontal shaker for 8 h and centrifuged for 20 min at 10,000 r.p.m. to obtain a clear supernatant. It was filtered through Whatman No. 42 filter paper. The filtrates were analysed for Cd using UNICAM 969 atomic absorption spectrophotometer at 228.8 nm wavelength. The Cd adsorbed by each soil type was calculated as the difference between the amount of Cd present in the solution initially and that remaining after equilibration, as described by Garcia-Miragaya & Page (1978). The adsorption data were fitted in Freundlich adsorption isotherm model, $x/m = K C_e^{1/n}$ [$\log (x/m) = \log K + 1/n \log C_e$], where, x/m is amount of Cd adsorbed per unit mass of soil (mg/kg), C_e is equilibrium concentration and, K and n are adsorption capacity or degree of affinity (mgCd/kg soil) and rate of adsorption, respectively.

Desorption studies (Sharma et al. 2005): Desorption studies were carried out in triplicate. After the supernatant was filtered, 20 mL 0.01 M $CaSO_4.2H_2O$ was added to the centrifuge tube. The retained solution in soil pellet was less than 0.3 mL and was not taken into account in calculation. The contents were thoroughly mixed and care was taken that no soil remained sticking to the tube. These tubes were shaken for 8 h and centrifuged to obtain a clear supernatant. The supernatant was analysed for cadmium. The process was repeated five times.

RESULTS AND DISCUSSION

Soil properties: The soil properties (Table 1) revealed a wide variability in pH 7.8, 5.1, 8.2; organic carbon 5.2, 3.4, 6.8 g/kg; $CaCO_3$ 6.5, 5.5, 8.0 %; CEC 13.7, 10.1, 26.8 cmol/kg; clay 21.87, 23.99, 40.85 %, respectively for alluvial, red and karail soil.

Adsorption-desorption isotherms of cadmium in alluvial soil: Curve of cadmium adsorption-desorption for alluvial soils as affected by different levels of cadmium are shown in Fig. 1. In general, the adsorption of cadmium followed a regular increase with increasing concentration of Cd up to 2.5 mg/L in the equilibrium soil solution. Beyond 2.5 mg Cd/L concentration in the equilibrium solution, the adsorbed amount of cadmium registered a relatively higher increase. This kind of adsorption pattern was suggestive of 'S' type adsorption isotherm (Giles et al. 1960) implying side-by-side association between adsorbed molecules or cooperative adsorption. It represents the case of physical adsorption on porous material and explains the formation of multi-molecular layer in the beginning. This isotherm indicates that there is tendency for saturation state to be reached in the multimolecular region. Desorption curve also followed a similar pattern to that of adsorption, however, the gap between adsorption and desorption isotherms was increased with increasing Cd levels. At higher concentrations of Cd the hysteresis loss is more, so less availability of Cd^{2+} in soil solution or less available to plants. This may be due to multilayer adsorption of Cd at soil surface. But at lower concentrations Cd will be easily desorbed and available in soil solution. The Freundlich adsorption-desorption isotherms are plotted in Fig. 2 and 3. The values of Freundlich adsorption- desorption parameters K (adsorption capacity) and K' (desorption capacity), and n (rate of adsorption) and n' (rate of desorption) are given in Table 2 as 0.239 and 0.204, and 1.14 and 1.15, respectively.

Adsorption-desorption isotherms of cadmium in red soil: The data on red soils on adsorption-desorption are plotted in Fig. 4. It is evident that the adsorption curve followed 'L' type adsorption pattern. Whereas 'S' type of desorption curve

Table 1: Physico-chemical characteristics of initial soil samples.

