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Adsorption of Zinc in Some Basmati Rice Growing Regions of Sub-Tropical Jammu

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Abstract: The behavior and Langmuir adsorption characteristics of Zn in basmati rice growing sandy clay loam to clay loam soils (pH 6.22-7.55, organic carbon 3.50-7.40 g kg^{-1}) were studied in the sub-tropical zones of Jammu Region. Increasing levels of Zn resulted in simultaneous increase in the supply parameter, Percentage saturation, Equilibrium concentration and adsorbed zinc but there was simultaneous decrease in Differential Buffering Capacity with an increase in the initial Zn supply. The highest Langmuir adsorption maxima and bonding energy of the soils were 1.21 mg kg^{-1} and 18.52 mg kg^{-1} respectively.

Key words: *Langmuir adsorption, adsorption maxima, bonding energy, differential buffering capacity, supply parameter, basmati rice growing soils*

Introduction

The term adsorption is commonly used for the processes of sorption of chemical elements from solutions at the surface of soil particles (Kabata and Pendias 1992). It is the phenomena in which adsorbates (atoms or molecules or ions) are adsorbed or bind to adsorbent (Soil particles or solid surface) from the soil solution by chemical or physical binding. It mostly controls the availability of Zn to plants from the soil solution or soil environment (Bairwa *et al.* 2018). The term sorption refers to all phenomena at the solid solution interface that may include adsorption and precipitation. The availability of micronutrients including Zn in the soil solution is regulated by adsorption-desorption process, and its partitioning between the solution and solid phases (Catlett *et al.* 2002) which in turn affects the capacity of soil to supply the plants with nutrients. The adsorption process is mostly influenced by the various soil properties *i.e.* texture, ion exchange, specific adsorption, organic matter complexation, precipitation, dissolution and clay content. Soil pH was observed to influence the adsorption process, where maximum adsorption was observed to takes place in the acidic medium around pH 4 (Mise *et al.* 2020). Adsorption of zinc was also represented by the clay content and CEC of soils (Sadat *et al.* 2019). Adsorption curves are useful for describing, studying and managing adsorption characteristics of the soil for an element. The adsorption characteristics *i.e.* adsorption maxima (a_{max}) and bonding energy (b) were calculated from the slopes and intercepts of the curves. Langmuir adsorption characteristics were generally studied by an adsorption isotherm which was a plot of the

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quantity of the ion adsorbed by solid phase as a function of the concentration of that ion in solution phase at equilibrium with solid phases. The buffering capacity of a soil for adsorption- desorption process usually affects quantity, intensity and kinetic parameters, which determine the capacity of the soil to supply plant nutrient (Diatta and Kocialkowski 1998).

Although research has been done on the DTPA extractable Zn, however, no information is available on adsorption of Zn in basmati rice (variety B370) growing soils of Jammu region. The Zn content of Jammu soils ranges between 0.1- 0.61 mg kg^{-1} and these soils have been reported to be deficient in Zn (Mondal *et al*. 2006; Spalbar *et al*. 2017). The present study was undertaken to understand the adsorption reactions with Zn and thereby their quantity, intensity and supply parameters.

Materials and Methods

Twenty (20) composite surface soil samples were collected from basmati (var 370) growing blocks (Bishna and R.S. Pura) of Jammu district. The soils were analyzed for pH (Jackson 1973); electrical conductivity (Richards 1954); Organic Carbon rapid titration method (Walkey and Black 1934) and Mechanical analysis by international Pipette method (Piper 1966). Available micronutrient Zn, Fe and Mn were determined by method described by Lindsay and Norvell (1978).

Adsorption studies

The adsorption studies of soil Zn were carried out as per the procedure outlined by Diatta and Kocialkowski (1998). To determine the adsorption characteristics of the soil samples, 0.5 mm sieved samples were divided into ten parts of 1g each. Different concentrations of $Zn(NO_3)_2$ from 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 mg kg^{-1} in 0.1 molar $Ca(NO_3)_2$ as background electrolyte was added to each sample at a ratio of 1:15 in a series of plastic bottles, shaken for two hours on a mechanical shaker and allowed to equilibrate overnight and filtered. The concentration of Zn was determined by atomic adsorption spectrophotometer (AAS) model Z.2300 (Hitachi, Japan). The amount of Zn adsorbed was calculated as the difference in the initial Zn and the remaining Zn in soil solution after equilibrium was attained. The data pertaining to the adsorption of Zn was fitted in to the Langmuir adsorption isotherm equation as follows:

