Egypt. J. Soil Sci. **44**, No. 2. pp. 185- 199 (2004)

Zinc Sorption on Organic Treated Soils

H. M. El-kouny
Soil Salinity and Alkalinity Research Department, Alexandria; Soil, Water and Environment Research Institute, Agricultural Research Center (ARC), Cairo, Egypt.

FIVE COMPOST organic materials namely farm animal manure (AMC), farm different plant residues (PRC), mixture of AMC/PRC), farm poultry manure (PMC) and humic substance (HS) and an alluvial and calcareous soils were used in this study. Organic material/ soil system for each was prepared to evaluate Zn sorption by the different OM/soil systems.

The data showed that Zn sorption by these OM/soil systems increased with pH increase up to pH 8 .The different systems showed marked variations in their capacity for Zn sorption. The relative increase or decreases for Zn sorption at pH 8 were 45.5, 36.4, 18.2, 9.1and 54.5% for AMC/soil, PRC/soil, AMPRC/soil, PMC/soil and HS/soil with soil No.1 (alluvial), respectively. In the case of soil No.2 (calcareous), these values were –7.6,-7.6, -18.47,-72.8 and 45.65 %, respectively.

The data also showed that Zn adsorption isotherm followed the Langmiur equation especially at low Zn concentrations.

The values of adsorption maximum (b) were higher with AMC/PRC and the least with PMCand PRC/soil systems for both the alluvial and calcareous soil. However, the bonding energy or affinity (a) of OM/soil systems to Zn were higher with PMC/soil systems than AMPRC/soil system for the two soils. These results suggest that applying PMC manure to both alluvial and calcareous soil would improve soil Zn supply to plants.

Keywords: Compost, Animal manure, Plant residues, Poultry manure, Humic substance, Alluvial soil, Calcareous soil, Zinc, Sorption, Adsorption, Isotherm, Bonding energy, Langmiur equation.

Organic matter of soil has an important role in improving the fertility of soil. Because soil organic matter is consisting of various sources of organic materials, its role for affecting nutrients status in soil, especially micronutrients, is very complex. Since soils in Egypt are mostly poor in organic matter content and that vast areas of cultivated soils are suffering Zn deficiency (Elsokkary, 1974), the incorporation of organic fertilizers to soil could improve its physical and chemical properties and consequently its fertility. Therefore, several studies have been carried out in order to investigate the effect of organic material incorporated with soil or clays on Zn adsorption, sorption, mobility from Zn added to these systems (Shuman, 1975; Elsokkary, 1980; Waller & Pickering, 1997,and Alvarez *et al.*, 1997). Therefore, the objective of this study was to evaluate the effect of incorporation of different composted organic materials with alluvial or calcareous soil on Zn sorption capacity of these soil systems from applied $ZnCl_2$.

Material and Methods

Used soils

Two soil samples (0-20cm) were collected from two different regions. The first soil (soil No.1) was collected from Bahr El-Bakar region, EL-Sharkia Governorate and it is an alluvial soil. The second soil (soil No.2) was collected from El– Noubriya region and it is calcareous soil . The two soils were air-dried, ground finely and passed through 2 mm sieve and stored in polyethylene bags for the experimental studies. The main chemical and physical characteristics of the soils were determined according to the methods outlined by Page *et al.* (1982) and the results obtained are shown in Table 1 .

Used organic materials

Five composted organic materials were used in this study which included: (i) farm animals manure compost (AMC), (ii) farm different plants residues compost (PRC), (iii) Mixture of farm animals manure compost and farm different plants residues compost with 1:1 ratio (AMC/PRC), (iv)Farm poultry manure compost (PMC) and (v) humic substance (HS)obtained from AMC / PRC mixture. Each organic material was air-dried, ground finely and passed through 0.2mm sieve and stored in polyethylene bags for the experimental studies. The main chemical characteristics of the five organic materials were determined according to the methods reported by Inbar *et al.* (1990); Bertran & Andreas (1994) ; Kaloosh (1995) and El - Kouny (1999) and the results obtained are given in Table 2.

