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Review

Adsorption study: A systematic approach to determine zinc availability in soils of divergent characteristics

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Imbalanced nutrient applications have resulted in failure of nutrient addition to keep pace with nutrient removal by crops especially in case of zinc (Zn). This resulted in productivity decline and malnutrition in humans due to their dependence of crops grown on these soils. This can be better solved by nutrient management practices as once the fertilizer is applied, it becomes available to the crop according to the Le chatelier's principle of chemical equilibrium but Zn being heavy metal, it is necessary to access the sorption characteristics of soils for healthy recommendation of Zn fertilization in soils of divergent characteristics. Due to paradigm shift of soil-plant-human from soil-plant study with respect to micronutrient malnutrition, the sorption study is gaining importance in recent research.

Key words: Zn fertilization, sorption characteristics, malnutrition, soil, nutrient, crops.

INTRODUCTION

Zinc supplying power of soil, extraction by leaching and uptake by plant roots depends essentially on the amount of zinc present at sorption sites (Sidhu et al., 1977; Joshi et al., 1983). Jurinak and Bauer (1956), classified zinc sorption into two types (i) non-specific sorption which occurred due to electrical attraction by active surface sites, and (ii) specific sorption which occurred as a result of strong chemical bond at nonorganic soil colloidal surfaces. In the later type of sorption, Zn^{2+} replaces O^{-2} and OH^{-1} ions in inter crystal structure of oxides and hydroxides (Shuman, 1977; Kalbasi et al., 1978).

Zinc sorption by soils can be influenced by soil reaction (Dahiya et al., 2005; Arias et al., 2005; Singh et al., 2008; Zahedifar et al., 2010; Pérez-Novo et al., 2011), clay content (Dahiya et al., 2005), clay minerals type (Dahiya et al., 2005), organic matter (Dahiya et al., 2005; Perez-Novo et al., 2008), total carbonate and active carbonate content (Al-Kaysi, 2000), amount of zinc applied and zinc carrier (Obrador et al., 2003). Zinc (Zn) sorption may also be affected by chemical composition of soil solution (Wang and Harrell, 2005; Zhao et al., 2010), ionic strength (Shuman 1986), ionic solution composition (Wang and Harrell, 2005; USDA-NRCS, 1996) and complex formation with inorganic ligands in soil solution (Mattigod and Sposito, 1977). Al-Hadethi et al*.* (2001) mentioned that extractable Zn recovered from the added were negatively correlated with clay content, CEC, $CaCO_3$, soluble calcium, and soluble magnesium. Zinc solubility also controlled by other reactions in soil such as mineral precipitation or adsorption onto Fe or Mn oxides (Catlett et al.*,* 2002) and phosphate-Fe oxides interactions (Wang and Harrell, 2005).

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Factors Affecting Zinc Adsorption in Soils

pH

The solubility of all Zn minerals decreases 100-fold for each unit increase in pH. Soil pH has been identified in many studies as one of the main factors affecting zinc mobility and sorption in soils (Pierangeli et al., 2003). Zinc becomes more soluble as pH decreases, therefore zinc is more mobile and increasingly available in low pH environments, especially below pH 5 (Duquette and Hendershot, 1990). At pH <7.7, zinc occurs as Zn^{2+} in soil solution, whereas at pH >7.7, the dominant form is $Zn(OH)_2$ (Giordano and Mortvedt, 1980). At higher pH values, it forms low solubility complexes with carbonate and hydroxyl ions (McGowen et al., 2001). Increasing soil pH increases the total number of negative sites on clay-minerals and organic matter, thereby increasing the capacity for Zn sorption (McBride, 1989). Saha et al. (2001) showed that the adsorption of Zn and Cd on the hydroxyaluminum- and hydroxyaluminosilicate-montmorillonite complexes is very strongly pH-dependent. Substantial fractions of these two metals were also adsorbed on complexes with a pH below 5. As the pH rose above 5, Cd and Zn adsorption on the complexes steeply increased, reaching plateau levels of almost 100% when the pH was between 6 and 7.

Soil pH exercised the largest influence on Zn buffer power (Dang et al., 1994); with increase in pH, zinc buffer power increased tremendously.

Type of clay mineral

It has been proven by many studies that among soil clay minerals, smectites have the greatest adsorption affinity to Cu and Zn (Helios-Rybicka et al., 1995; Shukla, 2002). Gypsiferous soils exhibited greater Zn adsorption than calcareous and acid soils (Hashemi and Baghernejad 2009). The high adsorption of Zn by gypsiferous soils could be related to the presence of a palygorskite mineral with a large surface area, but for acid soils with high contents of kaolonite and illite minerals, minimum Zn sorption was observed.

