SORPTION AND RELEASE OF CADMIUM-FULVIC ACID COMPLEXES IN SLUDGE TREATED SOILS

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Abstract
A batch experiment was conducted with ten sludge treated soils wherein soils were equilibrated with various amounts of ^{115}Cd tagged Cd–fulvic acid (FA) for time intervals upto 72 h. The equilibrium models, including the Langmuir, two-surface Langmuir and Freundlich models and kinetic models including irreversible zero, first, second, two rate constant equation, second approximate and Elovich models, were evaluated for their ability to describe the retention of Cd–FA in sludge treated soils. The relationship between the amount of Cd–FA retained by soil and the concentration of Cd–FA in soil solution was described by either two-surface Langmuir or Freundlich models. The maximum sorption capacity of Cd–FA in soils at two sites of reaction obtained from the two-surface Langmuir adsorption isotherm equation was found to be positively correlated with the organic matter content and cation exchange capacity of the soils. In general, none of the equations describing the order of reaction could explain the data over the entire time and concentration ranges studied. The Elovich equation provided the best fit of the data indicating, thereby, that the sorption of Cd–FA might be due to complex reactions involving more than one site of reaction with different rates and energetics. The desorption of Cd–FA sequentially through $0.5 M$ $Ca(NO_3)_2$ and $0.005 M$ KCl showed that a significant fraction of the Cd–FA complex retained by the soil was released to the solution but that some irreversible retention of Cd–FA occurred. The possible mechanisms of retention of Cd–FA in soils are discussed. © 1998 Elsevier Science Ltd. All rights reserved.

Key words: metal-complexes, sludge, sorption, soil pollution.

INTRODUCTION

The fate of the heavy metals added to the soils through disposal of city or industrial wastes depends

upon the equilibria governing their solubility, persistence in the soil solution and ease of their release into the soil solution if they are temporarily inactivated by the solid matrices of the soil or by sludge. The process of metal retention by the solid matrices of the soil may include ion exchange, adsorption and precipitation. All these reaction mechanisms have been defined by fitting the data into the various equilibrium and kinetic models. The reaction of organically complexed metal cation, in all probability, may be different from those of inorganic ions because of the facts that the complexation of metal cations by naturally occurring humic substances neutralizes the positive charges of the cations and the size of the ion becomes enlarged on complexation. The interaction of humic substances and metal complexes with inorganic matrices of soils has been studied by various workers (Greenland, 1965; Theng, 1979; Pandeya, 1991). The process of metal complex retention by soils has been demonstrated by them through retention by physical forces, ion exchange and clay–metal–humus bridging by metal cations. The data on reaction of metal complexes with naturally occurring humic substances is still very limited though, such information is vital in understanding the behaviour of sludge borne heavy metal cations in soils. The present study aimed at describing the retention and release of organically complexed Cd in soils.

METHODS

Ten bulk surface soil samples (0–15 cm) of old alluvium non-calcareous non-saline (Vertisol) of Patna (India) which had received sewage effluent for > 100 years were collected for the studies. The ten sampling sites were located in the sewage sludge disposal area starting from point of discharge of the effluents to a distance of nearly 3 km away from it.

The organic matter content of the soils was estimated by the rapid titration method of Walkley and Black as described by Jackson (1978) and the

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pH and electrical conductivity (EC) were determined in 1:2 soil water ratio. The International Pipette method (Piper, 1966) was adopted for the analysis of the textural class of soils. The properties of the soils are presented in Table 1. The variation in the organic matter content of the soil was primarily due to variation in the amount of wastes they received and the distance from the point of discharge of the effluents. As, the land from where the samples were collected remained submerged for 3–4 months in a year, the variation in the texture was primarily due to the deposition of the washings it received during flooding. The Cd in aqueous extracts of the soils was below detection limits. The diethylene triamine penta acetic acid (DTPA) extractable Cd was in the range of $0\cdot027$–$0\cdot189$ mg kg^{-1}. Total Cd in these soils, however, did not vary much and was found to be around $1\cdot0$ mg kg^{-1}. The humic matter of the soils was, by and large, insoluble in water. The fulvic acid (FA) component of humus, therefore, was below detection limits in the water extract of the soils.