Soil properties	Alluvial soil	Red soil	Karail soil
Taxonomic Class	Fine loamy, mixed hyperthermic, Typic Ustochrepts	Fine loamy, mixed hyperthermic, Typic Rhodustalfs	Fine loamy, mixed hyperthermic, Entic Chromusterts
pH (1:2.5)	7.8	5.7	8.2
EC (dSm^{-1})	0.113	0.135	0.165
OC (g/kg)	5.2	3.4	6.8
CaCO$_3$ (%)	6.5	5.5	8.0
CEC [cmol (P$^+$) kg^{-1}]	13.7	10.1	26.8
Sand (%)	28.53	16.59	1.53
Silt (%)	49.60	59.42	57.62
Clay (%)	21.87	23.99	40.85
DTPA-extractable Cd (mg/kg)	0.054	0.080	0.005

Table 2: Adsorption and desorption coefficients of alluvial, red and karail soil.

Soil	Adsorption				Desorption			
	logK	K$^{\square}$	1/n	n$^{\lozenge}$	logK'	K$^{\boxdot}$	1/n'	n'*
Alluvial	-0.62	0.239	0.87	1.14	-0.69	0.204	0.87	1.15
Red	-0.76	0.174	0.91	1.10	-1.18	0.066	0.96	1.04
Karail	-0.48	0.331	0.83	1.2	-1.1	0.079	0.89	1.12

$^{\square}$Adsorption capacity; $^{\lozenge}$Intensity of adsorption; $^{\boxdot}$Desorption capacity; *Intensity of desorption

is seen. It explains multi molecular layer in capillary space and represents the case of physical adsorption on porous materials, accompanied by capillary condensation. This isotherm indicates that there is tendency for saturation state to be reached in the multimolecular region. The amount of cadmium adsorbed (K) is noted 0.174, while the intensity of adsorption (n) is 1.102. The amount of cadmium desorbed (K') is 0.066 and the intensity of desorption (n') is 1.04 as given in Table 2 and plotted in Figs. 5 and 6, respectively.

Adsorption-desorption isotherms of cadmium in karail soil: The data on adsorption-desorption of cadmium in karail soil are plotted in Fig. 7. Curve revealed that both the adsorption and desorption pattern followed 'S' type curve. At low concentrations, the amount adsorbed is directly proportional to concentration. The extent of adsorption increases with concentration and ultimately reaches a limiting value. This explains the adsorption to be monolayer. One possible explanation for slow desorption is that chemisorption reactions usually require a much higher activation energy in desorption direction than sorption, to break the energetically very favourable bonds of the sorbate with the surface (McBride 2000, Appel & Ma 2002). The amount of cadmium adsorbed (K) is found to be 0.331 and intensity (n) as 1.2, whereas the amount of cadmium desorbed (K') is 0.079 and intensity of desorption (n') is 1.12 as given in Table 2 and Figs. 8 and 9. In general, the adsorption capacity of

soils for Cd increased with an increase in pH or alkalinity of the soils. The observed high adsorption of Cd by karail soils may be attributed to the increase in negative soil charge, less competition between Cd and H$^+$ for ion sorption sites, as well as the formation of moderate amounts of the Cd(OH)$^+$ species in solution (Garcia-Miragaya & Page 1978). The larger gap in hysteresis shows that there is more attenuation of the Cd^{2+} on surface. Hence Cd^{2+} is less available in soil solution and thus less available to plants.

