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Adsorption Dynamics of Nitrate in an Inceptisol of the Indo-Gangetic Plain of India

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A B S T R A C T

The laboratory experiment was conducted at Department of Soil Science and Agricultural Chemistry, Banaras Hindu University, Varanasi, Uttar Pradesh, India. In this experiment, the adsorption of nitrate onto soils of different cropping systems viz. rice-wheat(R-W), rice-vegetable (R-V), pulse-pulse (P-P) and sugarcane(S) was carried out in a batch equilibrium system. Surface soil samples were collected for adsorption study from each cropping system. Results showed that the adsorption isotherms were L- type (Langmuir type) in most of the soils. Adsorption data for soils were found to obey the Freundlich adsorption equation over the entire range of concentrations studied (50-300 mg NO_3^--N/L). In all the cases, the values of coefficient R^2_F were in the range of 0.71 to 0.99. Considering the K_F values, the order adsorption of nitrate on surface soils was: P-P> R-W (Cholapur)> S> R-W (Pindra)>R-V. The surface soil adsorption capacities were comparatively higher in R-W and R-V cropping system areas. In comparatively to the different surfaces of adsorption on soils, contribution of organic matter was found very higher (2.22 to 4.31) in these soils.

Introduction

Nitrate contamination of surface and groundwater is one of the major problems associated with agricultural activities in many parts of the India as well as globally (Mahvi *et al.*, 2005; Prasad and Raha, 2015). Most agricultural soils found in arid and semi-arid regions have a very low variable anion exchange capacity due to low in organic matter content. Therefore, nitrate easily leaches through the soil profile. Because Ion exchange reactions are important processes for controlling the fate of nitrate as well as dissolved nutrients such as nitrate, chloride and sulphate in agricultural fields (Ishiguro *et al.*, 1992; Prasad and Raha, 2016). Nitrate adsorption in soil may be influenced by environmental conditions (Mikkelsen, 1992) as well as fertilization practice. The prevailing environmental conditions such as temperature, humidity, type of natural soil, and common irrigation practices, are all considering to the migration of nitrate in soil. Thus, the dynamics of nitrate i.e. adsorption in soil should be studied for better understanding of the mechanisms of nitrate movement through soil profile in aquifer. The NO_3^- adsorption process has been studied in many different soil orders in tropical climate (Kinjo and Pratt 1971), including Oxisols (Dynia, 2000) as well as in ultisols of the southeastern and mid-Atlantic United States (Eick *et al.*, 1999), andisols (Tani *et al.*, 2003; Katou 2004) and in forest soils of the American northwest (Strahm and Harrison, 2006). However, none of these investigated NO_3^- adsorption dynamics for the Inceptisol soil order, in particular the soils of the Indo- Gangetic Plain, which is considered to be one of the most important crop production areas in India. The aim of this study was to investigate the NO_3^- adsorption capacity of Inceptisol and effect of different cropping systems on adsorption capacity of these soils.

Materials and Methods

Collection of soil samples

The soil samples were collected from cultivated lands of different cropping systems *viz*. rice-wheat, rice-vegetable, pulse-pulse and sugarcane in Varanasi district. The soils were collected from 0-15 cm depth during pre-monsoon period from cultivated areas with high intensity cropping systems. The total samples were 84 from different locations for adsorption study. Five representative soil samples in different cropping systems were selected for the adsorption study of nitrate. Selection of the soil samples was based on variation of clay content, organic matter content, calcium carbonate content as well as coverage of cropping systems in Varanasi district (Table 1).

The climate is predominantly sub humid and subtropical with annual temperature between 5 and 46° C and with an average rainfall 1100 mm per year of (90 % of rainfall is distributed during June to September). The soil samples were air dried, ground in wooden pestle and mortar and passed through a 2 mm stainless steel sieve.

Adsorption experiment

Adsorption experiments were carried out by using batch equilibrium technique. A 20 mL of graded concentration sorbate solution of potassium nitrate solutions as 50,100, 150, 200, 250 and 300 mgL^{-1} (50-300 mg NO_3^--N/L according to native NO_3^--N content in soil) were added to 100 mL plastic bottles in duplicates containing 10g of each soil. The contents were shaken for 2 hr (equilibrium time) at room temperature 25^0C. The samples were then centrifuged at 4000 rpm for 10 minutes, filtered and concentration of nitrate was measured colorimetrically.