Cd–FA complex

Fulvic acid was extracted from the city sludge of Patna sewage treatment plant by the modified fractionation procedure of Kononova (1966) and purified by the modified procedure of Forsyth (1947) as adopted by Pandeya (1992). The properties of FA are presented in Table 2. In absence of reliable data on the molecular weight of FA, an approximation of the molarity of FA was made from

the threshold value for flocculation of Fe–fulvate on titration of FA by FeCl$_3$. The method described by Pandeya (1991) and Pandeya (1993) was followed.

Equimolar concentrated solutions of FA adjusted to pH $7\cdot0$ and CdCl$_2$ were mixed thoroughly. The carrier free ^{115}Cd isotope in the form of cadmium chloride in $0\cdot05$ M HCl was added to the Cd–FA stock solution to give an approximate sp. act. of ^{115}Cd of $0\cdot25$. The stock solution of ^{115}Cd tagged Cd–FA was stored in amber coloured bottles at $0°$C. The stock solution of Cd–FA was diluted to provide working solutions having a range of cadmium concentration from 1 to 80 mg l^{-1}. The sorption study was carried out in a batch experiment with 4 g of soil in 40 ml of Cd–FA solution in centrifuge tubes. All samples were shaken for 1, 3, 6, 12, 24, 48 and 72 h and at every time interval, the samples were centrifuged for 10 min at 2000 rpm in a centrifuge with diameter of 30 cm. Two millilitre aliquots were taken out at each time interval for measuring the activity of Cd in solution by a gamma ray spectrometer with a well type scintillation head. The pH of the equilibrium soil solutions were measured and remained in the range of $7\cdot3$–$7\cdot9$ during equilibration. The desorption of Cd from soils was by equilibrating the soils sequentially with $0\cdot5$ M Ca(NO$_3$)$_2$ and $0\cdot005$ M KCl taking the samples used for sorption study. At the end of the equilibration period of sorption study supernatant liquid was decanted from each centrifuge tube and 20 ml of Ca(NO$_3$)$_2$ solution was added. It was shaken for 1 h. Two millilitres of the aliquot was taken out from the

Table 1. Physical and chemical properties of soils used for the various studies

Soil No.	pH	EC dSm^{-1}	Organic carbon (%)	CEC (cmol kg^{-1})	DTPA extractable Cd (mg kg^{-1})	Sand (%)	Silt (%)	Clay (%)	Textural class
1	7·46	1·75	2·50	23·60	0·189	52·01	28·70	8·60	SL
2	7·69	1·80	2·22	20·80	0·135	55·25	34·11	9·20	SL
3	7·77	2·00	2·13	19·65	0·078	54·93	34·20	9·40	SL
4	7·28	2·05	1·92	19·90	0·118	36·69	49·30	12·40	ZL
5	7·58	1·85	1·80	18·05	0·027	44·60	40·80	12·80	ZL
6	7·74	1·85	1·74	16·26	0·034	55·80	22·40	14·00	SL
7	7·90	1·95	1·61	14·30	0·076	34·68	45·00	18·40	ZL
8	7·87	1·92	1·47	14·01	0·064	38·16	40·50	19·21	ZL
9	7·92	1·90	1·44	10·95	0·056	23·98	52·00	21·80	ZL
10	7·35	1·75	1·32	7·70	0·032	22·20	50·00	25·30	ZL

SL, Sandy loam, ZL, Silty loam.

Table 2. The elemental composition and properties of fulvic acid extracted from sludge

Ash content (%)	E_4/E_6* (%)	Elemental compositions (%)				Acidic functional groups (m-equiv/100 g)**		
		C	H	N	O	Carboxyl groups	Phenolic −OH	Total acidity
1·00	10·41	30·03	6·18	5·58	58·21	359	189	548

*E_4/E_6 indicates the ratio of optical densities of fulvic acid at 465 and 665 nm wavelengths. This has been reckoned as the measure of aromocity and structural condensation due to humification (Kononova, 1966).
**Measured by potentiometric titration method (Pandeya, 1991).

tube after centrifugation and used for measuring [115]Cd activity. The solution from the centrifuge tube was decanted and 20 ml of KCl solution was added and vortex mixed on a shaker for 24 h. At the end, the content of the centrifuge tube were centrifuged, 2 ml of aliquot withdrawn, the rest decanted and another 20 ml of KCl was added. The equilibration processes with KCl was repeated thrice.