Preparation of organic material /soil systems

Organic material soil/ system (except HS) was prepared by mixing 12 gm organic material with 1 kg soil. This system was kept wet, with addition of distilled water to about 50% water holding capacity at room temperature ($20\pm3^{\circ}$). The soil organic material system was let to stand for 3 months at constant moisture content, then air-dried and ground to pass through 0.5 mm sieve and stored in polyethylene bags for the experimental studies. According to this technique, the obtained systems were (i) AMC /soil,(ii) PRC/soil , (iii) AMC-PRC/soil , (iv) PMC/soil.

TABLE 1. The main chemical and phyiscal characterstics of the used soils .

Soil parameter		Soil No.1	Soil No.2
EC *	dS /m	1.30	4.10
PH**		7.50	8.50
Na^+	meq /l	8.50	4.50
K^+	meq /l	1.00	1.50
Ca++	meq /l	1.90	33.50
Mg^{++}	meq /l	1.60	1.60
HCO^-_3	meq /l	3.50	3.50
CL^-	meq /l	6.90	32.00
SO^{--}_4	meq /l	2.60	5.50
O.M	%	4.75	1.75
CEC	meq/100gm	24.20	13.50
Total Zn	mg/kg	46.00	35.00
Total Carbonate	%	4.10	28.50
Particle size distribution:			
C. sand	%		
F. sand	%		
Silt	%	15.25	55.01
Clay	%	36.50	25.11
		12.75	4.48
Soil texture		35.50	15.40
		Loamy Clay	Sandy Loam

* Measured in water satured soil paste extract.
** Measured in 1:2.5 soil water suspension.

With respect to HS / soil system , 1 mg HS was mixed with 1 Kg soil. This system was treated as previously mentioned with respect to temperature, moisture content, preservation period, and storage. The main chemical characteristics of the obtained organic material / soil systems were determined according to the methods described by Schnitzer *et al.* (1981); Shuman (1985) and EL-Kouny(1999)

Zn sorption studies

Zn adsorption isotherm

One gram OM/Soil system was placed in a 50 ml centrifuge tube , an aqueous solution containing 15 ml 0.1M Ca Cl_2 and 15 ml Zn Cl_2 (1.0m MLZ) was added to the system. The pH of the system was adjusted as required by dilute solution of HCl or KOH . The suspension was shaken for 10 min using reciprocal shaker and then placed in water bath at 25 ^{0}C for 24 hr. The tubes were shaken for 10 min , centrifuged for 10 min , and the supernatant solution was filtered through Whitman filter paper No.42 . The concentration of Zn was measured in the filterate by atomic absorption spectrophotometer according to Li and Shuman (1997). The amount of Zn sorbed was obtained by the difference between Zn added and that measured in the supernatant solution. The same technique was used to investigate the effect of pH and Zn concentration on Zn sorption by OM/Soil systems . Each treatment was repeated in triplicates.

TABLE 2. The main chemical characteristics of the used organic materials .

Parameter	AMC	PRC	AMPRC	PMC	H.S
Bulk density (gm/m)	550	370	450	520	n.d.
PH*	6.31	7.11	6.71	6.65	8.45
EC** (ds/m)	6.06	3.79	4.89	5.51	n.d
O.C(%)	35.86	44.40	40.50	32.00	56.60
T.N(%)	2.65	2.05	2.86	3.12	1.40
O.M(%)	61.82	76.54	69.82	58.62	90.68
C/N ratio	13.53	21.65	14.16	9.97	40.50
CEC(meq/100g)	95.30	85.50	102.20	75.50	180.00
T-Zn(mg/kg)	250.00	90.00	170.00	325.00	25.00

* Measured in 1:10 organic material- water ratio (extract).

** Measured in 1:5 soil water ratio (suspension).

n. d. – not determined

Effect of pH on Zn adsorption

The above same procedure used with Zn sorption isotherm was followed. The required pH of the organic material/ soil system of the suspension was adjusted using either dilute HCl or dilute KOH . The tested pH range varied from 4 to 8 with constant Zn concentration of 1.0 mML^{-1} .The control treatment was carried out using only soil without Zn addition. Each treatment was repeated in triplicate

Effect of Zn concentration of Zn adsorption

Zinc sorption isotherm was carried out at a constant pH and with increasing Zn concentrations:(0.0, 0.1, 0.25, 0.50, 1.00, 2.0 and 4.00 mM^{-1}).The sorption procedure was as the same as followed with Zn sorption isotherm. The sorbed Zn was calculated as the difference between the Zn added and that measured in the supernatant solution. Each treatment was repeated in triplicates. The Zn sorption was examined for fitting the following Langmiur adsorption isotherm equation :

$$c/x/m = \frac{1}{ab} + \frac{1}{b} C$$

Where:

c/x/m : amount of Zn adsorbed

b: adsorption maximum constant

a: affinity constant (bondy energy)

The Langmiur coefficient was calculated and the treatment coefficient was separated using the homogeneity of slope test.

