Annals of Plant and Soil Research 16(1): 15-20 (2014)

CADMIUM ADSORPTION BY VERTISOL AND INCEPTISOL IRRIGATED WITH TUBEWELL WATER AND SEWAGE EFFLUENT

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Received: September, 2013; Revised accepted: January, 2014

ABSTRACT

The present study was conducted to assess the adsorption of cadmium (Cd) in surface and subsurface samples of Vertisol and inceptisol of district Indore, Madhya Pradesh. Soil samples were collected from 0-15 and 15-30 cm depths and representing Sarol series of Vertisol (Typic Haplusterts) and Malikheri series of Inceptisol (Fluventic Ustochrepts) orders irrigating with tubewell and sewage effluents respectively. Soil samples (pH 7.3 to 8.0), were subjected to Cd treatment at various concentrations (0 to 90 mg L^{-1}) and equilibrated at temperature (25 ± 1°C). 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. Results indicated that the adsorption capacity of the soils for Cd was more in Vertisol representing Sarolseries (Typic Haplusterts) as compared to Inceptisol representing Malikheri series (Fluventic Ustochrepts) when irrigated with sewage effluents. Equilibrium concentration (mg L^{-1}) obtained in soil solution as influenced by Cd application increased with increased Cd levels but the lower values of it was observed in Sarol soil series as compared to Malikheri that ultimately reflected the higher adsorption of Cd (mg kg^{-1}) in Sarol series soils either irrigated with sewage effluents or tubewell water. Experimental soils used in this study followed Langmuir adsorption isotherms with highly significant positive correlations (0.981 to 0.996). Adsorption isotherms showed that Cd adsorption was linearly related to Cd concentration in the equilibrium solution. The adsorption maxima were higher in Sarol series soil irrigated with sewage effluents. The standard free energy ($\Delta G°$) data showed the lowest values in (S3) Sarol series soils irrigated with sewage effluents (-15.57 and -13.85) for long run. The data related to effect of Cd levels on the Cd distribution coefficient (Kd) showed higher values in 0-15 cm depth soil irrigated with sewage effluents of Sarol series (2490 L kg^{-1}) equilibrated with lower concentration of cadmium (2 mg L^{-1}). These values were decreased with increase in concentration of Cd levels in both the soils either irrigated with tubewell water or sewage effluents. The data on per cent adsorption of Cd (X_{Ad}) in experimental soils followed the same trend as obtained distribution coefficient. The adsorption data, in general, indicated that Cd adsorption was more in soils having higher CEC values and organic matter content. The results of the study further suggested that Langmuir isotherm equation was found to provide an excellent fit to the experimental data.

Key words: Adsorption, distribution coefficient, Inceptisols, Langmuir isotherm, Vertisols

INTRODUCTION

Among various toxic metals cadmium (Cd) plays an important role that contaminates plants and enters the food chain, thereby posing health problems to human beings. The behaviour of heavy metals present in sewage sludge and industrial wastes that are used in agricultural practices has been the center of much attention during the last decade. Since the soil works as an adsorbent, it adsorbs heavy metals from the soil solution. So, the process of Cd adsorption is mainly due to the force imbalance existing on the solid and liquid surfaces. The dynamic equilibrium of various heavy metals between soil constituents and the adsorbed phase depends on the pH, the chemical nature of the metal species, stability of metal complexes, the binding power of the functional groups and ionic strength. Cadmium is recognized as one of the mobile heavy metals circulating in the environment and can readily enter the human food chain, being more weakly bound to soil constituents compared to many other metals (Mench *et al*., 1994). It normally occurs in concentration of 0.08 to 0.50 mg kg^{-1} soil. Its adsorption in soil is strongly controlled by soil pH, clay minerals, Mn, Al, and Fe oxides and hydroxides and soil organic matter (Gray *et al*., 1999). The term adsorption is commonly used for the process of sorption of chemical elements from solutions at the surface of soil particles (Kabata-Pendias and Pendias, 1984). The adsorption of Cd from the soil solution by the solid soil particles is generally accompanied by the simultaneous desorption of equivalent amounts of other cations from the solid phase to the soil solution. This process is called ion exchange or equivalent adsorption. Cadmium adsorption can easily be understood by following the adsorption isotherm. It essentially expresses the relation between the concentrations of Cd adsorbed on to the soil at constant temperature. So, the present study was framed out to understand the mechanism of adsorption reaction in Vertisol and Inceptisol receiving sewage effluent and tube well water.