The adsorption capacity of the three soils was in order of karail soil (0.331) > alluvial soil (0.239) > red soil (0.174). It was noted that karail soil has 47% more capacity to adsorb Cd in comparison to red soil. Rate of adsorption is also recorded highest in karail soil (1.2) and is 8% more than red soil (1.1). In case of red (acidic) soils, the amount of Cd adsorbed was lower than that of karail (alkaline) soils, since the amount left on the adsorbent (soil) after desorption is higher in clay rich (karail followed by alluvial) soils as compared to red soil. The specificity of the adsorbate (Cd^{2+}) is higher in the former type of soils and hence the availability on those soils would be lower. This finding was in accordance with the work of Garcia-Miragaya & Page (1978) who reported that with an increasing concentration of H$^+$ and Al^{3+} in solution, the competition between these ions and Cd for non sorption sites on the soil sorbent surfaces, together with the concomitant decrease of negative charge of the same
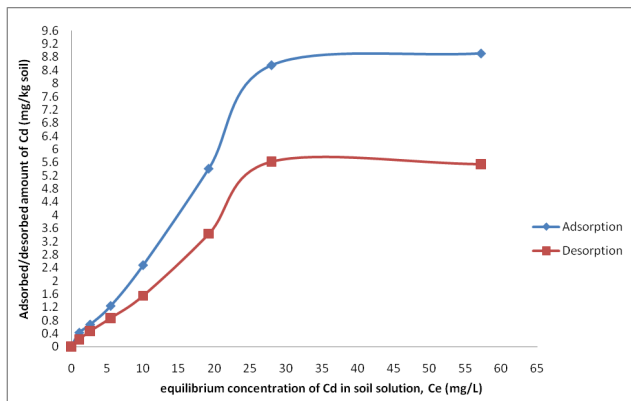
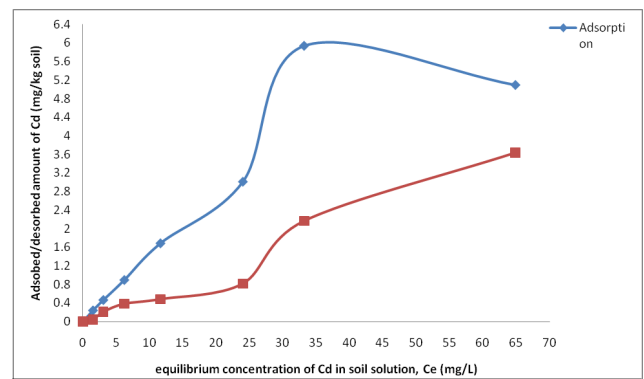Fig. 1: Adsorption-desorption curve in alluvial soil.

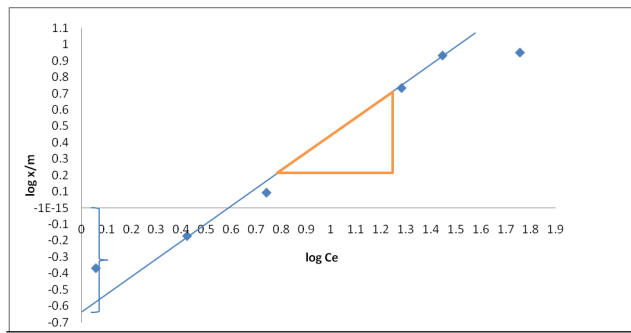Fig. 4: Adsorption-desorption curve in red soil.

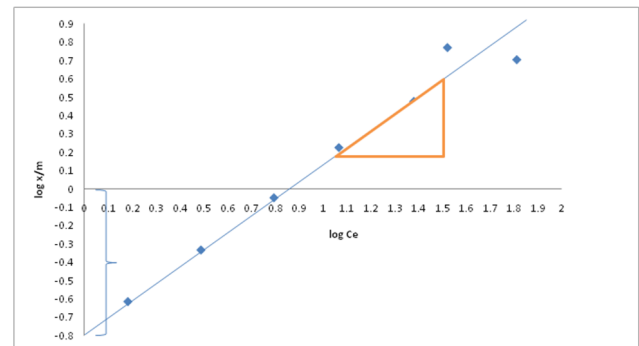Fig. 2: Adsorption isotherm in alluvial soil.

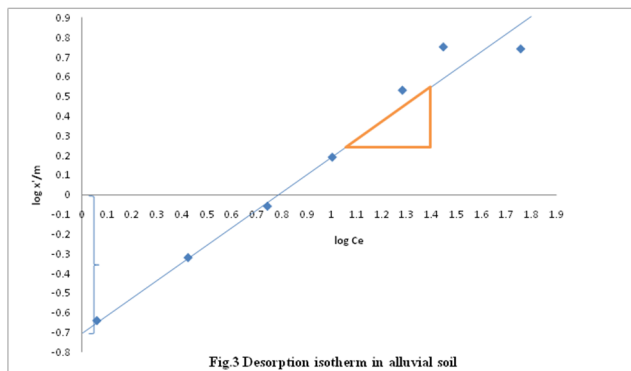Fig. 5: Adsorption isotherm in red soil.
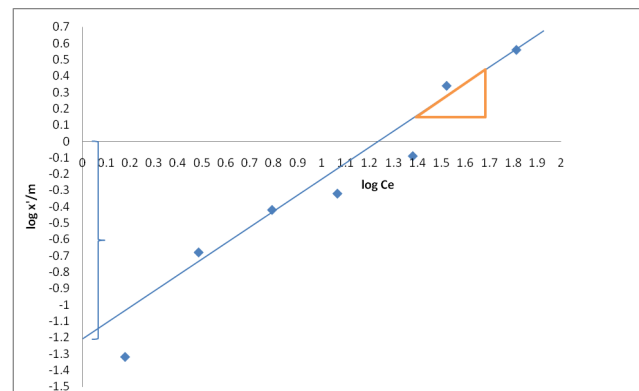