Langmuir equation

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

where,

C- Equilibrium concentration of Zn in soil solution (mg kg^{-1})

x/m- Amount of Zn adsorbed (mg kg^{-1})

a_{max} - Adsorption maxima (mg kg^{-1})

b- Bonding energy constant (L mg^{-1})

DBC- Differential Buffering Capacity

$$(\text{mg kg}^{-1}) = \frac{a_{max} * b}{(1 + bEqC)^2}$$

Results and Discussion

Physical and chemical properties of soil

The salient physical and chemical properties of soils are given in table 1. The pH ranged from 6.22-7.55. The organic carbon ranged from 3.50-7.40 g kg^{-1} with an average value of 6.00 g kg^{-1}. The EC ranged between 0.22-0.47 dS m^{-1} (mean 0.36 dS m^{-1}). The soils were sandy clay loam to clay loam in texture. The DTPA extractable Zn, Fe and Mn ranged from 0.26 - 0.74, 9.80-30.50 and 4.40-12.40 mg kg^{-1} with an average of 0.47, 22.05 and 7.26 mg kg^{-1}, respectively. Zn is predominantly bound to hydroxyl-Al interlayer's sandwiched between 2:1 vermiculite layer in the fine soil matrix and also tends to associate with the ferro-manganiferous mottles in paddy soils. These paddy soils would promote the formation of insoluble Zn which was also reported by Manceau *et al*. (2005). The DTPA extractable Fe and Mn were in sufficient range. These results are in close agreement with results reported by Spalbar *et al*. (2017)

Table 1. Physicochemical properties of soils

	pH	EC	OC	Sand	Silt	Clay	Zn	Fe	Mn
		(dS m^{-1})	(g kg^{-1})	-------------------%-----------------			----------mg kg^{-1}----------------		
Minimum	6.22	0.22	3.50	23.20	14.00	27.70	0.26	9.80	4.40
Maximum	7.55	0.47	7.40	56.70	38.40	48.80	0.74	30.50	12.40
Mean		0.36	6.00	40.00	25.90	33.61	0.47	22.05	7.26

Table 2. Multiple regression equations relating supply parameter with the adsorption characteristics in Jammu district