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MATERIALS AND METHODS

A laboratory study was conducted in the AICRP on Management of Salt Affected Soils & Use of Saline Water in Agriculture, Rajmata Vijayaraje Scindia Krishi Vishwa Vidyalaya, College of Agriculture, Indore Madhya Pradesh during 2009-10. The soil samples were collected from the four cultivated fields, irrigated with sewage effluent and tubewell waters from two depth 0-15 and 15-30 cm under two soil series *viz* Sarol (Vertisols) and Malikheri (Inceptisols). Tubewell water irrigated field in Sarol soil series is situated at 22° 47’ 70.9” N latitude, 75° 52’ 16.7” E longitude and sewage effluent irrigated field at 22° 46’ 18.9” N latitude, 75° 52’ 40.0” E longitudes. In Malikheri soil series tubewell water irrigated field is situated at 22° 47’ 19.2” N latitude, 75° 52’ 07.2” E longitude and sewage effluent irrigated field at 22° 45’ 21.4” N latitude, 75° 52’ 32.9” E longitude. These soil samples were processed for cadmium adsorption study. The data related to quality of irrigation water and experimental soils are presented in Table 1 and 2.

Table 1: Chemical characteristics of sewage effluent (SE) and tubewell water (TW)

Parameters	SE	TW
pH	7.4	7.3
EC (dSm^{-1})	1.82	1.10
SAR ($(mmol\ L^{-1})^{1/2}$)	3.6	1.5
Cd ($mg\ L^{-1}$)	0.073	0.002

EC – Electrical conductivity, SAR – Sodium adsorption ratio

Table 2: Initial physico-chemical properties of experimental soils

Parameters	**Tubewell Water Irrigated**				**Sewage Effluent Irrigated**			
Soil Series	**Sarol (Vertisol)**		**Malikheri (Inceptisol)**		**Sarol (Vertisol)**		**Malikheri (Inceptisol)**	
Soil Depth (cm)	0-15	15-30	0-15	15-30	0-15	15-30	0-15	15-30
Code	S1	S2	M1	M2	S3	S4	M3	M4
Cd ($mg\ kg^{-1}$)	0.146	0.096	0.140	0.072	0.450	0.386	0.272	0.192
pHs (1:2)	7.3	7.4	7.8	7.7	7.4	7.4	8.0	7.9
EC(dSm^{-1}) (1:2)	0.76	0.73	0.80	0.74	1.42	0.71	1.20	0.87
Org.Carbon ($g\ kg^{-1}$)	5.1	4.9	4.6	4.0	8.4	8.0	8.1	7.0
$CaCO_3$ ($g\ kg^{-1}$)	35	50	75	80	40	53	100	120
CEC [$cmol(p+)kg^{-1}$]	43.1	42.7	36.4	34.8	39.1	38.2	34.4	33.4
Sand %	22.0	19.9	21.9	20.9	30.0	28.2	18.4	17.3
Silt %	31.4	30.0	48.4	43.4	29.4	27.0	45.3	42.7
Clay %	46.6	50.1	39.6	38.6	40.6	44.8	36.3	40.0

The experiment was carried out in the laboratory by taking 40 ml of 0.01*M* $CaCl_2$ solution, containing each of 2, 5, 10, 15, 30, 45, 60, 75 & 90 mg Cd L^{-1} obtained by dissolving $CdCl_2.8H_2O$ (AR grade) and added to 4 g of soil on oven-dry basis in 50 ml polypropylene centrifuge tubes. These tubes were shaken on a reciprocating shaker for 2 hours and allowed to equilibrate at 25 ± 1°C for 24 hours in incubation chamber. The temperature was selected to be close to the yearly average soil temperature in the district (25°C). An equilibrium time of 24 hours was chosen for Cd adsorption as reported by Christensen (1984). Samples were centrifuged and the supernatant liquid was filtered and analyzed for Cd by Atomic Absorption Spectrophotometer using Perkin-Elmer Make (AAS-100). The Cd adsorbed was calculated as the difference between the amounts of Cd present in the solution initially and that remaining after equilibrium. The data was fitted in Langmuir’s adsorption isotherm.

The Langmuir adsorption equation is given by –

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{C}{b}$$

where,

C = Cd concentration of equilibrium soil solution (mg L^{-1}),

x/m = The amount of Cd adsorbed (mg kg^{-1} soil),

b = The adsorption maxima (mg Cd kg^{-1} soil) and

k = A constant related to the bonding energy of soil with Cd (mg L^{-1})

The adsorption maxima (b) and bounding energy (k) were calculated as inverse of the slope and slope/intercept, respectively of the Langmuir adsorption isotherm.