Fig. 3: Desorption isotherm in alluvial soil.

Fig. 6: Desorption isotherm in red soil.

surfaces may be the contributory factor for this phenomenon.

As reported by McBride et al. (1981), in calcareous or alkaline soils, $CdCO_3$ precipitation or chemisorption on carbonates may also be responsible for the present findings of high adsorption of Cd by alkaline soils. Furthermore, these findings are also in agreement with Soon (1981), who reported that with increasing soil pH, the surface charge and potential become more negative, thereby increasing the adsorption of metal cations such as Cd^{2+}. The alkaline soils i.e. alluvial and karail selected for this study mainly belong to the soil group 'Inceptisols' and 'Vertisols', respectively where 2:1 type of clays like montimorillonite are predominant. This might have favoured the high adsorption of Cd as reported earlier by Frost & Griffin (1977). The high pH, high CEC and high $CaCO_3$ content of alkaline soils may have favoured the conditions for high adsorption of Cd.
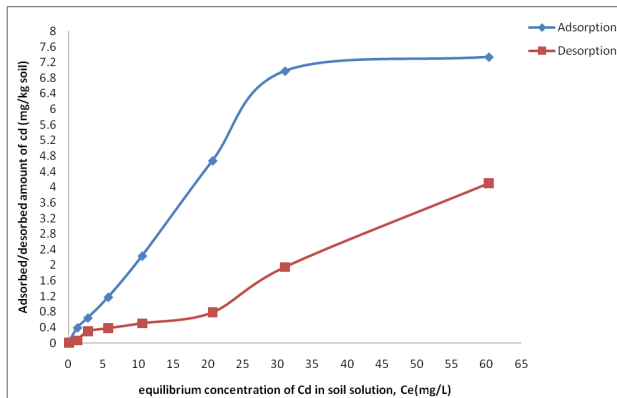
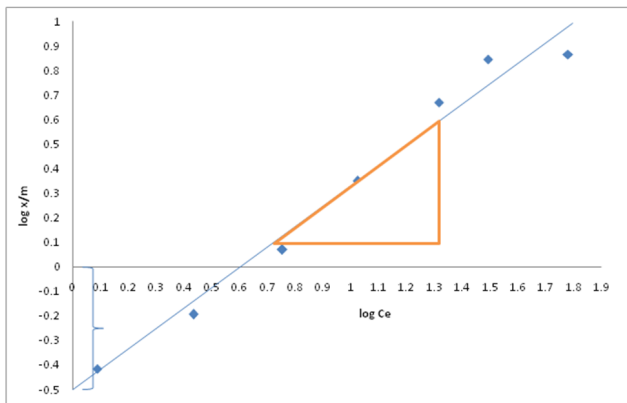Fig. 7: Adsorption-desorption curve in karail soil.
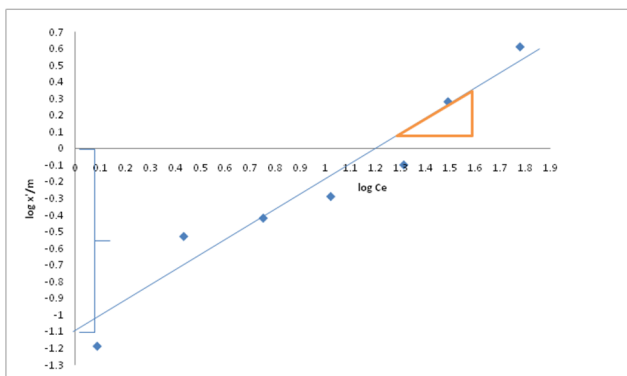

Fig. 8: Adsorption isotherm in karail soil.

