

Differential response of clay-organic complex and organic-free clay isolated from mulberry growing brown forest soils towards phosphorus adsorption

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ABSTRACT

Clay-organic complexes (COC) and organic-free clays (OFC) have been isolated from different locations under mulberry growing brown forest soils of Kalimpong. Homo-ionic suspension of isolated COC and OFC has been equilibrated with graded concentrations of phosphorus (P) at $300 \pm 1^{\circ}$ K to study the adsorption pattern of the latter. The P adsorption data obtained for both the COC and OFC have been significantly fitted to Freundlich adsorption isotherm ($R^2 = 0.60^*$ to 0.93^{**}) while Langmuir adsorption isotherm is mostly fitted to the adsorption data pertaining to OFC ($R^2 = 0.82^*$ to 0.99^{**}). OFC registers higher strength of adsorption (K) and affinity of adsorbate to adsorbent (n) over COC in terms of Freundlich isotherm and thus confirms the positive effect of organic matter in association with clay towards the reduction of P fixation. Poor fit of Langmuir isotherm to the P adsorption data by COC corroborates the above finding. However, P adsorption by OFC in terms of Langmuir isotherm registers varying bonding energy (K) and adsorption maxima (b) for the soils of different locations. Interestingly, OFC isolated from the soils of Reshambari, Sangsey and Bhalukhop exhibit similar adsorption maxima but differentiate each other substantially in terms of tenacity for retention of P as evinced by varying K values. Attempts have also been made to relate the adsorption parameters with relevant soil characteristics.

Key words: Brown forest soil, clay-organic complex, mulberry, organic-free clay and phosphorus adsorption.

Kalimpong has been sustaining as the principal seed crop zone for mulberry sericulture in Eastern India for decades (Datta, 2000). Soils of this zone come under the broad group *brown forest soils* and the nutritional status of the same is suffering from the problem of phosphorus (P) fixation due to acidic soil reaction (Mandal and Roy, 1985). Sub-optimal availability of P in soil impairs the nutrient balance in mulberry plant and, in turn, may interfere with the enzyme regulated metabolic processes responsible for the development and functioning of silk gland in silk worm, *Bombyx mori* L. (Majumder *et al.*, 1997). On the other hand, high level of organic matter in the soils concerned (Kar *et al.*, 2008) is likely to affect the adsorption of P by clays in association with the former. Such complementary postulations justify the initiation of the present study with a view to compare the response of clay-organic complexes (COC) with that of organic-free clays (OFC) towards adsorption of soluble P.

MATERIALS AND METHODS

Soil samples (0 – 0.30 m) were collected following the method of ‘composite soil sampling’ (Chopra and Kanwar, 1982) from five locations under mulberry vegetation of Kalimpong viz., Mahakaldara-1, Reshambari, Sangsey, Mahakaldara-2 and Bhalukhop for undertaking the investigation during 2006-2007. Relevant characteristics of each of the soil samples are presented in Table 1.

For isolation of OFC, collected soil samples were treated with 6% H₂O₂. The clay-sized particles were then separated by following the principle of settling velocities of the different sized particles falling in a liquid (water) medium (Chopra and

Kanwar, 1982). In contrast, COC were isolated from the soil samples by physical exertion through vibration. Soil – water (1:2) suspensions were vibrated for 2 minutes in each installment for a total of 8 minutes. Thereafter, clay sized COC were separated following the same principle as those of OFC. Homo-ionic suspensions of isolated COC and OFC were prepared following the standard analytical protocol (Sanyal and Kar, 1990) for adsorption study.

For estimation of P sorption, COC and OFC suspensions of each soil sample (in triplicate) were equilibrated with graded concentrations of P (25, 75, 150, 225, 300, 375, 450 and 525 mg P₂O₅ l⁻¹) at $300 \pm 1^{\circ}$ K for definite period of time (Singh and Tomar, 1996). After equilibration, each suspension was centrifuged and phosphorus was analyzed in the supernatant obtained on centrifugation. The amount of P adsorbed was calculated by depletion and data were fitted to Freundlich and Langmuir adsorption isotherm equation (Singh and Tomar, 1996).