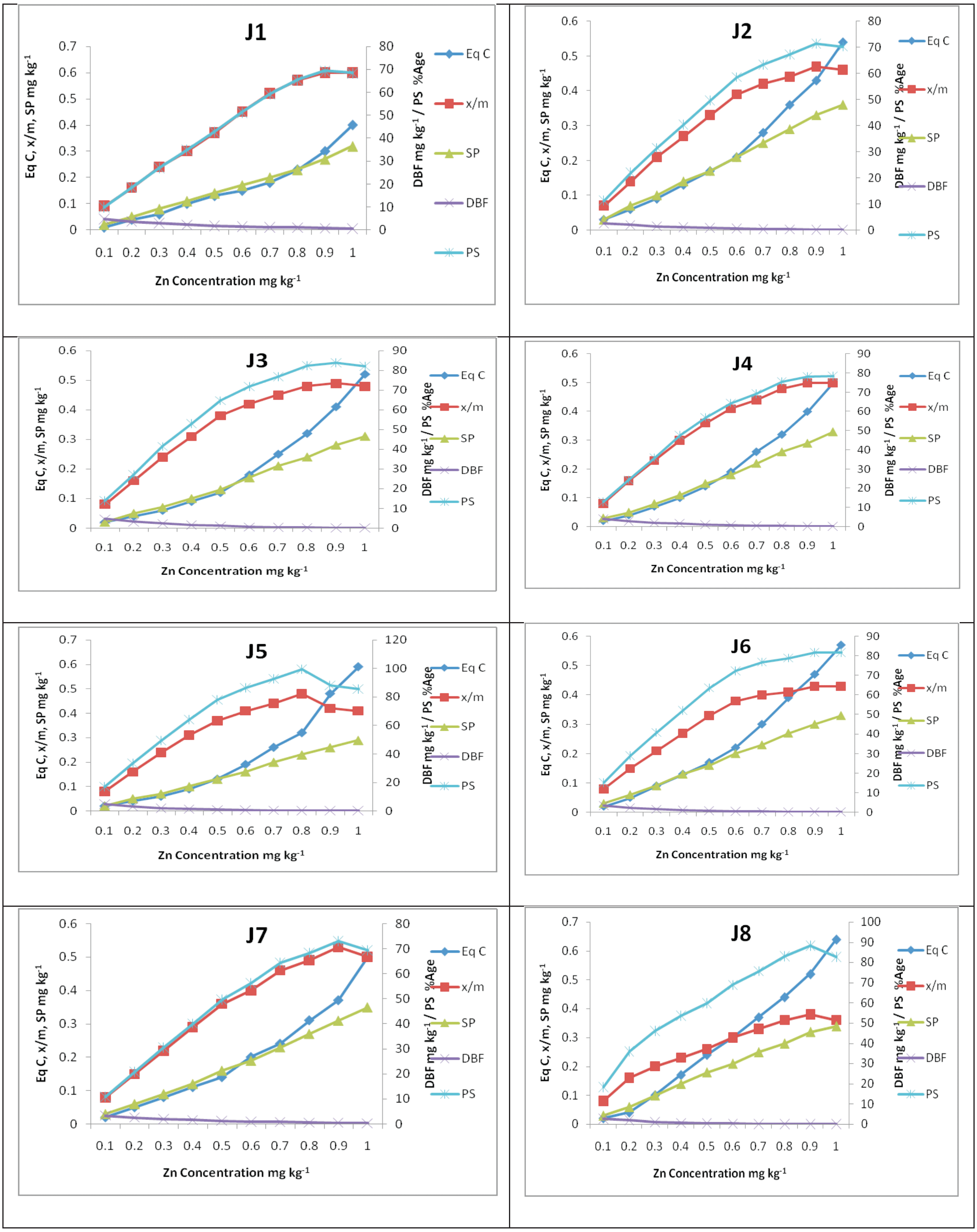
Parameters	Beta Wt	Reg. Coefficent	Standard Error	t- value	p-value
Intercept a		0.057	0.006	8.968	0.000
X_1	-0.158	-0.014	0.001	8.594	0.000
X_2	-0.235	-0.001	0.001	12.80	0.000
X_3	0.247	0.162	0.015	10.84	0.000
X_4	0.817	0.290	0.009	30.55	0.000