Results and Discussion

Effect of pH on Zn sorption

Table 3 shows the amounts of Zn sorbed by the different organic material/ soil systems. It is clear that Zn sorption had increased with increasing pH of these systems. It has been reported that Zn is probably retained on nonspecific sites throughout the pH range of soils (Harter, 1983). Also, Anderson and Chritensen (1988) showed that the pH is the most important in controlling Zn mobility in soils. Elssokkary (1980) found that high soil pH decreased the solubility of Zn and that the amount of sorbed Zn usually was high . Shuman (1980) has attributed that, at near-neutral alkaline pH, Zn is retained either to surface precipitation or sorption by soils .It has been also, reported that organic matter plays a major role in the soil retention of Zn (Shuman, 1980 & 1997, and Kabata-Pendias and Pendias, 1992) . However, organic complexation could lead to increased mobility in the soil since Zn is known to form stable complexes with fulvic acid (Kabata-Pendias and Pendias, 1992) .As shown in Table 3, increased Zn sorption occurred by organic material/ soil system. The increased sorption capacity of mineral soil organic system is attributed to exposed edges as well as to the presence of carboxylate and phenolic groups on the surfaces. Goh *et al.*, (1986) demonstrated decreased Zn sorption by semectite in the presence of fulvic acid. Evidenece of bonding mechanisms seems to be related to carboxylate groups, phenolic OH groups, and N pair electrons which are dominant sites (Stevenson & Fitch, 1981 and Fitch & Du,1996).

Table 3 showed that the untreated soil No.1 (alluvial; loamy clay soil) sorbed lower levels of Zn than soil No.2 (calcareous; sandy loam soil) especially at pHs 7 and 8. This could be due to the presence of higher portion of carbonate in soil No.2 and consequently to higher sorption sites for Zn. It can be suggested that chemosorption of Zn or combination of chemosorption and preciptation of Zn at high pHs (7,8) are the mechanisms increasing Zn sorption by these two soils. Pulford(1986) has argued that Zn reactions with soils involve both surface adsorption and a precipitation mechanisms. The highest sorption of Zn by soil No.2 (calcareous, sandy clay soil) is due to Zn co-precipitation with carbonate of soil (Jurinak and Bauer, 1956).

Figures 1and 2 showed that incorporating the organic materials with soils increased Zn sorption by the organic material/soil system at all pH values. It is clear that the effect of organic materials was more pronounced at all pH values. For soil No.1 and at pH 8, the incorporated HS/soil system sorbed the highest Zn level while PMC/soil system sorbed the lowest. The Zn sorption capacity of the different organic materials incorporated with No.1 can be arranged in the order: HS>AMC>PRC>AMPRC>PMC .It is clear that incorporation of PMC decreased Zn sorption by soil No.1 at pH 8 form 55 (the control soil) to 50mM/ kg (the PMC/soil system) . The selection of pH 8 for this comparison is due to that this value is dominant for alluvial Egyptian soils. In the case of soil No.2 (calcareous soil) it is clear from Fig. 2 that the untreated soil (control soil) sorbed the highest level of Zn as compared with the organic material treated soil systems. The PMC/ soil system showed the lowest capacity for Zn sorption while the AMC/soil system showed the highest. The sorption capacity for Zn by the different organic material /soil system of soil No.2 can be arranged in the order: AMC=PRC>AMPRC> HS>PMC at soil of pH 8. This indicated that incorporation of PMC with the calcareous soil decreased significantly the amount of Zn sorbed by soil .