Freundlich equation: $x/m = KC^{1/n}$ or $\log x/m = 1/n \log C + \log K$

Where, ‘x/m’ is amount of P adsorbed per unit weight of COC/ OFC (mg kg⁻¹), ‘C’ is equilibrium solution P concentration (mg l⁻¹), ‘K’ and ‘n’ are constants. Parameter ‘n’ is the affinity of adsorbate to adsorbent while ‘K’ is strength of adsorption (Venkatesh *et al.*, 2005). One-way ANOVA has been employed to ascertain the role of organic matter, in association with clay, on the adsorption parameters, viz., ‘n’ and ‘K’ (Table 2).

Langmuir equation: $C/(x/m) = (1/Kb) + (C/b)$

Where, ‘x/m’ is amount of P adsorbed per unit mass (mg kg⁻¹), ‘K’ is a constant related to bonding energy,

'C' is equilibrium P concentration (mg l^{-1}) and 'b' refers to sorption maxima and is the reciprocal of the slope of the line.

RESULTS AND DISCUSSION

Freundlich adsorption parameters

Freundlich adsorption isotherm for P obtained for COC and OFC for each soil sample gave good fit ($R^2 = 0.60^*$ to 0.93^{**}). Freundlich constants 'n' and 'K' are furnished in table 2 along with the corresponding regression equations. The isotherms obtained for COC and OFC of different soils showed that solid phases of these soils were having varying affinity (n) for adsorption with varying strength (K). It is also interesting to note that OFC exhibited significantly higher P adsorption capacities registering higher 'n' and 'K' values compared with those of COC. The finding might be explained in terms of 'clogging' of adsorption sites (Kar *et al.*, 2008) by organic polyanion through the formation of ligand exchange with the divalent 3d transition metal ions and ion-dipole interactions with alkali as well as alkaline earth metal ions (Raman and Chandrasekhar Rao, 1996). The postulation was further substantiated by the study of Sanyal *et al.* (1993) inferring loss of effective P-sorbing surface area due to association of clay and organic colloidal component of the soils.

Among the locations, COC isolated from the soils of Mahakaldara-2 registered the highest strength of P adsorption (6.374 l kg^{-1}) with the greatest affinity (0.960 kg l^{-1}) and the same may be correlated with clay/ organic matter ratio, extractable aluminum and iron (Table 1). For OFC, the sample collected from Sangsey recorded the highest K value ($119.895 \text{ l kg}^{-1}$) while Mahakaldara-2 showed the greatest affinity (2.468 kg l^{-1}) for P adsorption. Besides extractable aluminum and iron for affinity, CEC might be correlated with the K value. As adsorption is essentially a surface phenomenon, conceptually, soil solid phases having higher CEC probably offered higher surface area for larger adsorption of P (Murthy *et al.*, 1996). However, Freundlich 'K' for COC was significantly influenced by clay/ organic matter ratio ($r = 0.89^{**}$) and extractable iron ($r = 0.66^*$) while for OFC, the same was correlated with CEC ($r = 0.94^{**}$), pH ($r = 0.76^*$), extractable aluminum ($r = 0.74^*$) and iron ($r = 0.57^*$). On the other hand, Freundlich 'n' for COC was only related to clay/ organic matter ratio ($r = 0.52^*$) while the same for OFC was related to pH ($r = 0.84^{**}$), extractable aluminum ($r = 0.76^*$) and iron ($r = 0.75^*$). It is relevant to mention that Freundlich 'K' and 'n' both for OFC was negatively correlated with the available P content of soils recording -0.86^{**} and -0.83^{**} 'r' value, respectively. The finding suggested that larger adsorption of P serves as a supply pool for subsequent fixation of the same and, in turn, rendered it less availability in the solution

phase. Results of Sanyal *et al.*, (1993) on the acidic soils of South and Southeast Asia also supported this finding, suggesting that the stability of the P-sorption reaction products contribute to the P-fixing characteristics. But, for COC, only Freundlich 'n' was related to available P content of soils ($r = 0.54^*$) that too positively. It emphasizes the reduced effect of organic matter in association with clay on P fixation. It is creditable to mention that several reports are available on the interdependence of sorption parameters and soil characteristics (Singh *et al.*, 1996; Singh and Tomar, 1996; Madan Lal and Minhas, 2005).