Calculations and Data analysis

The concentrations of Cd in the sample solution were calculated at each sampling time using the following equation:

$$C = C_0 \left[\frac{(A - Bkg)}{(A_0 - Bkg)} \right] \tag{1}$$

where C is the concentration of metal in solution at time of sampling (mg l^{-1}), C_0 is the concentration of metal in solution before reaction with soil (mg l^{-1}), A is the activity of radionuclide in solution at time of sampling (cpm), A_0 is the activity of radionuclide in solution before reaction with the soil (cpm) and Bkg is the background activity (cpm).

For the retention part of the study, the amount of metal retained by the soil at the first sampling time was calculated by the following equation:

$$S' = \frac{(C_0 - C)V}{W} \tag{2}$$

where S' is the amount of metal retained by the soil (mg kg^{-1}); V is the initial total solution volume (l) and W is the weight of soil (kg).

The necessary corrections were made to take care of the amount metal lost due to removal of the small volume of solution at each sampling for counting.

In the release and exchange part of the study where the soil solution was sampled with time, the amount of metal retained by the soil was calculated by using the following equation:

$$S = \left[\frac{C(V' + V) - C'V')}{W} \right] \tag{3}$$

where S is the amount of metal extracted from soil (mg kg^{-1}), C is the concentration of metal in extract solution (mg l^{-1}), C' is the concentration of metal in solution at last sampling time in release part of experiment (mg l^{-1}), V' is the volume of entrained soil solution at the end of the release experiment (l) and V is the volume of extracting solution (l).The equilibrium and kinetic models tested for the fit of data are reported in Table 3.

RESULTS AND DISCUSSION

Sorption isotherm of Cd–FA in soils

The sorption isotherms were developed from the data on equilibrium concentration of Cd–FA in soils and the amount of Cd–FA retained by the soils. The isotherm curves obtained from all ten soils at different periods of incubation (results not shown) were of similar nature. This suggest that similar mechanisms for Cd–FA retention were operative in all the soils under study. The equilibrium concentration of Cd was observed to be dependent upon the levels of Cd–FA complex application, the period of incubation and nature of the soils. The metal retention reactions appeared to approach quasi equilibrium at *ca* 72 h of equilibration. The experimental data were tried for fit into different adsorption isotherm models (Table 3). The values of coefficient of determination of the fit of the equations at 72 h of equilibration are presented in Table 4. The linear and Langmuir models did not fit the data for the concentration range studied and periods of incubation. The experimental data on Cd–FA retention for all the ten soils showed a good fit to the Freundlich equation (representative plots in Fig. 1, other lines

Table 3. Equilibrium and kinetic models employed in the studies

Equilibrium models	Equations
Linear	$S = KdC$
Langmuir	$\dfrac{C}{S} = \dfrac{1}{Kb} + Cb$
Two surface Langmuir	$S = \dfrac{K_1 b_1 C}{1 + K_1 C} + \dfrac{K_2 b_2 C}{1 + K_2 C}$
Freundlich	$\log S = \log K + \dfrac{1}{n} \log C$

Kinetic	Integrated form
Zero order	$C_t = C_0 - Kt$
First order	$\ln C_t = \ln C_0 - Kt$
Second order	$\dfrac{1}{C_t} = \dfrac{1}{C_0} + Kt$
Two rate constant equation	$\ln C_t = \ln K + \left(\dfrac{1}{m}\right)\ln t$
Second approximate	$\ln(C_0 - C_t) = \ln C_0 - Kt$
Elovich equation	$(C_0 - C_t) = \dfrac{1}{\beta} \ln(\alpha\beta) + \dfrac{1}{\beta} \ln t$

S, Concentration of metal retained by soil (mg kg^{-1}).
C, Concentration of metal in solution (mg l^{-1}).
C_t, Concentration of metal ions after time t (mg l^{-1}).
C_0, Concentration of metal in solution before reaction with soil (mg l^{-1}).
Kd, K_1, K_2, b, b_1 and b_2 are curve fitting parameters for equilibrium models.
α, β and K are rate coefficients for kinetic models.
t, Time.

