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Effect of Calcium Carbonate, pH and Time on the Adsorption and Desorption of Ni in Soils of Shikar Block of Mirzapur District of Uttar Pradesh

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ABSTRACT: Nickel is considered as the essential nutrient for plants its deficiency is reared under field condition, but some reports of its deficiency is found in the Shikar block of Mirzapur district in Uttar Pradesh. So, in order understand the deficiency we need to know the factor affecting availability of Ni in the soil and for this a laboratory experiment of adsorption and desorption was done in which three factors were taken *i.e.* pH (2, 4, 6, 8, 10, 12), Calcium carbonate ($CaCO_3$) (0.25, 0.5, 1.0, 1.5, 2.0g) and time (1 to 24 hours). The result indicated that as the time increased the adsorption of Ni increased in the soil and saturated around 24 hours and two kinetic models were taken pseudo second order and intra diffusion model. The model that fitted best was pseudo second order with coefficient of determination (R^2= 0.944). Also different values of pH were taken and the result showed that as pH increased the adsorption increased but desorption of nickel decreased. The similar trend reported for the $CaCO_3$, as the amount of $CaCO_3$ increased from 0.25 to 2.0g the adsorption increased while desorption decreased. This study would help in understanding the factors that affect the adsorption and desorption of nickel in soil, especially under Ni deficient condition.

Keywords: Adsorption, $CaCO_3$, Intraparticle diffusion, pH, Pseudo second order.

INTRODUCTION

The most recently identified essential nutrient for plants is nickel (Ni) (Brown *et al.*, 1987). Following the discovery of its necessity in the lab, a deficiency of Ni has now been observed in a few perennial plants in field settings (Wood *et al*., 2004). Regarding this, Kumar *et al*. (2018) assessed the crop response to applied Ni for determining the amount of Ni in soil using barley as the test crop and reported the DTPA extractable critical limit of soil was 0.22 $mgkg^{-1}$ and in barley was 2.40 $mgkg^{-1}$. The DTPA extractable critical limit for soil was reported to be 0.17 $mgkg^{-1}$ and for soybeans to be 0.20 $mgkg^{-1}$ in a related study by Barman *et al*. (2020). The positive yield response to Ni application in field crops (Brown *et al.*, 1987) highlights the necessity for Ni addition, especially in deficient soils. Depending on the Ni affinity properties of various soil constituents, Ni can be dispersed between solid and solution phases when added to soil. Sorption, desorption, precipitation, ionic retention, and other phenomena are involved in its retention and decrease in mobility. For managing deficiency, understanding the adsorption and desorption of Ni in the soil and their quantification is crucial (Barman *et al*., 2013). According to several scientists, the pH primarily regulates the sorption and availability of nickel (Gomes *et al*., 2001). The availability and solubility of metals in the soil are known to be controlled by adsorption mechanisms, despite the possibility of all these events taking place at once. Some significant factors that influence the adsorption and subsequent plant absorption of Ni from soil are the pH, cation exchange capacity, and $CaCO_3$ content of the soils. Soil pH is the main factor affecting on Ni solubility, mobility, and sorption, while clay content, Fe and Mn oxides, and soil organic matter (OM) being in the secondary of significance (Anderson and Christensen 1988; Ge *et al*., 2000; Suavé *et al*., 2000; Tye *et al*., 2004; Iyaka 2011). Tahervand and Jalali (2016) reported that the sorption of Ni showed the predictable trend of increased metal sorption with increasing equilibrium pH (the minimum and maximum sorption of them occurred at pH 2 and 8, respectively in all soils). According to some observations, especially at high pH levels, sorption of Ni is very hysteric and sorbed Ni is difficult to remove from the soil matrix (Liao, 2010). Increased level of $CaCO_3$ content in used soils significantly increased the adsorption of pollutant (Ni, Pb and Cr) regardless the concentration used, this result was observed the increasing of the rate constants of used models (Mourid, 2014). According to the GIS and GPS survey, 7.16 % of soils in the Mirzapur district were Ni deficient. However, the largest deficiency was found in Sikhar (31.67 %), followed by Kon (27.78 %), and Majhawa (24.32 %). However, Sant Ravidas Nagar (22%) has the largest potential threat, followed by Mirzapur (19%) (Singh and Patra 2020). Adsorption and desorption of Ni in deficient is not studied yet under Indian conditions. As the soils of Sikhar block are deficient in nickel it is important to know the exact sorption mechanism and the factor that affect the sorption of nickel in the soil. In this consideration an experiment was done to know the effect of calcium carbonate, pH and time on the adsorption and desorption of Ni in soils of Sikhar block**.**

MATERIAL AND METHOD

Soil samples collected from the Sikhar block of Mirzapur district (with latitude 23.52º to 23.32º and longitude 82.72º to 83.33º) located in Uttar Pradesh district deficient in nickel. Soil samples were ground, air dried, and passed through a 2 mm sieve. Utilizing accepted techniques, processed soil was used to identify a few specific soil qualities. The hydrometer method was used to evaluate the mechanical composition of soils (Bouyoucos (1962), and a 1:2 soil: water suspension was used to determine the pH of soil samples (Spark (1996). The wet oxidation method (Walkley and Black 1934) was used to determine the amount of organic carbon in the soil.