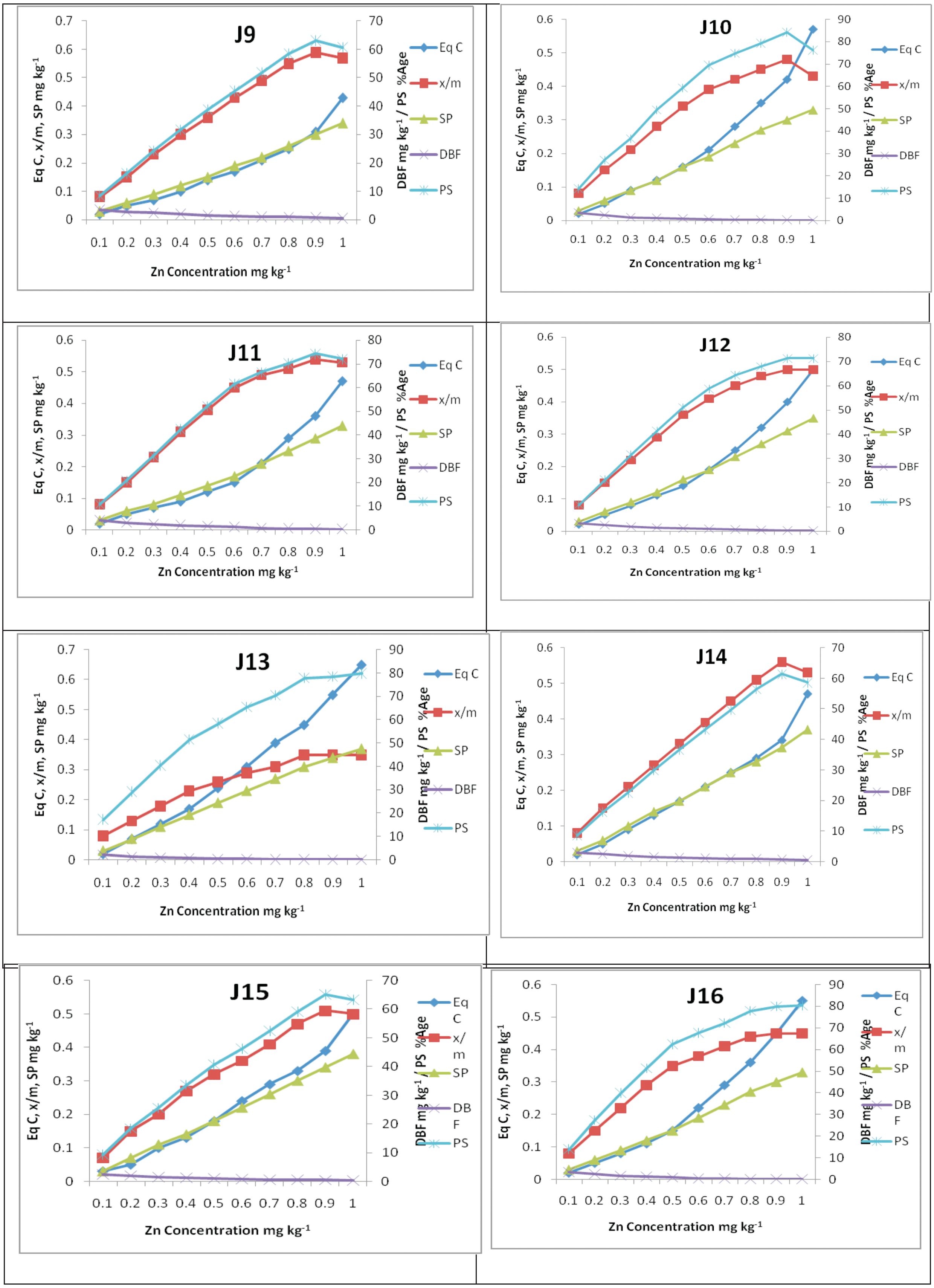
p - value < 0.01 indicates highly significant
p- value < 0.05 indicates significant
X_1- DBC, X_2- % saturation, X_3- Eq. Con, X_4- Zn supplied

Langmuir adsorption characteristics of zinc

The effect of Zn added on various adsorption characterizes are given (Fig.1 and 2). The Equilibrium Concentration (Eq C), Zinc adsorbed (x/m), Supply Parameter (SP) are depicted on the primary axis whereas, Differential Buffering Capacity (DBC) and per cent Saturation (PS) are shown on the secondary axis. Zinc adsorption was described well with Langmuir model over the range of Zn concentrations (0.1 to 1.0 mg kg^{-1}) for all soils. With the addition of increasing amounts of Zn to soils, there was an increase in adsorbed amount of Zn. This may be attributed to the fact that as the supply of Zn increased, the soils saturation level also increased, thus limiting the adsorption ability of the soil. With an increase in the equilibrium concentration, there was an increase in amount of Zn adsorbed but the adsorbed percentage decreased with an increase in the initial Zn supplied. This may be due to increase in the ratio of adsorbate to adsorbent. The amount of Zn adsorbed in these soils, irrespective of their treatments, increased with a rise in Zn concentration in equilibrium solution but magnitude of increase varied in soils. Diatta and Kocialkowski (1998), Ashraf (2008) and Casagrande *et al*. (2008) reported similar results. Adsorption maxima (a^{max}) which was the maximum adsorption capacity of soil, ranged between 0.43-1.21 mg kg^{-1}. The adsorption maxima had a positive correlation with soil pH, higher pH increased the adsorption maxima as a result of complication of Zn by OH ions and a higher net negative charge (Shuman 1986). Clays have high adsorption sites that allow the non-exchangeable adsorption of Zn (Randal and Bruce 1991). Similar results were also reported by Diatta and Kocialkowski (1998) and Ashraf (2008).

Bonding energy (b), the mean of strength could hold Zn and it ranged between 3.42-18.52 L mg^{-1}. Bonding energy was positively correlated with soil pH.