The percentage of the added Cd sorbed (xad) and distribution coefficient (Kd) were calculated. Distribution coefficient, which is related to the relative affinity of adsorbate for the adsorbent and solvent, is defined by Thakur *et al.* (2004) and Alloway (1995).

$$\text{Kd} = \frac{\text{Cd sorbed (mg kg}^{-1}\text{) of sorbent used}}{\text{Cd in solution (mg L}^{-1}\text{) at equilibrium}}$$

Where the equilibrium metal concentration adsorbed is given per unit weight of soil and the equilibrium metal concentration in solution per unit volume of liquid.

Thermodynamic parameter: The thermodynamic parameter as standard free energy (ΔG°) was determined using the following equation as given by Geetha *et al.* (2009).

$$\Delta G° = -2.303 \text{ RT } \log_{10}K$$

Where, R = Universal gas constant (KJ mol^{-1}), T = Absolute temperature (°K) and K = k × b (k and b are Langmuir constants obtained at 25°C temperature).

RESULTS AND DISCUSSION

Equilibrium concentration (C) as influenced by Cd levels

Equilibrium concentration (C) in the soil solution increased significantly with increasing Cd levels in the experimental soils of 0-15 and 15-30 cm depths (Table 3 & 4).

Table 3: Effect of Cd levels on the equilibrium concentration (C) in two soil series (0-15 cm depth soil)

Cd levels	Vertisol (Sarol)		Inceptisol (Malikheri)	
	TW (S1)	SE (S3)	TW (M1)	SE (M3)
		(mg L^{-1})		
2	0.074	0.008	0.194	0.136
5	0.208	0.048	0.512	0.364
10	0.499	0.168	1.125	0.800
15	0.910	0.397	1.829	1.357
30	2.221	1.218	4.076	3.092
45	4.055	2.579	6.851	5.486
60	6.617	4.607	10.390	8.417
75	9.991	7.656	14.566	12.286
90	14.400	11.396	20.303	18.006
CD (P=0.05)	0.0033	0.0033	0.0202	0.0048

The increasing trend was very less at lower levels (upto 15 mg L^{-1}) of Cd in both the soil series irrigated with TW or SE. The equilibrium concentration (C) at 0-15 cm depth soil samples was comparatively very low in S3 soil followed by S1, M3 and M1 soils. Similar trend of C was obtained in soils of 15-30 cm depth. The results clearly indicated that the soil irrigated with sewage effluents denoted less concentration of Cd in the equilibrium solution. The values of equilibrium concentration in soils of 15-30 cm depth were higher than surface soils of 0-15 cm depth either irrigated with TW or SE. This might be due to the lower per cent of organic carbon. The lower values of equilibrium concentration of Cd directly reflected the higher adsorption of Cd by the soil. Patel *et al.* (2004) also obtained high Cd concentration in soils irrigated with sewage effluents.

Table 4: Effect of Cd levels on the equilibrium concentration (C) in two soil series (15-30 cm depth soil)

Cd levels	Vertisol (Sarol)		Inceptisol (Malikheri)	
	TW (S2)	SE (S4)	TW (M2)	SE (M4)
		(mg L^{-1})		
2	0.121	0.052	0.236	0.167
5	0.317	0.144	0.614	0.451
10	0.705	0.374	1.324	0.995
15	1.232	0.713	2.150	1.654
30	2.823	1.832	4.672	3.711
45	4.975	3.504	7.396	6.329
60	7.825	5.846	10.983	9.581
75	10.787	8.999	15.488	13.763
90	16.182	13.186	21.207	18.832
CD (P=0.05)	0.0029	0.0045	0.0046	0.0034

Per cent adsorption (X_{Ad}) of Cd

A decreasing trend in X_{Ad} values was observed with increasing Cd levels in both the soil series either irrigated with TW or SE (Table 5).

Table 5: Effect of Cd levels on the per cent adsorption of Cd (X_{Ad}) in experimental soils

Cd (mg L^{-1})	Sarol (Vertisol)				Malikheri (Inceptisol)			
	TW (S1) (0-15)	TW (S2) (15-30)	SE (S3) (0-15)	SE (S4) (15-30)	TW (M1) (0-15)	TW (M2) (15-30)	SE (M3) (0-15)	SE (M4) (15-30)
2	96.28	93.93	99.60	97.40	90.28	88.20	93.22	91.67
5	95.83	93.65	99.03	97.11	89.77	87.72	92.72	90.97
10	95.01	92.95	98.32	96.26	88.75	86.76	92.00	90.05
15	93.93	91.78	97.35	95.25	87.81	85.67	90.95	88.97
30	92.60	90.59	95.94	93.89	86.41	84.43	89.69	87.63
45	90.99	88.94	94.27	92.21	84.77	83.56	87.81	85.93
60	88.97	86.96	92.32	90.26	82.68	81.70	85.97	84.03
75	86.68	85.62	89.79	88.00	80.58	79.35	83.62	81.65
90	84.00	82.02	87.34	85.35	77.44	76.44	79.99	79.08