Hydrous Oxides

Zinc sorption capacity correlates with soil contents of aluminosilicate clays, metal oxides and carbonates (Kalbasi et al., 1978, Saha et al., 2001). The interaction between Zn and Fe or Al oxides through the formation of a covalent bond with surface aqua and/or hydroxy groups has been cited as the major mechanism of Zn retention by acid soils (Bolan et al., 1999; Kalbasi et al., 1978, McBride, 1989). However, Zn sorption by $CaCO_3$ and precipitation as Zn hydroxide or Zn hydroxyl carbonates control Zn solubility in calcareous soils (Papadopoulos and Rowell, 1989).

Presence of cations and anions

The presence of Na^+ increased total Zn adsorption as opposed to K^+ in all soils (Hashemi and Baghernejad, 2009). Wang and Harrell (2005) showed that NH_4^+ and K^+ equally decreased Zn sorption as opposed to Na^+ in acid and calcareous soils; NH_4^+ yielding 4 to 12% more adsorbed Zn in the labile pool as compared to K^+ in acid soils. They showed that the effect of background ions on the lability of adsorbed Zn varied between acid and calcareous soils. According to Bolland (1997), high rates of P addition may increase Zn sorption on soils dominated by variable charge surfaces by increasing the net negative charge on the surface.

Amount of clay

Absorption and adsorption are two properties related to the surface area of clay minerals. The bio-availability of trace elements including Zn, decrease with the clay mineral content in soils (Sipos, 2003). Zinc may be irreversibly fixed by clay through isomorphus substitutions or solid-state diffusion into the crystal structure of layer silicates.

Ionic strength

The effect of major cations and ionic strength on the chemistry of Cd, Cu, and Zn in alkaline sodic and acidic soils has been investigated by (Fotovat and Naidu, 1998). Increase in ionic strength decreased Zn retention in acid soils but did not have any significant effect in calcareous soils (Shuman, 1986).

Buffering capacity

Activity of zinc ions in the ambient soil solution bathing plant roots is controlled by simultaneous equilibra of several competing reactions such as specific bonding, surface exchange, lattice penetration, precipitation reaction and the processes leading to desorption of surface and lattice bound ions. Characterization of the solid phase supply of zinc in relation to surface chemical reaction provides the net effect of all simultaneous equilibra controlling the activity of zinc ions in the ambient soil solution. This enables calculations of parameters such as quantity, intensity and buffering capacity of the soil, which when combined into a united expression, called a supply parameter, can be related to the uptake of zinc by crops (Khasawneh and Copeland, 1973). In other words, the buffering capacity of a soil for adsorption-desorption processes usually affects quantity, intensity and kinetic parameters, which determine the capacity of the soil to supply plant nutrients. Attempts have been made to relate the growth and nutrition of crops to changes in these factors in soils (Maskina et al., 1980). The three mutually dependent factors namely quantity, intensity and buffering capacity may be integrated using linear form of Langmuir equation into an unifying term called supply parameter has been shown to adequately describe the zinc supplying capacity of soils (Sidhu et al., 1977; Sinha et al.,1975). Appreciable fractions of total soluble zinc may be in equilibrium with specially adsorbed forms associated with insoluble organic matter (Bourg, 1995; McBride, 1989). The hydrolysis constant of zinc is $10^{-9.6}$ so at pH greater than 7.0 the hydrolyzed species $Zn(OH)^+$, $ZnHCO_3^+$, $Zn(OH)_3^-$ will be present in sufficient amounts relative to Zn^{2+} to be important in adsorption reactions. In the same way, the hydrolysis process favours chemisorption by allowing zinc to interact with the surface as a monovalent cation (Stahl and James, 1991). The rate of zinc sorption from solution to solid surfaces is a dynamic factor that directly or indirectly regulates the amounts of Zn in solution and its availability (Taylor et al., 1995). Diatta and Kocialkowski (1997) concluded that with the addition of increasing amounts of zinc there was a simultaneous increase in the equilibrium concentration, adsorption, and percent saturation of adsorption capacity and supply parameter of zinc. Also, through multiple regression analysis revealed that in all soils quantity, intensity and equilibrium concentration were the main parameters accounting for the supply of zinc. Further, Karimian and Moafpourian (1999) and Reyhanitabar et al. (2007) reported a range of maximum buffering capacity, 309 to 3509 for the calcareous soils of southern Iran and 212.7 to 625.0 for the calcareous soils of central Iran. Maskina et al. (1980) reported that a value of supply parameter around unity is optimum for sustaining proper growth and zinc nutrition of rice in paddy growing soils of India.

