Review

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

Girija Veni V., Rattan R.K and Datta S.P

Indian Agricultural Research Institute, New Delhi-110012, India.

Accepted 07 October, 2013

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, Zn²⁺ 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, CaCO₃, 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).

Factors Affecting Zinc Adsorption in Soils

рΗ

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 Zn²⁺ 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 clayminerals 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 CaCO₃ 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.

lonic 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 adsorptiondesorption 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 I^{-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 (AI-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° both for Pb and Cd indicated that both reactions are spontaneous. Also, the values of ΔH° 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° 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° and ΔS° 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° to be negative indicated Zn sorption to be spontaneous and ΔH° 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° , ΔG° , ΔH° and ΔS° .

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.

REFERENCES

Adhikari T, Singh MV (2003). Sorption characteristics of

lead and cadmium in some soils of India. Geoderma (114): 81-92.

- Al-Kaysi SCh (2000). Effect of physical and chemical properties of carbonate minerals in some Iraqi soils in zinc fixation. 1: Properties of carbonate minerals. Iraqi J. Agric. Sci. (30): 53-72. (in Arabic).
- Al-Tamimi RA (2006). Zinc sorption by some Torrifluvents of sub-Saharian region south of Libya. Emirates J. Agric. Sci. (18): 1-10.
- Anyika CC, Ninyo A, Kparmwang T (2010). Sorptiondesorption of Zn by a RhodicKhandiustult in the northern guinea Savanna of Nigeria. Continental J. Agronomy (4): 15-22.
- Arias M, Perez-Novo C, Osorio F, Lopez E, Soto B (2005). Adsorption and desorption of copper and zinc in the surface layer of acid soils. J. Colloid Interface Sci. (288): 21-29.
- Ashraf MS, Ranjha AM, Yaseen M, Ahmad N, Hannan A (2008). Zinc adsorption behaviour of different textured calcareous soils using Freundlich and Langmuir models. Pakistan J. Agric. Sci. (45): 6-10.
- Biggar JW, Cheung MW (1973). Adsorption of picloram (4-Amino-3,5,6-Trichloropicolinic acid) on panocheephrata, and palouse soils: A thermodynamic approach to the adsorption mechanism. Soil Science Society of America Proceedings (37): 863- 868.
- Bolan NS, Naidu R, Syers JK, Tillman RW (1999). Surface charge and solute interactions in soils. Adv.Agron. (67): 87–140.
- Bolland MDA (1997). Comparative phosphorus requirement of canola and wheat. J. Plant Nutr. (20): 813-829.
- Bouberka Z, Kacha S, Kameche M, Elmaleh S, Derriche Z (2005). Sorption study of an acid dye from an aqueous solutions using modified clays. J. Hazard. Mater (119): 117-124.
- Bourg ACM (1995). Mobility of heavy metals in agricultural soils following long-term land application of sewage sludge from the Paris-Acheres water treatment plant. International Conference on Heavy metals in the Environment, Hamburg (1): 252-255.
- Dahiya S, Shanwal AV, Hedge HAG (2005). Studies on the sorption and desorption characteristics of Zn(II) on the surface soils of nuclear power plants sites in India using a radiotracer technique. Chemosphere (60): 1253-1261.
- Dali-youcef N, Oddane B, Drriche Z (2006) Adsorption of zinc on natural sediment of Tafna River. J. Hazard. Mater. (137): 1263–1270.
- Dandanmozd F, Hosseinpur AR (2010). Thermodynamic parameters of zinc sorption in some calcareous soils. J. Ameri. Sci. (6): 1-7.
- Dhillon SK, Sinha MK, Randhawa NS (1975). Chemical equilibria and Q/I relationship of zinc in selected alkali soils of Punjab. J. Indian Soc. Soil Sci. (23): 38-47.
- Diatta J, Kocialkowski W (1997). Adsorption of zinc in some selected soils. Pol.J. Environ. Stud. (7): 195-200.