In general, the X_{Ad} was more in the surface soils as compared to sub-surface soils. X_{Ad} values ranged from 96.28-84.00, 99.60-87.34, 90.28-77.44 and 93.22-79.99 per cent in S1, S3, M1 and M3 soils respectively with increasing Cd levels. Whereas, these values ranged from 93.93-82.02, 97.40-85.35, 88.20-76.44 and 91.67-79.08 per cent in S2, S4, M2 and M4 soils respectively. These data clearly indicated that at lower levels of Cd its adsorption was more in both the soil series under study irrigated with TW and SE. Kaur *et al*., (2004) also got 53.5 to 89.3 per cent Cd adsorption of the initially added cadmium. Correlation coefficient (r) was also worked out between X_{Ad} and different levels of Cd (Table 6). Cation exchange capacity (CEC), OC, clay and EC values were positively correlated with X_{Ad} values obtained from 2-90 mg Cd L^{-1}. Significant negative correlation coefficient was obtained between pH and X_{Ad} values. Calcium carbonate content of the soil also showed a negative correlation with X_{Ad}.

Table 6: Correlation coefficient (r) between different parameters of experimental soils and per cent adsorption of Cd (X_{Ad})

Parameter	**pH**	**EC**	**CEC**	**OC**	**$CaCO_3$**	**Clay**
$X_{Ad}2$	-0.667*	0.444	0.567	0.658	-0.651	0.400
$X_{Ad}5$	-0.681*	0.423	0.583	0.645	-0.667*	0.420
$X_{Ad}10$	-0.678*	0.430	0.586	0.647	-0.664	0.422
$X_{Ad}15$	-0.673*	0.436	0.578	0.651	-0.663	0.411
$X_{Ad}30$	-0.676*	0.433	0.585	0.648	-0.665	0.419
$X_{Ad}45$	-0.709*	0.421	0.597	0.624	-0.694*	0.427
$X_{Ad}60$	-0.701*	0.429	0.586	0.634	-0.684*	0.417
$X_{Ad}75$	-0.731*	0.385	0.641	0.593	-0.711*	0.489
$X_{Ad}90$	-0.741*	0.379	0.612	0.597	-0.704*	0.465

**Significant at the 0.05 probability levels*

Distribution coefficients (Kd)

The evaluation of the influence of Cd application on distribution coefficient (Kd) for the experimental soil was calculated and presented in Table 7.

Table 7: Effect of Cd levels on the Cd distribution coefficient (Kd) L kg^{-1} in experimental soils

Cd (mg L^{-1})	**Sarol (Vertisol)**				**Malikheri (Inceptisol)**			
	TW (S_1) (0-15)	**TW (S_2) (15-30)**	**SE (S_3) (0-15)**	**SE (S_4) (15-30)**	**TW (M_1) (0-15)**	**TW (M_2) (15-30)**	**SE (M_3) (0-15)**	**SE (M_4) (15-30)**
				L kg^{-1}				
2	259.0	154.8	2490.0	374.6	92.9	74.7	137.4	110.0
5	230.0	147.5	1024.4	336.4	87.7	71.4	127.3	100.7
10	190.5	131.7	584.0	257.3	78.8	65.5	115.0	90.5
15	154.8	111.7	367.8	200.3	72.0	59.7	100.5	80.6
30	125.0	96.2	236.2	153.7	63.6	54.2	87.0	70.8
45	100.9	80.4	164.5	118.4	55.6	50.8	72.0	61.1
60	80.6	66.6	120.2	92.6	47.7	44.6	61.2	52.6
75	65.0	59.5	87.9	73.3	41.4	38.4	51.0	44.4
90	52.5	45.6	68.9	58.2	34.3	32.4	39.9	37.7