Langmuir adsorption parameters

Langmuir adsorption isotherm for P gave a good fit to OFC ($R^2 = 0.82^*$ to 0.99^{**}) but failed to describe P adsorption by COC satisfactorily (Table 3), except the sample isolated from Mahakaldara-2 ($R^2 = 0.99^{**}$). The findings were in well conformity with that of Freundlich's out put. The probable reason might be the interference of organic radicals with the linearity of Langmuir adsorption curves. For satisfactory response of Langmuir equation, linearity of the curves was mostly observed at lower concentrations, indicating thereby the presence of adsorption sites with a uniform bonding energy and a single adsorption maximum (Murthy *et al.*, 1996).

Location wise P adsorption data registered the largest Langmuir 'b' value ($454.55 \text{ mg kg}^{-1}$) for OFC isolated from the soils of Mahakaldara-2, but, recorded the greatest bonding energy (0.7941 l mg^{-1}) for the OFC isolated from Sangsey soils. For OFC, Langmuir 'b' was significantly influenced only by extractable aluminum ($r = 0.79^*$) while 'K' was only influenced by soil pH ($r = 0.66^*$). It is interesting to note that OFC isolated from the soils of Reshambari, Sangsey and Bhalukhop exhibited similar adsorption maxima but differentiated each other substantially in terms of tenacity for retention of P as evinced by varying K values. The finding might be correlated with the extractable aluminum content of the soil samples concerned (Table 1). It is also imperative to mention that Langmuir 'K' was negatively correlated ($r = -0.78^*$) with the available P content of soils which, ultimately dissolves the above contention. However, the samples had identical P adsorption capacity but different buffering capacities and thus, OFC of Sangsey ($K = 0.7941$) seemed to replenish the solution P concentration better (Murthy *et al.*, 1996) than Bhalukhop ($K = 0.5510$) and Reshambari ($K = 0.2030$).

Adsorption isotherm curves

Adsorption isotherms of P on homo-ionic COC and OFC of different locations are presented in fig. 1 and fig. 2, respectively. The values of the sorption intensity ($1/n$), which reflected the non-

linearity of adsorption (Bansal and Chaturvedi, 1996) were more than unity for COC (1.2221 to 1.0560), indicating 'S' type isotherms but, less than unity for OFC (0.5640 to 0.4052), indicating 'L' type isotherms with higher degree of linearity than COC. Moreover, 'S' type isotherm was indicative of vertical orientation of adsorbed molecules at the surface (Krishnasamy, 2003) and lesser degree of linearity of the same envisaged that new sites became available to the solution P as adsorption occurred resulting competition of the same for sites on the adsorbing surface as discussed earlier. On the other hand, 'L' type isotherm for OFC favoured the process of adsorption exhibiting initial steep increase owing to the adsorption of large amount of the solution P at lower concentration, since more active sites of adsorbent were available for adsorption. Due to formation of monolayer, it became increasingly difficult for the solute molecule to find further vacant site available as more sites in the adsorbent were already filled (Arora *et al.*, 2004).