Fig. 9: Desorption isotherm in karail soil.

As compared to the Vertisols and Inceptisols, Alfisols exhibited lower adsorption of Cd. According to John (1972), as reported by Cavallaro & McBride (1978), the presence of Al^{3+} in acid soils and its competition for exchange sites might have resulted in reduced Cd adsorption in these soils. In addition, low pH of acidic soils has the effect of increasing the fractions of functional groups in soil organic matter that is

associated with protons or Al^{3+}, thereby reducing the ability of Cd^{2+} to be adsorbed (Cavallaro & McBride 1978). Cowan et al. (1992) and Zachara et al. (1992) have suggested that Fe oxides decrease Cd sorption by blocking access of Cd to exchange sites. The presence of high amounts of Al^{3+} and Fe^{3+}, may therefore, be responsible for the low adsorption capacity of Cd in these soils.

Desorption capacity was recorded highest in alluvial soil (0.204) followed by karail (0.079) and red soil (0.066). Rate of desorption is also seen highest in alluvial soil (1.15) and lowest in red soil (1.04). As the clay content bearing negative charge in soil matrix is least in alluvial soils thereby Cd desorption will be more providing more Cd^{2+} in soil solution and making them more available to plants in comparison to karail soil which are rich in clay content. Similar findings for different tropical soils ranging in pH for 4.8-8.2 have been reported by Rattan & Sehgal (1989).

CONCLUSIONS

In general, the Freundlich adsorption isotherm was found to fit better for Cd adsorption in all the three soils selected for this study. Karail soil favoured high adsorption of Cd possibly due to precipitation as $CdCO_3$ and high clay content, which may lead to less availability of Cd for plant uptake, whereas, red soil adsorbed less Cd and more Cd was present as Cd^{2+} in solution, which may result in high availability of Cd for plant uptake. This clearly indicates that irrespective of origin of soils, Cd adsorption is mainly dependent on pH, CEC, clay and $CaCO_3$ content of soils.

ACKNOWLEDGEMENTS

REFERENCES

Adhikari, T. and Singh, M.V. 2003. Sorption characteristics of lead and cadmium in some soils of India. Geoderma, 114: 81-92.
Alloway, B. J. 1990. The Origins of Heavy Metals in Soils. Heavy Metals in Soils. Blackie and Sons Ltd., U.K., pp. 339.
Appel, C. and Ma, L. 2002. Concentration, pH and surface charge effects on cadmium and lead sorption in three tropical soils. J. Environ. Qual., 31: 581-589.
Cavallaro, N. and McBride, M.B. 1978. Copper and cadmium adsorption characteristics of selected acid and calcareous soils. Soil Sci. Soc. Am. J., 42: 550.
Cowan, C.E., Zachara, J.M., Smith, S.C. and Resch, C.T. 1992. Individual sorbent contributions to cadmium sorption on Ultisols of mixed mineralogy. Soil Sci. Soc. Am. J., 56: 1084-1094.
Frost, R.R. and Griffin, R.A. 1977. Effect of pH on adsorption of copper, zinc and cadmium from landfill leachate by clay minerals. J. Environ. Sci. Health., 12: 139-156.
Garcia-Miragaya, J. and Page, A.L. 1978. Sorption of trace quantities

of cadmium by soils with different chemical and mineralogical composition. Water Air and Soil Pollution, 9: 289-299.

Giles, C.H., McEvan, T.H., Nakhwa, S.N. and Smith, D. 1960. Studies in adsorption, Part XI, A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms of specific surface area of solid. J. Chem. Soc., 3973-3993.

Hesse, P.R. 1971. A Textbook of Soil Chemical Analysis. Prentice Hall of India Pvt. Ltd., New Delhi.