Experiment procedure: For sorption study, 20 mL of 0.01 M $Ca(NO_3)_2$ solution containing $NiSO_4.6H_2O$ (10.0 mg/L Ni) with different pH values from 1 to 12 and 1 gm of soil sample were transferred in the duplicate into 60 mL polypropylene centrifuge tubes . For calcium carbonate different amount was taken for sorption (0.25, 0.5, 1.0, 1.5 and 2.0) and added to the 1gm soil prior adding nickel sulphate solution. A wrist action shaker was used to shake the tubes for 24 hours. 10 mL aliquot of the clear supernatant from centrifuging the suspension was obtained, and it was filtered through Whatman No. 42 filter paper. AAS was used to determine nickel. According to the Datta and Bhadoria (1999), protocol, the desorption of Ni was started for each sorption soil suspension by substituting the removed 10 mL aliquot with a Ni-free 0.01 M $Ca(NO_3)_2$ solution . The mixture was stirred ferociously for 24 hours on a wrist action shaker to achieve equilibrium. A 10 mL sample of the crystal-clear supernatant solution from the centrifuged suspension was taken for Ni analysis. For the kinetic adsorption tests, a fixed soil dosage of 1 gm and 20 mL of $NiSO_4.7H_2O$ solution were placed in a 60 mL centrifuge tube and agitated in a rotary shaker at a speed of 180 rpm at 25° C.10 mL aliquot of the clear supernatant from centrifuging the suspension was obtained at various time intervals, and it was filtered through Whatman No. 42 filter paper. AAS was used to determine nickel content in filtrate.

The amount of adsorption q (mgkg^{-1}) can be calculated as

$q = (Cinit - Ceq) * V / M * 1000$

Where Cinit and Ceq are the initial concentration and equilibrium concentration of Ni, respectively (mg L^{-1}), V is the volume of aqueous phase (mL), and M (g) is the mass of soil.

Desorbed Ni = Equilibrium Ni at desorption-Equilibrium Ni before desorption/2.

Table 1: Showing initial properties of soil.

Soil texture	Sandy Clay Loam
pH	7.63
Organic Carbon (%)	0.55 %
$CaCO_3$ (%)	15 %
DTPA Ni (ppm)	0.175

RESULT AND DISCUSSION

A. Kinetics of adsorption

The results of kinetic adsorption of Ni are presented in Fig. 1. As shown in this figure the adsorption Ni was slow during the initial hours but it increases as the time increased from 5 to 10 hours but slowly. After 10 to 15 hours the increase in adsorption of nickel was high but as the time increased up to 24 hours adsorption is nearly completed and no more adsorption is there. This happened as the soil is deficient in Ni increasing the time occupied the vacant sites in the soil and as time increases the no of vacant sites were occupied due which no more adsorption of Ni took place in the soil system. Ni will eventually adsorb on the surfaces of the interiors of small pores as time goes on. In the meanwhile, a chelate or stable complex is formed; this will lead to slower adsorption rate. The similar, thing reported by Xie *et al*. (2018) in copper. The kinetic model is used to evaluate the adsorption process' mechanism. Here, we adopted the intraparticle diffusion model and the pseudo-second order model for the kinetic adsorption. The pseudo second order kinetic model, which is depicted in Fig. 1, had the best fit to this data. Its coefficient of determination (R^2) was 0.9944. The pseudo-second order (PSO) kinetic model is represented by $t\ qt = 1/q_e^2K_4 - t/q_e$ where K_4 is the pseudo-second order rate constant for sorption and qt(mg kg^{-1}) is the amount adsorbed at time(t) (Ho and Mckay, 2003).Values of q_e and K_4 can be obtained by plotting t/qt vs t, where q_e is the slope and K_4 is the intercept. For this model, the sorption process is controlled by chemisorption, and the sorption capacity is controlled by the number of active sorption sites. Between adsorbates and adsorbents, electrons are shared or transferred as part of this chemisorption action. The intraparticle diffusion model was depicted in Fig. 2, and its coefficient of determination (R^2) sis 0.831. The intraparticle diffusion model, which was developed from Fick's second law of diffusion (Lin *et al*., 2009; Zhang and Stanforth, 2005), is represented as follows: $qt = C_1 + K_1t^{1/2}$, where C_1 is an intercept constant indicating the effect of boundary layer to adsorption and K_1 is an intraparticle diffusion rate constant. Values of K_1 and C_1 are calculated from the plot of t/qt against $t^{1/2}$.