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Table 4. Coefficient of fit of data on sorption of Cd–FA in soils at 72 h of equilibration in different models

Soil No.	Linear	Freundlich	Langmuir
1	0·706	0·959	0·743
2	0·829	0·909	0·064
3	0·802	0·978	0·796
4	0·807	0·990	0·640
5	0·805	0·989	0·038
6	0·806	0·969	0·230
7	0·704	0·974	0·342
8	0·684	0·991	0·318
9	0·793	0·990	0·378
10	0·763	0·962	0·303

were within the limits of these lines). In the Freundlich adsorption isotherm, the log–log nature of the plots often leads to an apparent good fit or, the flexibility of two constants allows for easy curve fitting. The limitations are that it is valid for a narrow range of concentrations and the maximum sorption capacity cannot be determined. The Freundlich equation parameters after 72 h of reaction between the metal and soils are summarized in Table 5. The fact that the Freundlich equation fitted

Fig. 1. Freundlich adsorption isotherm plots of Cd–FA in soil No. 3.

the retention data at all times might have been the result of an almost instantaneous reversible reaction between the metal fulvate and soils, even though the overall retention reaction was not at equilibrium. This is why studies by earlier workers like O'Connor *et al.* (1983), on adsorption of heavy metals by sludge-treated soils were confined to only 2–4 h of equilibration. The fast reaction rate at initial periods of incubation is evident from Fig. 3. The Freundlich equations thus, fits the data at all equilibration times. The reaction is too fast to observe and only its result is seen. Evidence for such a reaction has been provided by Harter (1984).

The relationship between the amount of organically complexed metal retained by the soil and the concentration of metal in solution was also described by the two-surface Langmuir models for all the ten soils and at all intervals of time. Initial estimates of the four two-surface Langmuir parameters, K_1, K_2, b_1 and b_2 were obtained by using the method of Sposito (1982). A computer programme for Gaussian non-linear regression procedure was used for the fitting of the curve for the two-surface Langmuir equation to the data. The test of goodness of fit of the data in the two surface Langmuir adsorption isotherm equation was done by plotting the data on the actual amount of Cd–FA sorbed and those, predicted by the equation (Fig. 2). The coefficient of determination for the fit of the data in the equation for all the ten soils were statistically significant at 99% level of confidence and the standard errors of estimates were low (0·05–0·053). This indicated that the data on retention of Cd–FA in soils conform to the two surface Langmuir adsorption isotherm equation.

The parameters of the two surface Langmuir equation are given in Table 6. The values of b_1 and b_2 provided the maximum sorption capacity of two reaction sites and ranged from 453 to 5840 and 392 to 5504 mg kg^{-1}, respectively. The two surface Langmuir parameters are best regarded as curve fitting parameters unless independent evidence is available to prove that two types of reaction sites actually exist (Veith and Sposito, 1977; Sposito, 1984). The b_1 and b_2 parameters of the two surface Langmuir equation for Cd–FA retention were positively and significantly correlated with organic

Table 5. Freundlich model parameters for Cd after reaction with soils for 72 h

Soil No.	Log K	1/n	Regression equation	R^2
1	109·99	0·724	$\log S = 109·99 + 0·724 \log C$	0·954
2	38·38	1·050	$\log S = 38·38 + 1·050 \log C$	0·909
3	151·45	0·725	$\log S = 151·45 + 0·725 \log C$	0·978
4	154·03	0·749	$\log S = 154·03 + 0·749 \log C$	0·990
5	69·14	1·030	$\log S = 69·14 + 1·030 \log C$	0·989
6	59·51	1·020	$\log S = 59·51 + 1·020 \log C$	0·969
7	52·57	0·957	$\log S = 52·57 + 0·957 \log C$	0·974
8	53·71	0·862	$\log S = 53·71 + 0·862 \log C$	0·991
9	39·23	0·981	$\log S = 39·23 + 0·981 \log C$	0·990
10	32·74	0·972	$\log S = 32·74 + 0·972 \log C$	0·963