Distribution coefficient (Kd) represents the adsorption affinity of metal cation in solution for the soil solid phase and can be used as valuable tool to study metal cation mobility and retention in soil systems. According to Anderson and Christensen (1988) high values of Kd indicate that metal has been retained by solid phase through sorption reactions while low values of Kd indicate that large fraction of the metal remain in solution. The data clearly show that Kd values increases with increase in Cd levels. The higher values of Kd were obtained in Sarol series soils irrigated with SE of 0-15 cm depth as compared to Maliheri soil series. The values of Kd ranged from 52.50-259.06, 68.98-2490.00, 34.33-92.92 and 39.98-137.42 L kg^{-1} in S1, S3, M1 and M3 soil respectively in 90 to 2 mg L^{-1} Cd application. Similar type of decreasing pattern was also obtained in sub-surface soil (15-30 cm) of the same series. Christensen (1989) also obtained the Kd values in the range of 15-2455 L kg^{-1}, whereas, Usman (2008) obtained Kd values in the range of 0.04-45 L kg^{-1}. Correlation coefficient (r) between Kd values of 2-90 mg L^{-1} Cd levels (Kd_2 to Kd_{90}) and soil parameters was also worked out (Table 8). The adsorption affinity of Cd represented by the Kd_2 to Kd_{45} was influenced mainly by EC and Kd_{10} to Kd_{90} by OC as shows by the positively significant correlated between these variables. Results indicated that parameters like CEC of soil were positively correlated with Kd. The Kd values of Cd was negatively correlated to pH and $CaCO_3$ from Kd_2 to $Kd_{90.}$ Clay content of soil was negatively correlated with Kd_2 to Kd_{10} and positively correlated with kd_{15} to Kd_{90} values of Cd. At lower level up to 10 mg L^{-1} Cd also showed negative correlation of Kd with clay content of soil. Christensen (1989) also obtained a significant positive correlation (r = 0.79) between Kd and organic matter content of the soil.

Table 8: Correlation coefficient (r) between different parameters of experimental soils and distribution coefficient (Kd)

Parameter	pH	EC	CEC	OC	$CaCO_3$	Clay
Kd_2	-0.376	0.787*	0.192	0.543	-0.444	-0.081
Kd_5	-0.416	0.784*	0.232	0.637	-0.484	-0.043
Kd_{10}	-0.446	0.769*	0.272	0.682*	-0.512	-0.001
Kd_{15}	-0.470	0.742*	0.305	0.713*	-0.532	0.038
Kd_{30}	-0.488	0.709*	0.344	0.740*	-0.547	0.085
Kd_{45}	-0.502	0.682*	0.371	0.742*	-0.559	0.115
Kd_{60}	-0.506	0.662	0.384	0.750*	-0.558	0.137
Kd_{75}	-0.547	0.601	0.460	0.725*	-0.591	0.236
Kd_{90}	-0.512	0.622	0.412	0.756*	-0.555	0.182

** Significant at the 0.05 probability*

Standard free energy (ΔG°) as influenced by Cd application

Free energy (ΔG°) is an important thermodynamic quantity that helps in predicting the spontaneity of a process. The free energy of a system is a measure of its capacity to do useful work. The free energy (ΔG°) of experimental soils under study was calculated by taking different parameters of thermodynamic as influenced by Cd application at 25°C (Table 9). Both the experimental soils *i.e.* Sarol and Malikheri series either irrigated with SE or TW water showed negative values of free energy due to Cd application. Thermodynamic parameters revealed that Cd adsorption increased as the value of (ΔG°) increased at a particular temperature. It ranged from -12.24 to -15.57 for Sarol soils and -10.57 to -11.95 KJ mol^{-1} for Malikheri soils. The soils irrigated with SE (S3 and M3) depicted higher values of ΔG°. Similarly higher ΔG° was also obtained by Deka *et al.*, (1997), and Adhikari and Singh (2003). The negative values of ΔG° for Cd indicated that the reaction is spontaneous. Such negative values in 25°C temperature under study suggest that the adsorption is more spontaneous. On the basis of thermodynamic parameters obtained by the study it can be concluded that Cd adsorption reaction was exothermic in the experimental soils.

Table 9: Standard free energy (ΔG°) of the thermodynamic parameter of experimental soil as influenced by Cd application at 25°C

Parameter	S1	S2	S3	S4	M1	M2	M3	M4
b	970.1	1073.1	836.7	926.0	1139.1	1270.7	1043.7	1117.3
k	0.209	0.130	0.642	0.289	0.076	0.056	0.119	0.088
K	202.4	139.7	537.4	267.4	86.4	71.2	124.6	98.66
ΔG°	-13.16	-12.24	-15.57	-13.85	-11.05	-10.57	-11.95	-11.37

ΔG°-Standard Free Energy (KJ mol^{-1})

On the basis of study, it may be concluded that Cd adsorption was more in Vertisol (Sarol series soil) as compared to Inceptisol (Malikheri soil series). On the other hand sewage effluents irrigated soils depicted more Cd adsorption as compared to tube well irrigated soils of the study area.

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