The finding of the study indicated that the predictability of P adsorption data for COC and OFC improved considerably by Freundlich equation than by Langmuir equation. Freundlich 'n' was strongly related to Freundlich 'K' both for COC ($r = 0.83^{**}$) and OFC (0.97^{**}) and thus, satisfied the relation of 'cause-effect' continuum. However, Freundlich 'K' (strength of adsorption) was significantly correlated ($r = 0.78^*$) with Langmuir 'K' (bonding energy) for adsorption of P by OFC and the finding was quite likely to justify each other in terms of buffering/replenishing capacities of P concentration in the bathing solution of soil. It suggested that P might be available to mulberry plants even after the quantity of available P in the soil solution was exhausted and the same might be confirmed by the desorption study of the same. The vision pokes the stakeholders towards the mission of probable utilization of the residual P fertilizer for economizing mulberry production. Nevertheless, the effect of organic matter in association with clay on the reduction of P fixation through lesser degree of adsorption coupled with poor retention of the same was also quite conspicuous from the present study.

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Table 1. Relevant characteristics of soil

Characteristics	Location				
	Mahakaldara-1	Reshambari	Sangsey	Mahakaldara-2	Bhalukhop
Clay (kg kg ⁻¹)	0.150	0.236	0.186	0.196	0.147
Organic matter (kg kg ⁻¹)	0.031	0.055	0.044	0.038	0.032
Clay/ Organic matter	4.839	4.291	4.227	5.158	4.594
Total N (kg kg ⁻¹)	0.0018	0.0035	0.0030	0.0021	0.0016
C:N ratio	9.99	9.12	8.51	10.50	11.60
pH	4.35	4.25	4.80	4.90	5.25
CEC [c mol (p+) kg ⁻¹]	24.332	21.230	28.494	26.663	24.611
Extractable Al (mg kg ⁻¹)	70.601	62.310	72.232	78.222	66.623
Extractable Fe (mg kg ⁻¹)	32.290	33.183	34.290	38.211	37.741
Available P (mg kg ⁻¹)	11.94	12.60	8.87	9.76	11.55

Table 2. Freundlich plot of P adsorption data along with Freundlich constant

Location	Strength of adsorption (l kg ⁻¹)		Affinity of adsorbate to adsorbent (kg l ⁻¹)		Regression equation (R ²)	
	COC	OFC	COC	OFC	COC	OFC
Mahakaldara-1	4.657	90.511	0.895	2.019	log x/m = 0.6681 + 1.1174 log C (0.93**)	log x/m = 1.9567 + 0.4952 log C (0.60*)
Reshambari	4.317	61.277	0.947	1.773	log x/m = 0.6352 + 1.0560 log C (0.92**)	log x/m = 1.7873 + 0.5640 log C (0.90**)
Sangsey	3.148	119.895	0.818	2.398	log x/m = 0.4981 + 1.2221 log C (0.91**)	log x/m = 2.0788 + 0.4171 log C (0.81**)
Mahakaldara-2	6.374	112.616	0.960	2.468	log x/m = 0.8044 + 1.0421 log C (0.89**)	log x/m = 2.0516 + 0.4052 log C (0.77**)
Bhalukhop	5.083	107.399	0.937	2.335	log x/m = 0.7061 + 1.0669 log C (0.92**)	log x/m = 2.0310 + 0.4283 log C (0.75**)

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** significant at P = 0.01

Table 3. Langmuir plot for P along with adsorption maximum (b) and bonding energy constant (K)

Location	Adsorption maximum (mg kg ⁻¹)		Bonding energy (l mg ⁻¹)		Regression equation (R ²)	
	COC	OFC	COC	OFC	COC	OFC
Mahakaldara-1	-	416.667	-	0.2034	C/(x/m) = 0.0538 + 0.0022 C (NS)	C/(x/m) = 0.0118 + 0.0024 C (0.82*)
Reshambari	-	370.370	-	0.2030	C/(x/m) = 0.2077 - 0.0002 C (NS)	C/(x/m) = 0.0133 + 0.0027 C (0.99**)
Sangsey	-	370.370	-	0.7941	C/(x/m) = 0.1984 - 0.0009 C (NS)	C/(x/m) = 0.0034 + 0.0027 C (0.99**)
Mahakaldara-2	434.783	454.545	0.0409	0.3793	C/(x/m) = 0.0563 + 0.0023 C (0.99**)	C/(x/m) = 0.0058 + 0.0022 C (0.98**)
Bhalukhop	-	370.370	-	0.5510	C/(x/m) = 0.1012 - 0.0015 C (NS)	C/(x/m) = 0.0049 + 0.0027 C (0.99**)