Fig. 3. Representative plot of change in Cd–FA concentration in equilibrium solution as a function of time.
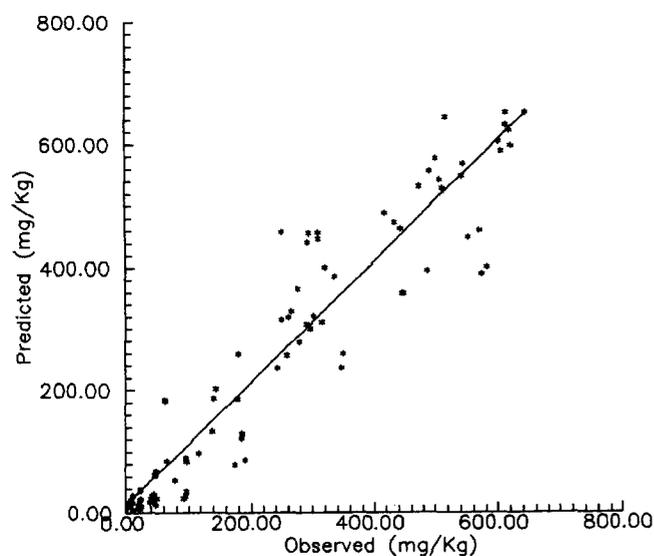
Fig. 2. Scatter diagram for the observed and predicted values of the amount of Cd–FA retained by the soils.

carbon content ($r = 0.857**$ and $r = 0.905**$) and with CEC of the soils ($r = 0.677*$, and $r = 0.837**$), respectively. The contribution of soil properties to the variation of maximum sorption capacity of Cd at two reaction sites b_1 and b_2 could be described by the following step-down multiple regression equations.

$b_1 = -1070.95 - 3.46$ pH $- 3.61$ EC $+ 4.75$ O.C.

$\quad + 4.31$ CEC $+ 4.18$ clay; ($R^2 = 0.936**$,

$\quad$ adj. $R^2 = 0.856**$)

$b_1 = -13831.44 - 3.73$ EC $+ 4.83*$ O.C. $+ 4.49$ CEC

$\quad + 4.35*$ clay; ($R^2 = 0.934**$, adj. $R^2 = 0.882**$)

$b_1 = -23121.57 + 6.73**$ O.C. $+ 3.44$ CEC

$\quad + 4.73*$ clay; ($R^2 = 0.907**$, adj. $R^2 = 0.860**$)

$b_2 = -13761.79 - 1.54$ pH $- 3.13$ EC $+ 9.06**$ O.C.

$\quad - 3.33$ CEC $+ 2.01$ clay; ($R^2 = 0.954**$,

$\quad$ adj. $R^2 = 0.896**$)

$b_2 = -7476.30 + 7.53**$ O.C. $- 2.39$ CEC $- 3.06$ clay;

$\quad$ ($R^2 = 0.936**$, adj. $R^2 = 0.904**$)

$b_2 = -7584.62 + 7.54**$ O.C. $- 2.36$ CEC;

$\quad$ ($R^2 = 0.936**$, adj. $R^2 = 0.918**$)

Nearly 93% of the variation in sorbed Cd at reaction sites (b_1) could be accounted by the combined effect of EC, organic carbon, CEC and clay content of the soils. The positive and high values of organic carbon followed by CEC in the equation emphasizes the dominant factors affecting the Cd retention in these soils. These two factors related to the extent of 93.6% to the variation in maximum sorbed Cd at other reaction sites (b_2). This indicates that organic carbon and CEC of the soils were the most effective factors influencing sorption capacity of Cd in these soils. The humic substances and clay fraction of the soils probably provided sites for retention of organically complexed Cd and the retention may predominantly have been due to ion exchange. The values of K_1 and K_2, which may be regarded as the bonding energy constants of

Table 6. Two-surface Langmuir parameters for Cd–FA after reaction with soils for 72 h

Soil No.	K_1 ($l\ mg^{-1}$)	b_1 ($mg\ kg^{-1}$)	K_2 ($l\ mg^{-1}$)	b_2 ($mg\ kg^{-1}$)	$b_1 + b_2$ ($mg\ kg^{-1}$)
1	0.008	5840.14	0.009	5504.17	11344.31
2	0.065	4155.96	0.026	4337.06	8493.02
3	2.692	1444.04	0.106	4192.54	5636.58
4	0.008	2699.45	0.007	2787.08	5486.53
5	0.027	1063.38	0.028	984.86	2047.84
6	0.063	1503.08	0.054	1669.14	3172.22
7	0.075	690.90	0.085	469.04	1159.94
8	0.108	604.16	0.110	462.50	1066.50
9	0.049	857.70	0.045	1276.89	2134.59
10	0.060	453.18	0.062	392.05	845.23

two reaction sites were, however, not related to soil properties.