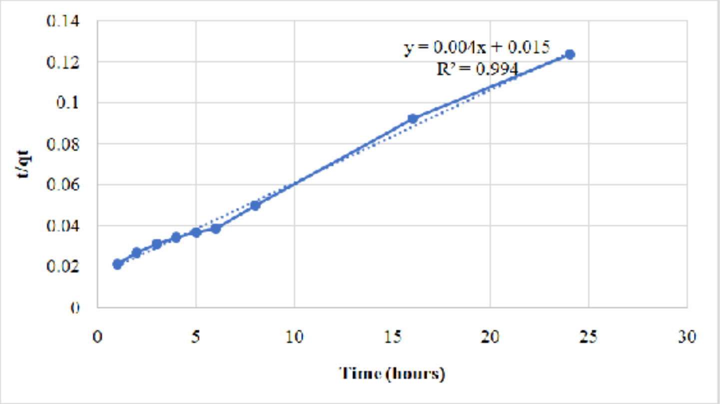

Fig. 1. Pseudo second order kinetic model for Ni in soil.

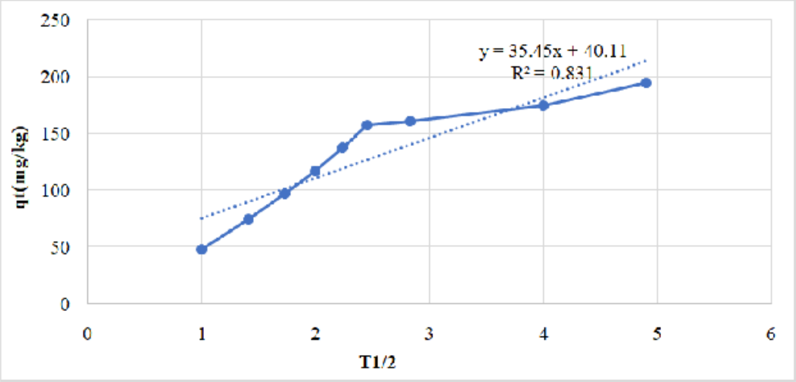

Fig. 2. Intraparticle diffusion kinetic model for Ni in soil.

Table 2: Fitting parameter of kinetic model.

Pseudo second order Kinetic model			**Intraparticle diffusion Kinetic model**		
$t\ qt = 1/q_e^2K_4 - t/q_e$			$qt = C_1 + K_1t^{1/2}$		
q_e	K_4	r^2	C_1	K_1	r^2
222.22	0.00131	0.9944	40.11	35.46	0.831

B. Effect of pH on Ni adsorption and desorption

Several experiments at pH levels of 2, 4, 6, 8, 10, and 12 were carried out to investigate the effect of pH on Ni adsorption. During initial phase adsorption was slow but as the pH rises the adsorption of Ni increased. Several viewpoints can be used to comprehend this feature. First off, a low pH concentration causes a high H^+ content, which causes soil minerals to dissolve and release ions like Mg(II), Fe(II), and Al(III) (Ozdemir and Yapar 2009). Second, the surface groups become protonated at low pH levels. As a result, it will generate a positive surface charge that might make it harder to combine with the Ni ion. Thirdly, with an increased pH, Ni ions may hydroxylate in the soil and change their ionic state. The amount of H^+ drops with an increase in pH, which causes more hydroxyl groups to interact with soil particles and speed up adsorption. The rate of adsorption ceases to rise once the soil's negative charge groups have reached equilibrium with Ni ions. Similarly, the result for desorption showed that as the pH increased the desorption of Ni decreased, this is due to fact as the pH increases negative charges increased on the surface of soil particles which resulted in less desorption of Ni ions from soil sites.

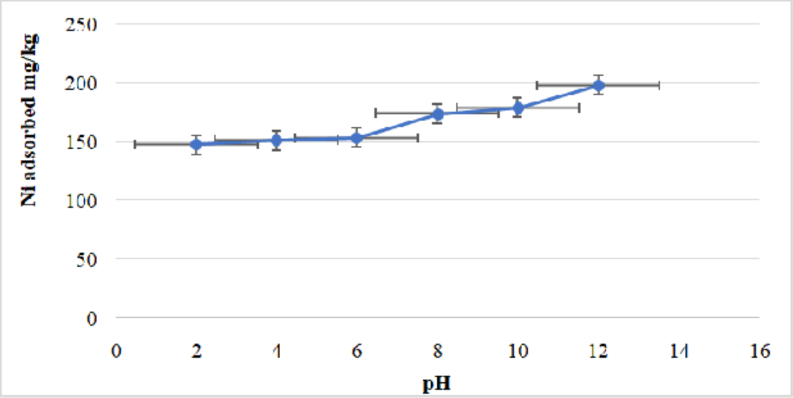

Fig. 3. Effect of pH on adsorption of Ni.