Adsorption Isotherms

Adsorption isotherms can be used to describe the equilibrium relationship between the amounts of adsorbed and dissolved species at a given temperature taking into account intensity, quantity and capacity factors, which are important for predicting the amount of soil nutrient required for maximum plant growth. Langmuir isotherm has been shown to be suitable for Zn adsorption studies (Pombo and Klamt, 1986; Machado and Pavan, 1987; Cunha et al., 1994; Nascimento and Fontes, 2004; Arias et al., 2005).

Adsorption of zinc in paddy growing soils of India conformed to the Langmuir adsorption isotherms (Maskina et al., 1980; Dhillon et al., 1975; Sinha et al., 1975). According to their reports, the order of variation of adsorption maxima in paddy growing soils was as follows: Bhatinda sandy loam>Pantnagarsilty clay loam>Ferozepur sandy loam>Jabalpur sandy loam>Hoshiarpur sandy loam>Ferozepur sand; adsorption maxima of Zn increased with increase in clay content of soils. Further reported that bonding energy constant (K) and the differential buffering capacity of zinc showed wide variations among soils. Soil texture and pH were evidently the important factors influencing the variations in the parameters of Zn retention in these soils.

In a laboratory study undertaken with concentrations between 0 to 50 mg Zn l^{-1} to determine the zinc retention and release capacity of a Rhodic Khandiustult was carried by Anyika et al. (2010). They found that the amount of zinc released in the Ap horizon was slightly more than that released in the Bt horizon, that is Zn was more difficult to release in the Bt horizon than in the Ap horizon. They also reported that adsorption data did not fit the linear form of either the Langmuir or Freundlich isotherms. But findings of several other workers regarding zinc adsorption in soils with divergent characteristics showed good fit to either Langmuir or the Freundlich isotherms (Al-Tamimi, 2006; Ashraf et al., 2008; Hashemi and Baghernejad, 2009; Gurpreet-Kaur et al., 2012). Failure of zinc adsorption data to conform to the linear Langmuir equation has been attributed to the existence of more than one type of zinc adsorbing sites.

Evaluation of thermodynamic parameters provide an insight into mechanism of Zn sorption in the soils. Adsorption increases with increasing temperature due to the increase in number of active sites (Yavuz et al., 2003; Bouberka et al., 2005). Thus, thermodynamic approach may be used to predict the final state of metal in the soil system from an initial non-equilibrium state (Jurinak and Bauer, 1956; Sposito, 1984). Evaluation of the free energy change corresponding to the transfer of element from bulk solution into the appropriate site of the double layer or clay mineral lattice are helpful to express the sorption process.

Adhikari and Singh (2003) showed that the high values of ΔG^o both for Pb and Cd indicated that both reactions are spontaneous. Also, the values of ΔH^o were negative for Cd and positive for Pb, indicating that Cd sorption reaction was exothermic while Pb sorption was endothermic in all the soils. The values of ΔS were found to be positive due to the exchange of the metal ions with more mobile ions present on the exchanger, which would cause increase in the entropy, during the adsorption process (Unlu and Ersoz, 2006). Dandanmozd and Hosseinpur (2010) studied Zn sorption using linear, Freundlich, Temkin and D-R models. They found that the values of K^o increased with rise in temperature from 25 to 45 °C in all the soils. The ΔG^o values at 25 and 45 °C were negative and ranged from -7.00 to -16.64 and -13.24 to-41.93 kJ mol^{-1}, respectively. The values of ΔH^o and ΔS^o were positive and ranged from 357.47 to 74.02 kJ mol^{-1} and 1255.97 to 281.79 J mol^{-1} K^{-1}**,** respectively. The values of ΔG^o to be negative indicated Zn sorption to be spontaneous and ΔH^o positive showed Zn sorption to be endothermic. Similar findings were also reported by (Biggar and Cheung, 1973; Adhikari and Singh 2003; Dali-youcef et al., 2006; and Unlu and Ersoz 2006. Zinc sorption increased with rise in temperature because of increase in the values of K^o, ΔG^o, ΔH^o and ΔS^o.

CONCLUSIONS

In this article, we reviewed the adsorption characteristics of Zn in soils. The adsorption behavior of Zn to soil is complicated due to number of factors affecting its availability, hence a clear understanding is very much necessary to overcome the Zn deficiency in crops and in turn in animals and humans as these crops are their daily food. This review article also focused on the thermodynamic parameters as they provide the insights of Zn sorption mechanisms in soil.

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