The amount of adsorbed nitrate on soil (C_s) was calculated from the difference between the initial and equilibrium concentration (C_e). The data was fitted to logarithmic from of the freundlich equation.

$$\log (C_s) = \log K_{f\,ads} + 1/n_{ads} \times \log(Ce)$$

$\log K_{f\ ads}$ and $1/n_{ads}$ are the constants representing the intercept and slopes of the isotherms, respectively. The distribution coefficient, K_D was calculated as C_s/C_e [total $C_s.C_e$ / $(C_e)^2$] to measure the adsorption extent. The adsorption constant $K_{f\ ads}$ normalized to soil organic carbon content, K_{oc} and soil calcium carbonate content, K_{cc}. These are important parameters that play a significant role in environmental fate assessment of nitrate and were evaluated using the following equation:

$$K_{OC} = \frac{KD}{\%OC} \times 100$$

$$K_{OM} = \frac{KD}{\%OM} \times 100$$

$$K_{cc} = \frac{KD}{\%CaCO_3} \times 100$$

Simple correlation and regression analyses were done using microstate package to correlate adsorption with various soil parameter.

The data were also fitted with Langmuir adsorption equation by calculated Ce/x/m, where x/m is the amount of adsorbed (µg NO_3^- g^{-1} soil).

Results and Discussion

The characteristic of the soils under adsorption study are presented in the Table 2 revealed that there were significant differences in the physical properties of the soils *viz*. bulk density water holding capacity and clay content of the soils. Moreover, there were wide variations in the electrochemical and chemical properties of the soils.

The batch equilibrium adsorption study on the soils was performed on selected soils of different cropping systems of Varanasi district, *viz*. rice-wheat of Pindra, rice-wheat of Cholapur, rice-vegetable, pulse-pulse, and sugarcane.

The data on adsorption of nitrate in the selected soils of district Varanasi are presented in Table 3 and isotherms of nitrate in surface are depicted in Figure 1. The adsorption isotherms were drawn between the amount of nitrate (x/m) adsorbed (µg g^{-1}) on soils and that in equilibrium (C_e) suspensions (µg mL^{-1}) at a fixed volume water, respectively. The data was fitted both Frendulich and Langmuir adsorption eqations.

Frendulich adsorption equation

Adsorption data for soils were found to obey the Freundlich adsorption equation over the entire range of concentrations studied and corresponding Freundlich adsorption isotherms are shown in Figure 2. In all the cases, the values of coefficient R^2_F (Table 4) were in the range of 0.70 to 0.99.

The values of K_F and 1/n for soil-nitrate adsorption combinations were estimated by linear regression of the logarithmically transformed data and the values so obtained were summarized in Table 4. The magnitude of K_F expresses the relative adsorption capacity on degree of adsorption for the adsorbate (NO_3^-) for a given system of adsorbent and 1/n values express the adsorption intensity. The values of 1/n provide an idea of the intensity of adsorption which varies with nature of the adsorbate. The 1/n value < 1 for the different soils indicate the non-linearity between solution equilibrium concentration and adsorption are in good agreement with the L-shape of the isotherms.

The lack of linearity may be attributed to specific interaction existing between the organic matters on the mineral fraction of the soils. The adsorption of nitrate initially increased with increasing nitrate concentration but at later stages of higher concentration adsorption rate decreased with increasing concentration of nitrate in all the investigated soils. Thus, the increasing rate was greater at lower concentrations than at higher concentration of applied nitrate solution. Thus, the adsorption isotherms were L-type (Langmuir type) in most of the soils of Varanasi district. In L-type isotherms on initial slope that is curvilinear and concave with respect to the amount of nitrate adsorbed. Nitrate adsorption in some soils of Turkey also has been shown to be described by L-type (Akosman and Özdermir, 2010).