J1
J2
J3
J4
J5
J6
J7
J8
Eq C, x/m, SP mg kg-1
DBF mg kg-1 / PS %Age
Zn Concentration mg kg-1
Eq C
x/m
SP
DBF
PS


J9
J10
J11
J12
J13
J14
J15
J16
Eq C, x/m, SP mg kg-1
DBF mg kg-1 / PS %Age
Zn Concentration mg kg-1
Eq C
x/m
SP
DBF
PS

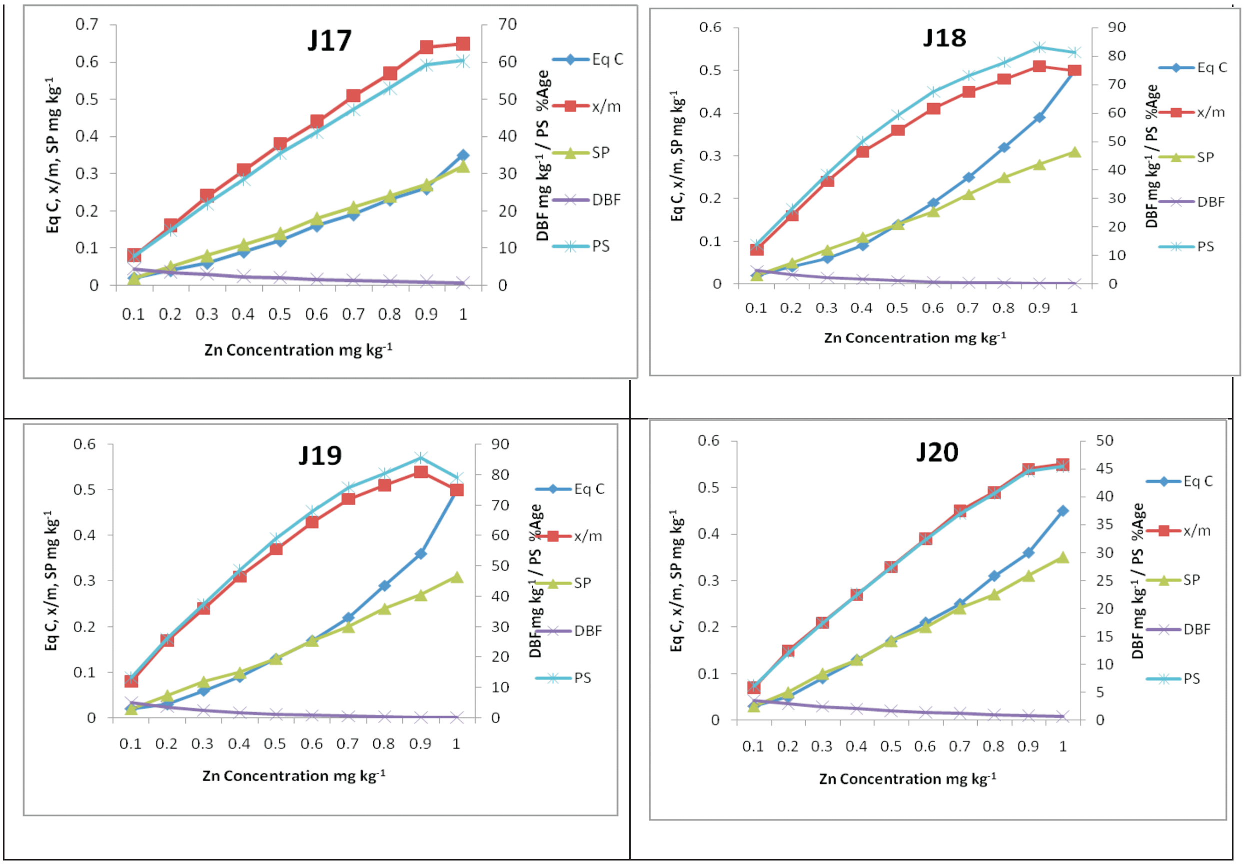


Fig. 1. Influence of Zn added on the Equilibrium Concentration (Eq. C, mg kg^{-1}), amount of Zn adsorbed (x/m, mg kg^{-1}), Supply Parameter (SP, mg kg^{-1}), Differential Buffering Capacity (DBC, mg kg^{-1}) and Per cent Saturation (PS %).