- Fotovat A, Naidu R (1998). Changes in composition of soil aqueous phase influence chemistry of indigenous heavy metals in alkaline sodic and acidic soils. Geoderma (84): 213–234.
- Giordano PM, Mortvedt JJ (1980). Zinc uptake and accumulation by agricultural crops. In: Zinc in the Environment, **Part II**, Health Effects (J.O. Nriagu, Ed.) John Wiley and Sons, New York.
- Gurpreet-Kaur, Sharma BD, Sharma P (2012). Zinc adsorption as affected by concentration, temperature, and time of contact in the presence of electrolytic and aqueous medium in benchmark Soils of Punjab in Northwest India. Comm. Soil Sci. Plant Anal. (43): 701-715.
- Hashemi SS, Baghernejad M (2009). Zinc sorption by acid, calcareous and gypsiferous soils as related to soil mineralogy. Iran Agric. Res. (28): 1-16.
- Helios-Rybicka E, Calmano W, Breegwer A (1995). Migration of Cu ions in Cu-montmorillonite heated with and without alkali halides. Clays Clay Miner (43): 738-743.
- Joshi DC, Sharma BK, Dhir RP (1983). Studies on the adsorption of Zn by fine textured alluvial soils of arid Rajasthan. Clay Res. (2): 39-45.
- Jurinak JJ, Bauer N (1956). Thermodynamics of zinc adsorption on calcite, dolomite and magnesite type minerals. Soil Sci. Soc. Am. Proc. (20): 466-471.
- Kalbasi M, Racz GJ, Lowen- Rudgers LA (1978). Mechanism of zinc adsorption by iron and aluminum. Soil Sci. Soc. Am. J. (39): 464-470.
- Karimian N, Moafpourian GR (1999). Zinc adsorption characteristics of selected soil of Iran and their relationship with soil properties. Commun. in Soil Sci. Plant Anal. (30): 1722-1731.
- Khasawneh FE, Copeland JP (1973). Cotton root growth and uptake of nutrients.Relation of phosphorus uptake quality, intensity and buffering capacity.Soil Sci. Soc. Am. Proc. (37): 250 -254.
- Maskina MS, Randhawa NS, Sinha MK (1980). Relation of growth and zinc uptake of rice to quantity, intensity and buffering capacity factors of zinc in soils. Plant Soil (54): 195-205.
- Mattigod SV, Sposito G (1977). Estimated association constants for some complexes of trace metals with inorganic ligands. Soil Sci. Soc. Am. J. (41): 1092-1097.
- McBride MB (1989). Reactions controlling heavy metal solubility in soils. Adv. Soil Sci. (10): 1-55.
- McGowen SL, Basta NL, Brown, GO (2001). Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter contaminated soil. J. Environ. Qual. (30): 493-500.
- Obrador A, Novillo J, Alvarez M (2003) Mobility and availability to plants of two zinc sources applied to calcareous soil. Soil Sci. Soc. Am. J. (67): 564-572.
- Papadopoulos P, Rowell OL (1989). The reactions of Cu

and Zn with calcium carbonate surface. J. Soil Sci. (40): 39-48.

- Pérez-Novo C, Fernández-Calviño D, Bermúdez-Couso A, López-Periago JE, Arias-Estévez M (2011). Phosphorus effect on Zn adsorption-desorption kinetics in acid soils. Chemosphere (83): 1028-1034.
- Perez-Novo C, Pateiro-Moure M, Osorio F, Novoa-Munoz JC (2008). Influence of organic matter removal and competitive and non-competitive adsorption of copper and zinc in acid soils. J. Colloid Interface Sci. (322): 33-40.
- Reyhanitabar A, Karimian N, Ardalan M, Savaghebi G, Ghannadha M (2007). Comparison of five adsorption isotherms for prediction of zinc retention in calcareous soils and the relationship of their coefficient with soil characteristics. Commun. Soil Sci. Pant Anal. (38): 147-158.
- Saha UK, Tanjguchi S, Sakurai S (2001). Adsorption behavior of Cd, Zn, and Pbonhydroxyaluminum-and hydroxyaluminosilicate-montmorillonite complexes. Soil Sci. Soc. Am J. (65): 694-703.
- Shukla LM (2002). Sorption of Zn and Cd on soil clays. Agrochemica. (44): 101-106.
- Shuman LM (1986). Effect of ionic strength and anions on Zn sorption by two soils. Soil Sci. Soc. Am. J. (50): 1438-1442.
- Shuman LM (1977). Adsorption of Zn by Fe and Al hydrous oxides as influenced by aging and pH. Soil Sci. Soc. Am. J. (41): 703-706.
- Sidhu AS, Randhawa NS, Sinha MK (1977). Adsorption and desorption of zinc in different soils. Soil Sci. (124): 211-218.
- Singh D, Ronald G, Mclaren, Cameron KC (2008). Effect of pH on Zinc Sorption–Desorption by Soils. Commun. Soil Sci. Plant Anal. (39): 2971-2984.
- Sinha M K, Dhillon SK, Pundeer GS, Randhawa NS, Dhillon KS (1975). Chemical equilibria and Q/I

relationship of zinc in some acid soils of India.Geoderma (13): 347-362.

- Sipos P (2003). Distribution of Cu, Ni, Pb and Zn in natural brown forest soil profiles from the Cserhat Mts., Ne Hungary. Acta Mineralogical- Petrografica, (44): 43-50.
- Sposito G (1984). The Surface Chemistry of Soils. Oxford Univ. Press, New York, USA.
- Stahl SR, James BR (1991). Zinc sorption by B horizons soils as a function of pH. Soil Sci. Soc. Am. J. (55): 1592.
- Taylor RW, Hassan K, Mehadi AA, Shuford JW (1995). Zn sorption by some Alabama soils. Commun. Soil Sci. Plant Anal. (26): 993–1008.
- Unlu N, Ersoz M (2006) Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. J. Hazard. Mater. (136): 272– 280.
- USDA-NRCS (1996). Soil survey laboratory methods manual. Soil Survey Investigations Report No. 42. v. 30. U.S. Gov. Print. Office, Washington, DC.
- Wang JJ, Harrel, DL (2005). Effect of ammonium, potassium and sodium cations and phosphate, Nitrate, and chloride anions on Zn sorption and lability in selected acid and calcareous soils. Soil Sci. Soc. Am. J. (69): 1036-1046.
- Yavuz O, Altunkaynak Y, Guzel F (2003). Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. Water Res. (37): 948–952.
- Zahedifar M, Karimian N, Yasrebi J (2010). Zinc desorption of calcareous soils as influenced by applied zinc and phosphorus and described by eight kinetic models. Comm. Soil Sci. Plant Anal. (41): 897-907.
- Zhao, Keli, Selim HM (2010). Adsorption-desorption kinetics of Zn in soils: influence of phosphate. Soil Sci. (175): 145-153.