Continued application of sewage sludge in the soils leads to enrichment of soils in organic carbon even though the tropical climate facilitates mineralization of organic carbon at very fast rates. The disposal of organic wastes, containing toxic heavy metals including cadmium may, therefore, result in further enrichment of cadmium in soils. As the organically complexed metal cations are held up by the solid matrices of the soils through ion bridging between the negatively charged clays and humic substances their persistence in the soil is high (Pandeya, 1991).

Kinetics of reaction of Cd–FA complexes in soils

A plot of change in Cd–FA concentration in the soil solution at various periods of reaction (Fig. 3) indicated a rapid loss of the metal complex in the initial stages of the reaction followed by a slow rate of loss, as time of reaction was increased. This suggested that: the reaction order might not be unity, the reaction might have been reversible; diffusion within the soil particles might have been a rate-limiting step and more than one reaction mechanisms might have been involved (Amacher et al., 1986).

Among the several kinetic equations tested to describe ability to fit the retention data, no single order of reaction could explain data over the entire time and concentration ranges studied for any of the soils. This indicates that the reaction might have been complex involving a number of reaction sites and mechanisms operating simultaneously as observed by Lahav and Hochberg (1975) and Dyanand and Sinha (1979). The first- and second-order models assume that the concentration of the reaction sites on the soil surface does not change significantly during the reaction. This may be true if the concentration of reaction sites is substantially greater than that of the metal in solution. The decrease in the rate of the reaction with time that was observed, suggests that the reaction was approaching equilibrium after longer times of reaction. Aringhieri et al. (1985) used a reversible second-order kinetic model in an attempt to describe the retention of Cu and Cd in soils. They attributed the failure of this model to fit their data to diffusion within the soil particles limiting the rate of reaction. A similar situation during the present studies may be suggested as the reason for failure of conformation of the present data to simple order of reactions.

The Elovich equation adequately described the kinetic data for retention of Cd–FA in the soils under study with statistically significant values of the coefficient of determination (R^2) ranging between 0·795* and 0·994**. A typical representative plot of data on the basis of the Elovich equation is depicted in Fig. 4. The equation has earlier been used by
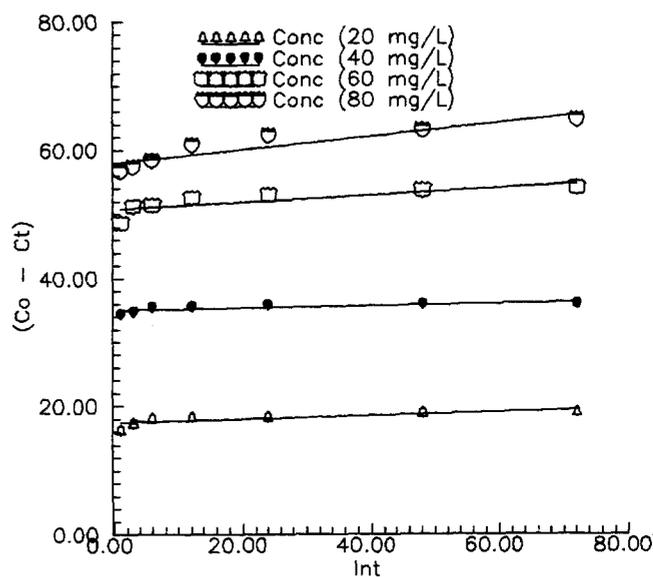
Fig. 4. Plots for kinetics of retention of Cd–FA in soil No. 3 as per Elovich equation.

Chien et al. (1980) to describe complex reactions involving more than one simultaneous reaction having different rates. The values of the rate constants of the reaction (α and β) are presented in Table 7. According to the assumptions of the Elovich equation, one of the two rate constant (α) may be regarded as the rate of an instantaneous rapid reaction not governed by exponential law. The higher the value of α is the faster the reaction will be. The instantaneous fast reaction may be assumed to have taken place due to the interaction of the Cd–FA molecules on the surface of the soil particles. The other rate constant (β), provides the rate of the exponential first-order reaction that took place simultaneously but extended over a period of time. A low value of β is indicative of a higher rate of reaction.