Fig.1 Adsorption pattern of nitrate on soils of different cropping system

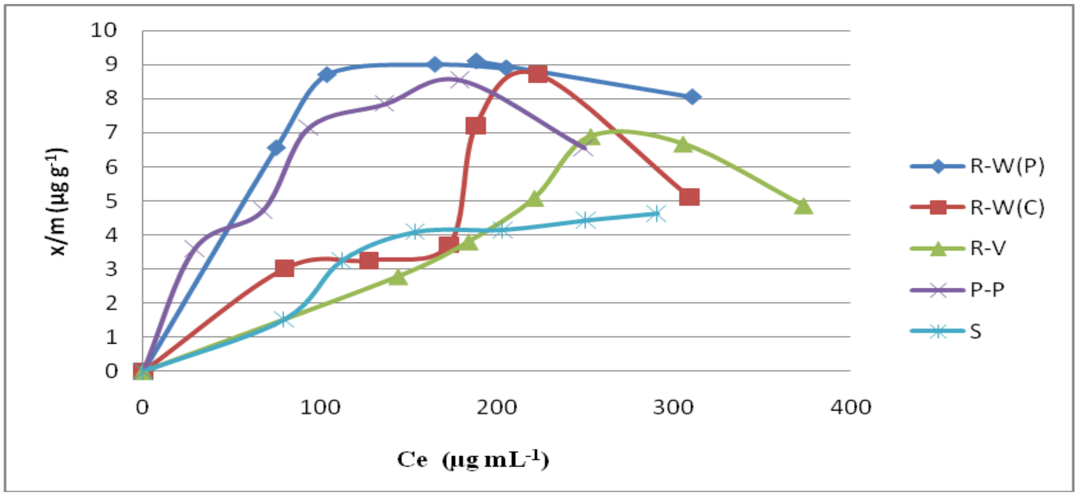

Fig.2 Freundlich adsorption isotherm of nitrate for soils of different cropping

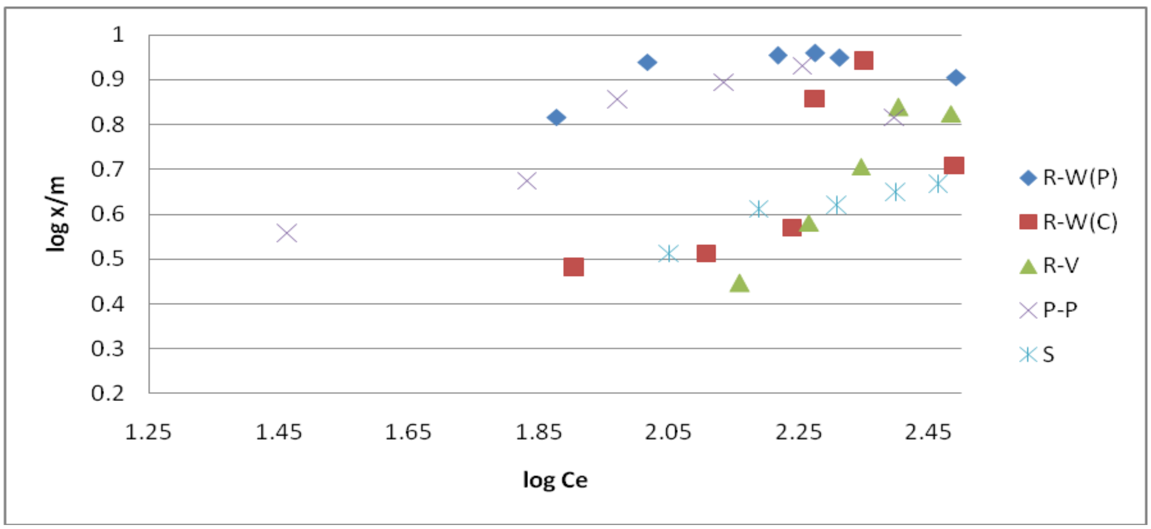

Table.1 Procedure followed for physico-chemical analysis of soil

Properties	Method adopted	references
pH	Glass electrode pH meter	Jackson 1967
EC(dSm^{-1})	Electrical conductivity meter	Jackson 1967
Organic Carbon (g/kg)	Wet oxidation method	Walkely and Black 1934
Bulk Density (Mg m^{-3})	Pycnometer method	Black 1965
Water Holding Capacity (%)	Keen Rackzowski box method	Black 1965
$CaCO_3$ (%)	Rapid titration method	Piper 1951
Soil Texture	Hydrometer method	Bouyoucos 1927
Cation Exchange Capacity (Cmol (p^+ kg^{-1}))	Neutral ammonium acetate	Jackson 1967
Nitrate content	Colorimetrically	Nelson *et al.*, 1954

Table.2 Physico-chemical characteristics of soils in different cropping systems

S. No.	Cropping system	pH	EC (dSm^{-1})	Organic Carbon (g/kg)	BD ($Mg\ m^{-3}$)	WHC (%)	$CaCO_3$ (%)	Sand (%)	Silt (%)	Clay (%)	Taxutural Class (USDA)	CEC [Cmol ($p^+ kg^{-1}$)]
1.	Rice-wheat (Pindra)	7.96	0.163	8.19	1.35	53.77	2.50	41.40	33.00	25.60	Sandy loam	14.65
2.	Rice-wheat (Cholapur)	7.80	0.198	8.58	1.36	46.65	6.25	35.40	36.00	28.60	Clay loam	16.41
3.	Rice- vegetable	8.20	0.173	11.05	1.39	47.08	6.25	33.68	40.00	26.32	Loam	9.65
5.	Pulse-pulse	9.03	0.327	1.95	1.18	48.77	3.00	41.40	35.00	23.60	Loam	8.47
7.	Sugarcane	8.16	0.289	6.37	1.26	47.48	1.25	38.24	36.00	25.76	Loam	10.07