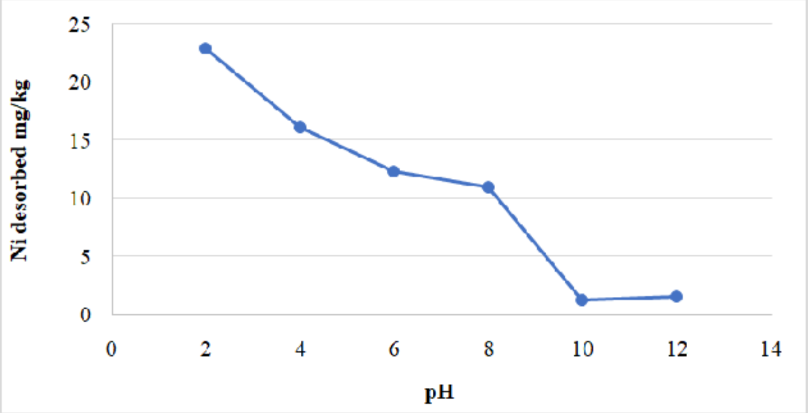

Fig. 4. Effect of pH on desorption of Ni.

C. Effect of Calcium carbonate on adsorption and desorption of Ni

An experiment were carried out using various amounts of $CaCO_3$ content, including 0.25, 0.50, 1, 1.5, and 2.0g, in order to examine the influence of $CaCO_3$ on Ni adsorption. The result from the Fig. 3 showed that as the amount of $CaCO_3$ content increased in the soil the adsorption of Ni increased in the soils specially during the initial phase the adsorption was slow but as $CaCO_3$ content increased from 1.0 to 2.0 g the adsorption of Ni increased at the faster rate. This happened due to the fact at higher $CaCO_3$ content the adsorption of Ni takes place on the surface of $CaCO_3$ as well as on the soil particles. Also carbonate may increase the soil pH due to which adsorption of Ni increased. Also, the result showed that Ni concentration adsorbed on calcareous soils was higher than Cd in the case of used (Cd & Ni) as a test solution (Mourid, 2014). Also during desorption the amount of Ni desorbed decreased when $CaCO_3$ content increased in the soil, which was shown in Fig. 4. This decrease may be due to fixation of Ni on the surface of $CaCO_3$ and soil particles.

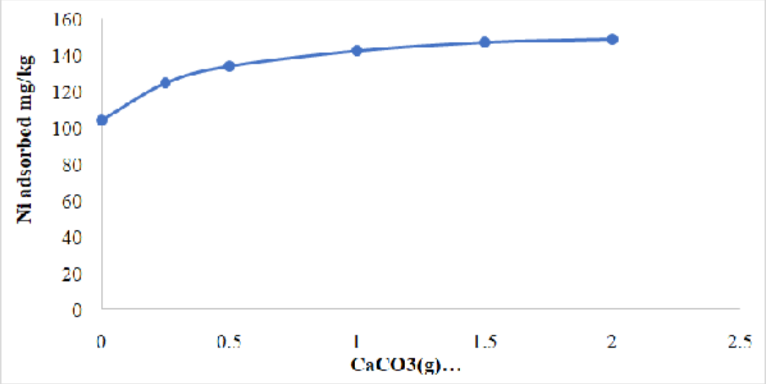

Fig. 5. Effect of $CaCO_3$ on adsorption of Ni.

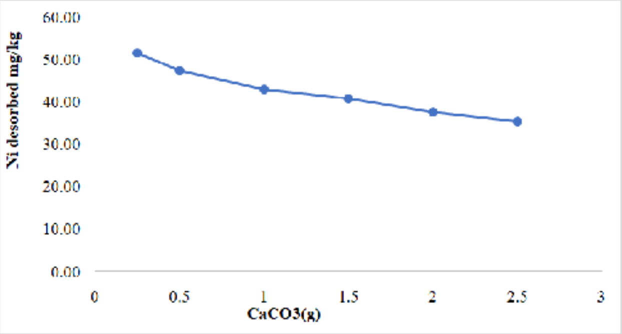

Fig. 6. Effect of $CaCO_3$ on desorption of Ni.

CONCLUSION

The study showed that the pH, $CaCO_3$ and time has effect on the adsorption and desorption of nickel. As the pH increased or decreased in the soil system the availability of nickel is affected which is showed at different pH conditions, similarly with $CaCO_3$ content? As the time has also influenced the adsorption of Ni as the time increased the adsorption of nickel increased with further saturation at longer interval. From this study sorption pattern of nickel can be clearly understood and the factors affecting it. This study would help us in understanding the factors that affect the nickel adsorption and how it can be used up by the plant.

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Conflict of Interest. None.

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