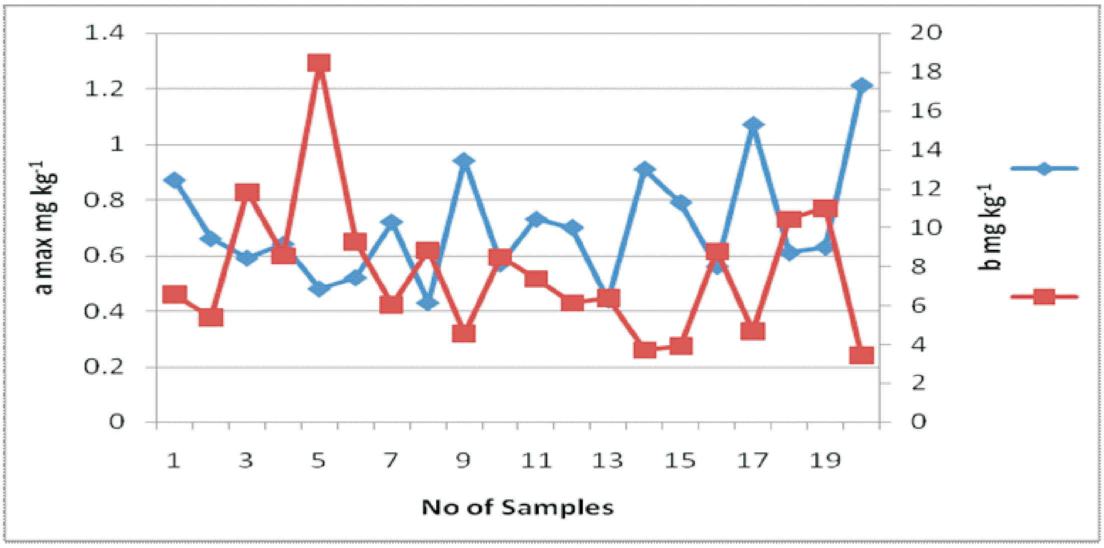


Fig. 2. Influence of Zn added on the adsorption maxima (a^{max} mg kg^{-1}) and bonding energy (b, L mg^{-1})

Tiwari and Kumar (1980) and Diatta and Kocialkowski (1998) reported similar results.The supply parameter, which was introduced by Khasawneh (1971), and Khasawneh and Copeland (1973) to integrate quantity, intensity and buffering capacity, were responsible for the supply of nutrients like zinc. Soils with high adsorption maxima, bonding energy and differential buffering capacity had a greater affinity for added Zn and thus, for any changes in the supply parameter, higher rates of Zn will be required. Supply parameter showed steady rise with an increase in the initial Zn supplied. Similar results were observed by Diatta and Kocialkowski (1998). Differential buffering capacity (DBC) of the soil is an indicator of the resistance to change in ions of the soil solution when they were added to or removed from it and once the processes controlling the quantity variables were saturated, Zn concentration in solution phase would increase. The differential buffering capacity showed a gradual decrease with an increase of initial Zn supplied. Similar results were observed by Diatta and Kocialkowski (1998). Percentage saturation indicates the nutrients retained by the soil after attaining equilibrium. The nutrients in solution were associated with colloidal surfaces which are important for plant growth. The solution fraction was readily available while adsorbed fractions may be gradually released as the ions in solution were depleted. A gradual increase in the Percentage saturation was observed with an increase in initial Zn supplied. Similar results were observed by Joshi (1986) and Diatta and Kocialkowski (1998).

Statistics

To analyze the impact of various independent variables (DBC, per cent saturation, Eq. Conc. Zn supplied) on the dependent variable (supply parameter), multiple regression (Table 2) models were developed. The results revealed that all the independent variables *viz.* (DBC (t=8.594, p=0.000), Per cent saturation (t=12.80, p=0.000), Eq. Concentration (t=10.84, p = 0.000), Zn supplied (t=30.55, p=0.000) have significant effect on supply parameter. Further, DBC and per cent saturation were negatively correlated, which means that with the increase in DBC and per cent saturation, the supply parameter decreases and *vice versa*. The other independent variables Eq. concentration and Zn supplied were positively significant. R^2 value of the model was 0.985 which is statistically significant (p-value= 0.000).

Conclusion

Adsorption of Zn was mostly depended on soil pH, clay content and CEC. In the Langmuir adsorption characteristics, the Eq. concentration and amount of Zn adsorbed and Langmuir adsorption and supply parameter increased with the increase of Zn application. Differential buffering capacity and per cent adsorbed decreased with the increase of Zn application. Langmuir adsorption model can be used to control and manage Zn deficiency in soils of basmati rice growing areas of the region where deficiency of Zn has been reported to be a limiting factor in basmati rice production.

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