Table 3 showed that incorporation organic material with the alluvial soil significantly increased Zn sorption except PMC/ soil system where it decreased. However, all organic materials decreased Zn sorption by the calcareous soil. It is clear that PMC was the must effective in decreasing Zn sorption by the two soils and consequently increasing Zn availability.

TABLE 3. The relative increase or decrease (%) of zinc sorption by the different organic material (OM)- soil systems with respect to the control soil at pH 8.

OM / Soil System	Studied soil	
	Soil No.1	Soil No.2
Control/soil	100.00	100.00
AMC/soil	45.50	-7.60
PRC/soil	36.40	-7.60
AMPRC/soil	18.20	-18.47
PMC/soil	-9.10	-72.82
HS/soil	54.50	45.65

Zn sorption isotherm

Figures 3-6 and Table 4 show Zn sorption by the different organic materials/ soil systems. It is clear that the data fit Langmiur adsorption isotherm especially at the low concentration of Zn in the equilibrium solution. For organic material/ soil system of soil No.1, it is clear that PRC /soil an PMC/soil systems showed low value of " b" (adsorption maximum) as compared with HS, AMC, AMPRC / soil systems. Thus, the values of "b" can be arranged in the order for the different organic material/soil systems: AMPRC > HS > AMC > PMC > PRC. However the bonding energy and affinity (a) of the systems to Zn can be arranged in the order: PRC>PMC>AMC>HS >AMPRC. For organic /soil system of soil No.2 , it is clear that PRC /soil and PMC/soil system showed low value of