Desorption of Cd from soils

The heavy metals added through manure and wastes undergo various chemical process leading to redistribution of ionic species of metal cations in various chemical pools with distinctly different solubility

Table 7. Kinetic parameters of the reaction of Cd–FA in soils as calculated from Elovich equation rate constants

Soil No.	ln α (mol min^{-1})	β (mol^{-1})
1	15·28	0·99
2	18·83	1·49
3	25·28	1·90
4	21·66	1·49
5	14·29	1·01
6	38·04	2·23
7	12·88	1·11
8	28·10	1·72
9	28·61	2·13
10	24·76	1·69

(Sims and Patrick, 1978; Sposito *et al.*, 1982). The data on release of Cd–FA by the extractants from soil No. 9 is presented in Fig. 5. Though the values are not presented here, the amount of Cd desorbed by these two extractants from different soils at the same levels of concentration of added cadmium differed widely. The total amounts of Cd–FA recovered from nine out of ten soils through release and extraction were not equal to the amount of metal retained by the soils. It might have been possible that precipitation of added cadmium into sparingly soluble compounds occurred in most of the soils which could not be extracted by either $Ca(NO_3)_2$ or KCl. The precipitation of cadmium might have resulted because of displacement of Cd^{2+} from the FA ligand by competing cations present in the soil solution and subsequent reaction with OH^- and CO_3^{2-}.

Reaction model

If the reaction of the complexed Cd species with soils conformed to the two-surface Langmuir adsorption isotherm equation and kinetic Elovich equation, it suggests that the reaction was complex in nature. As in assumptions of the two models, the reaction might have involved more than one site of reaction with distinctly different energetics and rates. Similarly, sequential extraction of adsorbed Cd species on soils by $Ca(NO_3)_2$ and KCl revealed that the reaction involves two distinct sites with dissimilar

energy for sorption. Failure to recover all the Cd sorbed on the soils by these two reagents in nine out of ten soils might possibly have been due to precipitation as sparingly soluble compounds. Thus, the situation can be explained on the basis of the diagrammatic model presented in Fig. 6. The metal complexes added to the soil may meet simultaneously more than one of the following situations:

1. the organically complexed molecule may get sorbed on the non-specific (S_1) or specific (S_2) sites of the soils (Greenland, 1965; Parfit *et al.*, 1977). The data on the two-surface Langmuir adsorption isotherm and kinetic Elovich model provided evidence for such effects.
2. It may co-precipitate as metal-chelate–Cd compounds (Lahav and Hochberg, 1975).
3. Competing metal cations may replace Cd from the ligand and be precipitated as hydroxides and carbonates (Dyanand and Sinha, 1979, 1980). The data on desorption of cadmium species indicates such a possibility.