Table.3 Adsorption of the nitrate in soils of different cropping systems

Soil depth (cm)	Nitrate applied ($\mu g\ g^{-1}$)*	Equilibrium concentration (Ce) ($\mu g\ mL^{-1}$)	Amount of nitrate adsorbed (x/m) ($\mu g\ g^{-1}$)	Ce/x/m	log Ce	log x/m
Rice- wheat (Pindra)	50	75.32	6.56	11.48	1.88	0.82
	100	103.9	8.70	11.94	2.02	0.94
	150	164.94	9.0	18.33	2.22	0.95
	200	205.19	8.9	23.06	2.31	0.95
	250	188.31	9.1	20.69	2.27	0.96
	300	310.39	8.05	38.56	2.49	0.91
Rice-wheat (Cholapur)	50	80.23	3.02	26.57	1.90	0.48
	100	127.91	3.26	39.24	2.11	0.51
	150	173.26	3.72	46.58	2.24	0.57
	200	188.37	7.21	26.13	2.28	0.86
	250	223.26	8.72	25.60	2.35	0.94
	300	309.3	5.12	60.41	2.49	0.71
Rice-vegetable	50	144.25	2.79	51.70	2.16	0.45
	100	184.07	3.81	48.31	2.26	0.58
	150	221.24	5.09	43.47	2.34	0.71
	200	253.1	6.90	36.68	2.40	0.84
	250	305.31	6.68	45.71	2.48	0.82
	300	373.45	4.87	76.68	2.57	0.69
Pulse-pulse	50	29.03	3.60	8.06	1.46	0.56
	100	67.74	4.73	14.32	1.83	0.67
	150	93.55	7.15	13.08	1.97	0.85
	200	136.56	7.85	17.40	2.14	0.89
	250	179.57	8.55	21.00	2.25	0.93
	300	249.46	6.56	38.03	2.40	0.82
Sugarcane	50	79.66	1.53	52.07	1.90	0.18
	100	112.36	3.26	34.47	2.05	0.51
	150	153.93	4.10	37.54	2.19	0.61
	200	203.37	4.16	48.89	2.31	0.62
	250	250.56	4.44	56.43	2.40	0.65
	300	290.54	4.64	62.62	2.46	0.67

*Native nitrate content in soil: Rice- wheat (Pindra): 90.91 $\mu g\ g^{-1}$, Rice-wheat (Cholapur): 60.47 $\mu g\ g^{-1}$, Rice-vegetable: 122.12 $\mu g\ g^{-1}$, Pulse-pulse: 15.05 $\mu g\ g^{-1}$, Sugarcane: 44.94 $\mu g\ g^{-1}$

Table.4 Partition coefficient, Freundlich and Langmuir constant data of nitrate adsorption on soils of different cropping systems

S. No.	Cropping system	K_D	K_{OC}	K_{OM}	K_{CC}	K_F	1/n	R^2_F	K_L	b	R^2_L
1.	Rice-wheat(Pindra)	0.045	3.30	1.91	1.80	0.399	0.924	0.999	1.295	8.772	0.802
2.	Rice-wheat (Cholapur)	0.026	2.22	1.29	0.42	0.979	0.260	0.920	0.007	7.194	0.944
3.	Rice-vegetable	0.020	2.33	1.35	0.32	0.098	1.287	0.931	0.005	7.937	0.727
4.	Pulse-pulse	0.042	4.31	2.50	1.40	1.055	0.365	0.719	0.040	8.130	0.900
5.	Sugarcane	0.023	3.00	1.74	1.87	0.816	0.358	0.854	0.012	5.988	0.972

Langmuir adsorption equation

The adsorption data of nitrate on soils of Varanasi district were also fitted in the Langmuir adsorption equation (R^2_L) over the entire range of concentration studied. The adsorption maxima (b) and index of bonding energy (K_L) were calculated from slope-^{1} slope/intercept of a straight line relationship, respectively between C_e and C_e / x / m in the Langmuir adsorption equation. The adsorption maxima (b) and Langmuir constant (K_L) i.e., index of bonding energy are presented in Table 4.