Hodgson, J. F. 1970. Trace substances in environmental health. In: D. D. Emphill (ed.), Vol.III. pp. 45-58. Univ. of Missouri Press, Columbia.

Jain, C. K. and Ram, D. 1997. Adsorption of lead and zinc on bed sediments of river Kali. Water Research, 31(1): 154-162.

John, M.K. 1972. Cadmium adsorption maxima of soils as measured by the Langmuir isotherm. Can. J. Soil Sci., 52: 343-350.

Kabata-Pendias, A. 1995. Agricultural problems related to excessive trace metal contents of soils. In: Salmons, W., Forstner, U., Mader, P. (Eds.) Heavy Metals. pp. 3-18. Springer., Berlin.

Lester, I. N. 1987. Heavy Metals in Wastewater and Sludge Treatment Processes. CRC Press. Inc., Boca Raton, Fl. U.S.A. pp. 1-40.

Lewis, G. P., Lyle, H. and Miller, S. 1969. Association between hepatic water soluble protein-bond cadmium levels and chronic bronchitis and/or emphysema. Lancet II, pp. 1330-1333.

Lindsay, W.L. and Norvell, W.A. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J., 42: 421-428.

Lisk, D. J. 1972. Trace metals in soils, plants and animals. Advan. Agron., 24: 267.

McBride, M. B. 2000. Chemisorption and precipitation reactions. In: Summer, M. E. (Ed.) Handbook of Soil Science. CRC Press, Boca Raton, Fl., pp. B265-B302.

McBride, M.B., Tyler, L.D. and Hovde, D.A. 1981. Cadmium adsorption by soils and uptake by plants as affected by soil chemical properties. Soil Sci. Soc. Am. J., 45: 739-744.

Nriagu, J. O. and Pacyna, J. M. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature, 333: 134-139.

Page, A. H. and Bingham, E. T. 1973. Cadmium residue in the environment. Residue Review, 98: 1-44.

Ramachandran, V. and D'Souza, T.J. 1999. Adsorption of cadmium by Indian soils. Water Air and Soil Pollut. 111: 225-234.

Rattan, R. K. and Sehgal, D. 1989. Investigations on cadmium adsorption on soils differing in physical and chemical characteristics. J. Indian Soc. Soil Sci., 37:2 84-289.

Schroeder, H. A. 1965. Cadmium as a factor in hypertension. J. of Chronic diseases, 18: 647-656.

Sharma, A., Srivastava, A., Bali Ram, Srivastava, P. C. and Singh, G. 2005. Effect of organic manure on adsorption-desorption of isoproturon herbicide in different soils. Pest. Res. J., 17(1):77-81.

Soon, Y.K. 1981. Solubility and sorption of cadmium in soils amended with sewage sludge. J. Soil Sci., 32: 85-95.

Sparks, D. L. 1996. Methods of Soil Analysis. Part 3, Chemical Methods. Soil Sci. Soc. Am. Inc. Am. Soc. Agron. Inc., Madison, Wisconsin, USA.

Swift, R. S. and McLaren, R. G. 1991. Micronutrient adsorption by soils and soil colloids. In: G. H. Bolt., M. F. De Boodt., M. H. B. Hayes, M. B. McBride (Eds.). Interactions at the Soil Colloid-Soil Solution Interface. pp. 257-292. Kluwer Academic Publishers, Drdrecht.

Tsuchiya, K. 1969. Causatiar of "Ouchi-Ouchi" disease. Rieo J. Med., 18: 181-194.

Yanai, J., Zhao, F. J., McGrath, S. P. and Kosaki, T. 2005. Cadmium uptake by the hyperaccumulator Thlaspi caerulescens on a range of contaminated soils. Environ. Pollu., 139: 167-175.

Zachara, J.M., Smith, S.C., Resch, C.T. and Cowan, C.E. 1992. Cadmium sorption to soil separates containing layer silicates and iron and aluminium oxides. Soil Sci. Soc. Am. J., 56: 1074-1084.