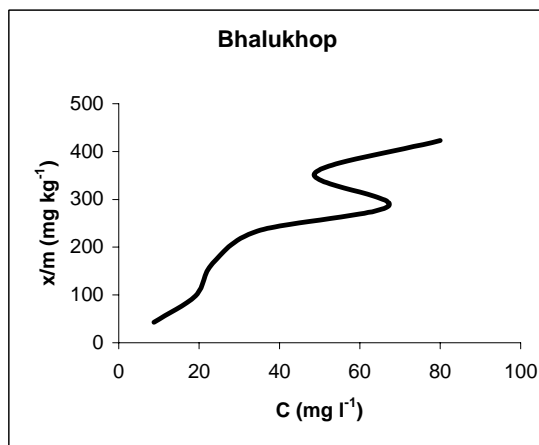
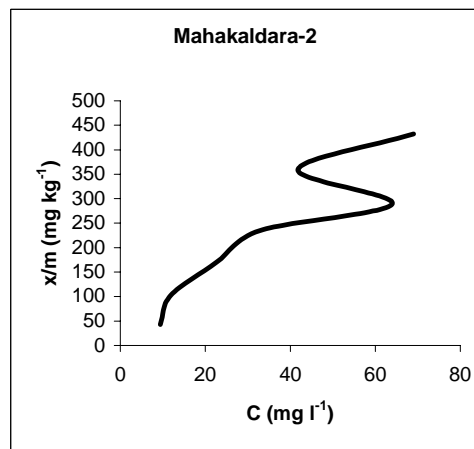
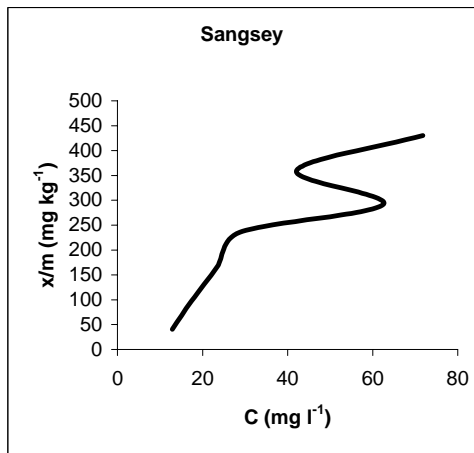
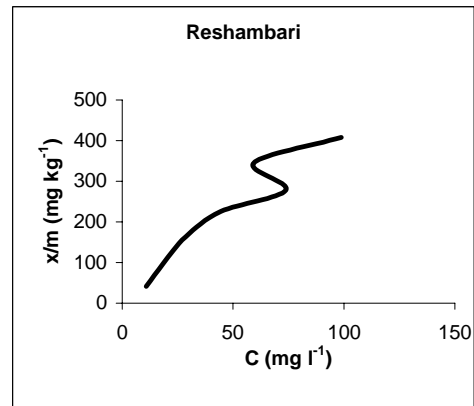
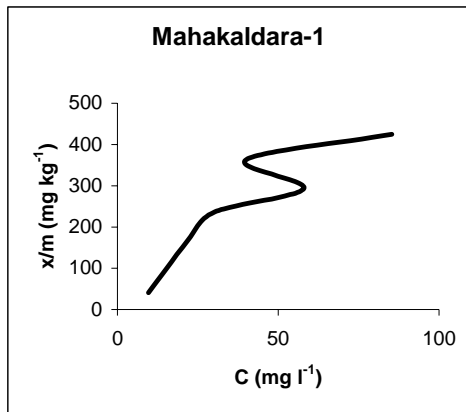


Fig. 1. Adsorption isotherms of P on COC.