The reaction in situation (1) may be considered to be reversible as in the results but situations (2) and (3) may not be truly reversible processes. Thus, on consideration of the multi-site reaction models of Selim *et al.* (1976), Cameron and Klute (1977) and Amacher *et al.* (1986), a multi-site reaction model of the following forms may explain the reaction of Cd–FA in soils.
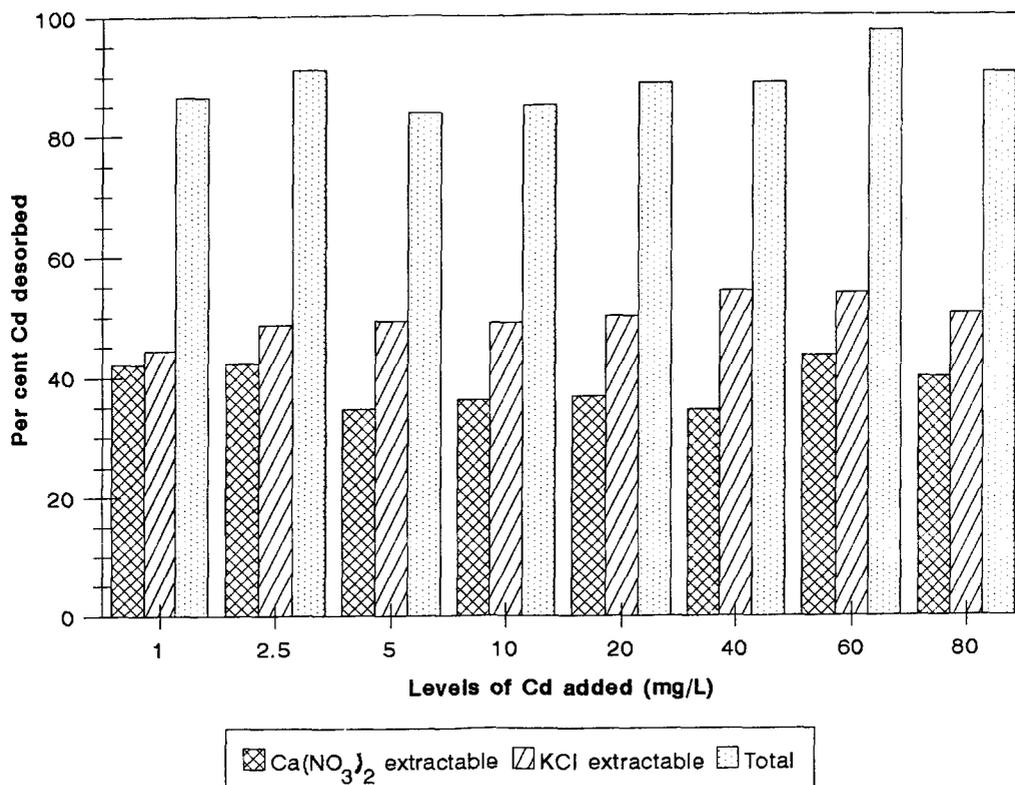
Fig. 5. Desorption of Cd by $Ca(NO_3)_2$ and KCl from Cd–FA treated in soil No. 9.
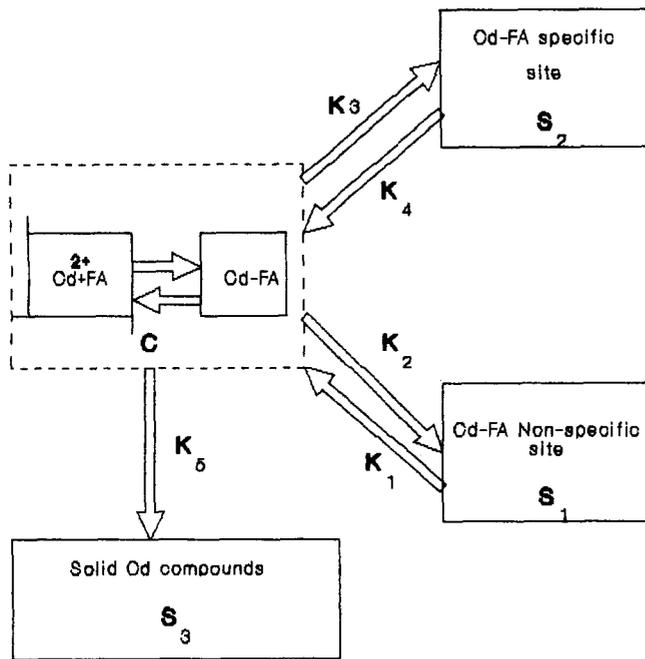
Fig. 6. Diagrammatic representation of the reactions controlling retention of Cd–FA in soils.

$$\left(\frac{\delta S}{\delta t}\right) = \left(\frac{\delta S_1}{\delta t}\right) + \left(\frac{\delta S_2}{\delta t}\right) + \left(\frac{\delta S_3}{\delta t}\right) \qquad (4)$$

where, S_1, S_2 and S_3 represent the concentration of metal-complexes retained by the soil for three different reactions. The displacement of metal cation from the ligand, and sorption of inorganic Cd species by soils independently has not been considered separately in the equation, because the independent identity of complexed Cd in soil solution in the absence of Cd^{2+} is not possible and quantification of Cd^{2+} and Cd–FA separately, is impracticable. Thus, simplification of the equation yields:

$$\left(\frac{\delta S}{\delta t}\right) = k_1C - k_2S_1 + k_3C - k_4S_2 + k_5S_3 \qquad (5)$$

The analytical or numerical solution to this model has not been attempted in the present investigation. The hypothesis, however, has indirect evidences in the present investigation and thus, needs to be verified in future research. Even if the data on reaction of Cd–FA in soils obey such a model, this does not prove that the model is correct, since different processes or mechanisms can produce the same observed results. Nevertheless, a model which can fit all the data over the entire time and concentration ranges for all the soils and a metal complex of interest would have a considerable value.

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