It was revealed from data the adsorption maxima ranges from 0.8 to 1000 µg g^{-1} and the bonding energy ranged from -0.001 to 1.295 mL $µg^{-1}$ NO_3^-. The negative values of bonding energy showed the exothermic reaction during equilibrium. The highest index of bonding energy was observed in the soils of rice-wheat (Pindra) cropping system and this indicated greater affinity of soil for NO_3^- of R-W (Pindra).

Giles *et al.*, (1960) suggested that isotherm shape provides an indication of the adsorption mechanism operating for a given solute – solvent adsorbent system. According to Giles, there are four types of adsorption mechanism *i.e.* solvent affinity type (S – type), Langmuir type (L – type), constant partition type (C – type) and high affinity type (H – type). In L – type, isotherm has an initial slope that is curvilinear and concave with respect to the amount of adsorbed nitrate. It was confirmed by 1/*n* values for soils under study *i.e.* 1/*n* < 1. The L-type isotherm has an initial slope *i.e.* non-linear and concave with respect to the abscissa.

The adsorptive capacity of organic carbon, organic matter and calcium carbonate content for the soil was evaluated by calculating K_{OC}, K_{OM} and K_{CC} values and results obtained are given in Table 4. It was revealed from the data that adsorption of nitrate was comparatively higher on organic matter (K_{OM}) than free $CaCO_3$ (K_{CC}) in most of soils of Varanasi district except soils of sugarcane cultivated soils. Contribution of organic matter was lowest in the surface soil of rice-wheat cultivated areas of Varanasi district.

Although the mineral phase is also responsible for a significant contribution to the total adsorption, but due to contribution of clay through anionic exchange surface obviously very low. Considering the K_F values, the order of adsorption of nitrate on surface soils was as follow: pulse-pulse > rice-wheat (Cholapur) > sugarcane > rice-wheat (Pindra) > rice-vegetable.

The surface soil adsorption (K_F) capacities were comparatively higher in rice-wheat, rice-vegetable cropping system areas of Varanasi district. In comparison to the different surfaces of adsorption of nitrate on soils, comparatively contribution of organic matter was found very higher in these soils.

Relationship between soil properties, partition coefficient, Freundlich and Langmuir parameters of adsorption of nitrate

Simple correlation coefficients were calculated to find inter-relationship between soil properties and NO_3^- adsorption constants (*viz*. K_F, 1/n, K_L and b) and partition coefficient (K_D, K_{OC}, K_{OM} and K_{CC}) in soils of Varanasi district. It was revealed that the adsorption intensity (1/n) of NO_3^- on the soils had a significant positive correlation with organic matter (0.742) and $CaCO_3$ (0.651). The adsorption capacity (K_L) of NO_3^- was negatively correlated clay content of surface soil. Thus, the major sites nitrate adsorption of the soils Varanasi obviously organic matter, $CaCO_3$ and might be Al/Fe hydroxides. Remya *et al.*, (2011) also observed that highest nitrate adsorption was on the soils containing highest organic matter (OM) content. This can be attributed to the greatest number of binding sites provided by chemically active OM and its extremely large surface area. These observations infer that OM content plays a major role in the nitrate sorption capacity of the soils. The soil OM has a polyelectrolytic character with various chemically reactive functional groups, hydrophilic and hydrophobic sites, which influences the soil-solution interaction. Moreover, it was reported that the mobility of pesticides and nitrate (Ndala *et al.*, 2006) often related to the active components of organic fraction.

The nitrate adsorption in five surface soils was investigated. The texture of the soils of different cropping systems was found loam to clay- loam. The ranges of organic carbon and $CaCO_3$ in soils were 1.95 -11.05 g/kg and 1.25 to 6.25 %, respectively. According to adsorption pattern, the adsorption of nitrate on different soils were observed Langmuir type ('L' type) isotherm, i.e. initial slope that were observed curvilinear and convex with respect to the amount of NO_3^- adsorbed. The adsorption isotherms of nitrate on soils were well fitted with both Freundlich's and Langmuir's adsorption isotherms but the Freundlich adsorption isotherm better described the NO_3^- adsorption in these soils. The order of adsorption of nitrate on surface soils was as follows: pulse–pulse >rice-wheat (Cholapur)>sugarcane >rice-wheat (Pindra) >rice-vegetable. Nitrate adsorption was found higher on organic matter in comparison to the different surfaces of adsorption. It was revealed that the adsorption intensity (1/n) of NO_3^- on the soils had a significant positive correlation with organic matter (0.742) and $CaCO_3$ (0.651). The adsorption capacity (K_L) of NO_3^- was negatively correlated clay content of surface soil.

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