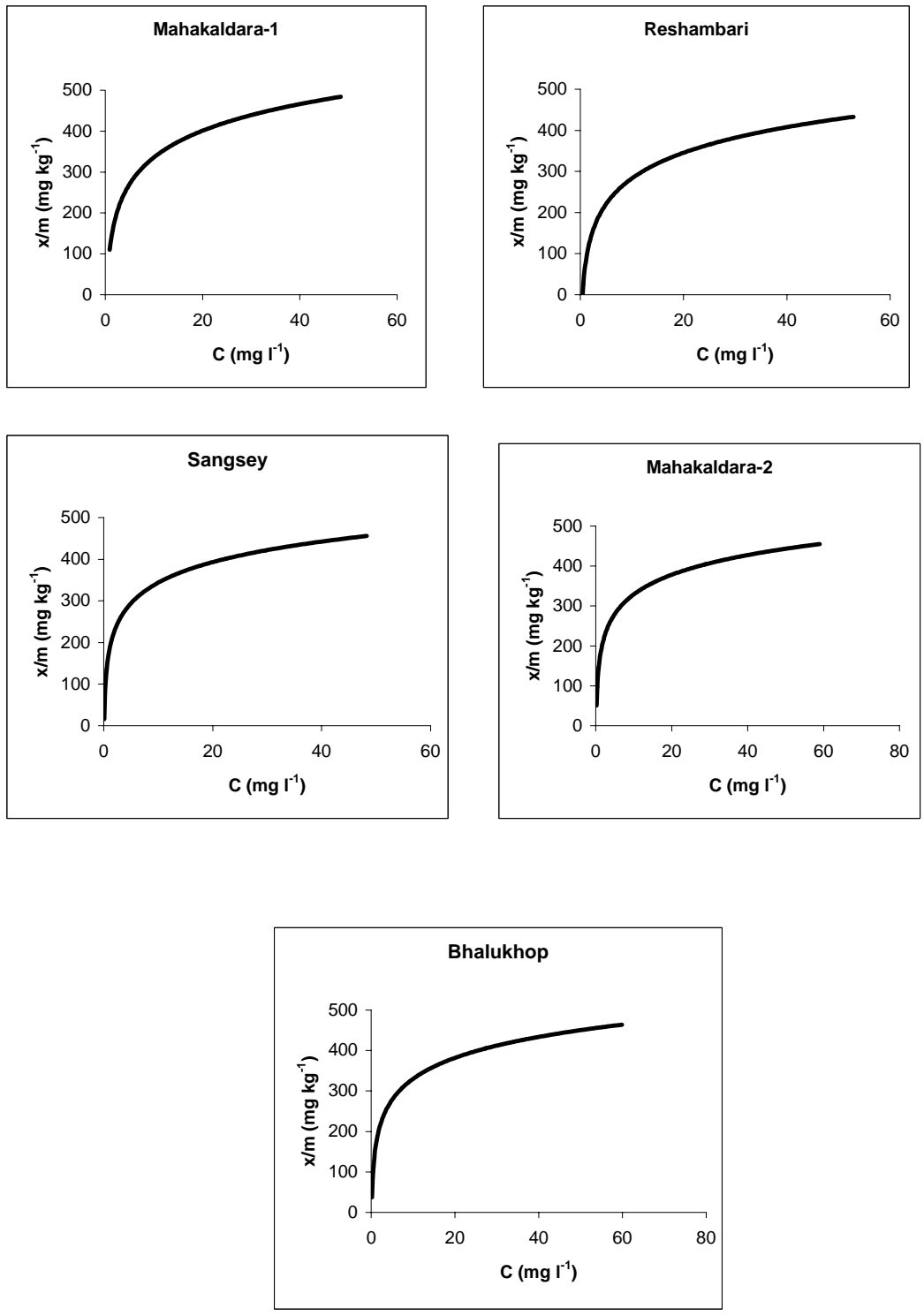


Fig. 2. Adsorption isotherms of P on OFC.