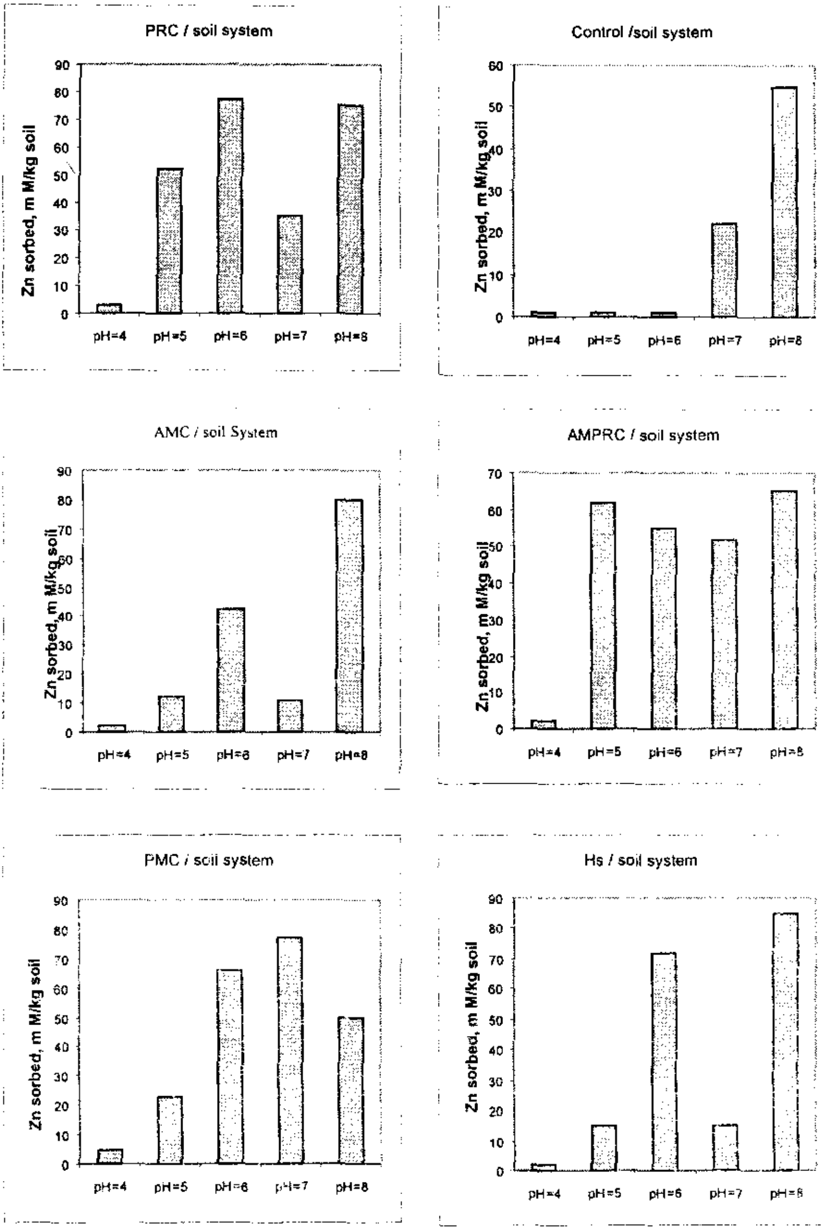

Fig 1. The relationship between pH of the equilibrium solution and amounts of Zn sorbed by different organic material system of soil No. (1).

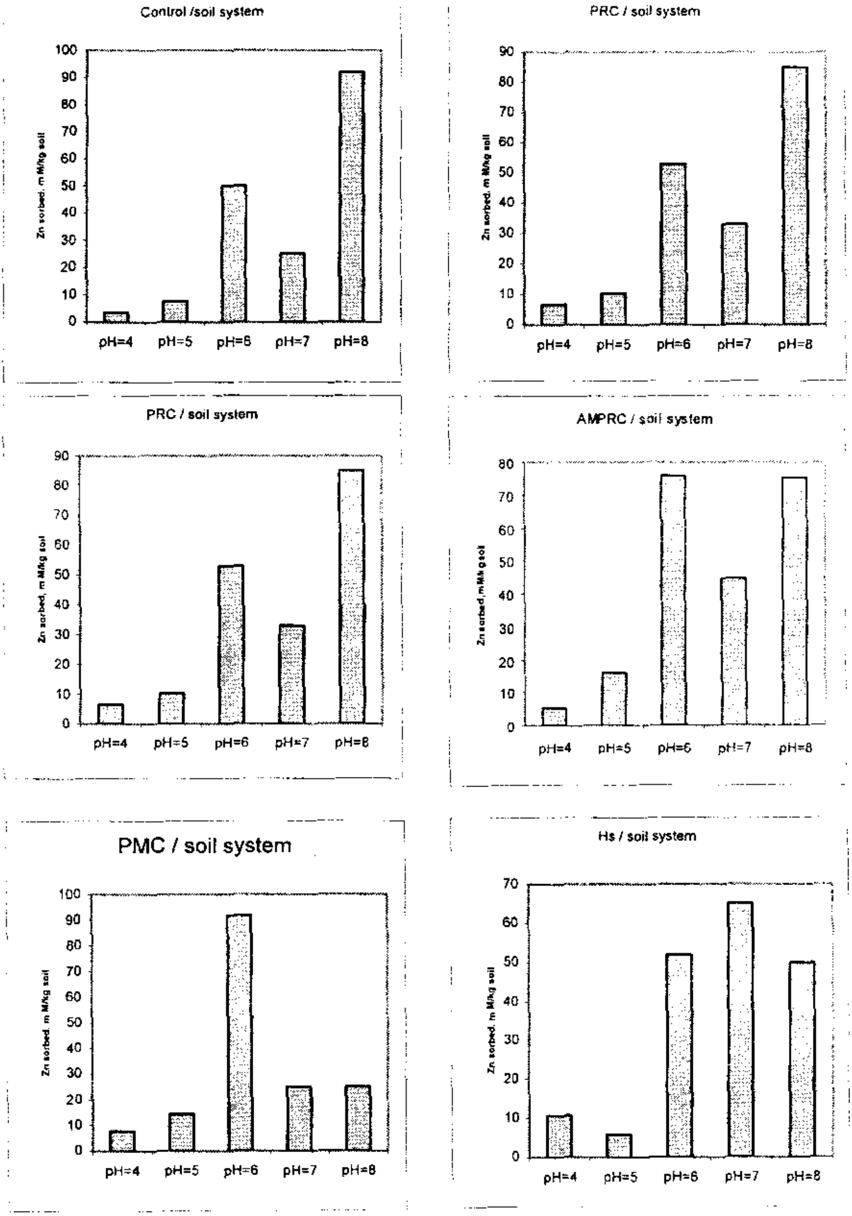

Fig 2. The relationship between pH of the equilibrium solution and amounts of Zn sorbed by different organic material system of soil No. (2).

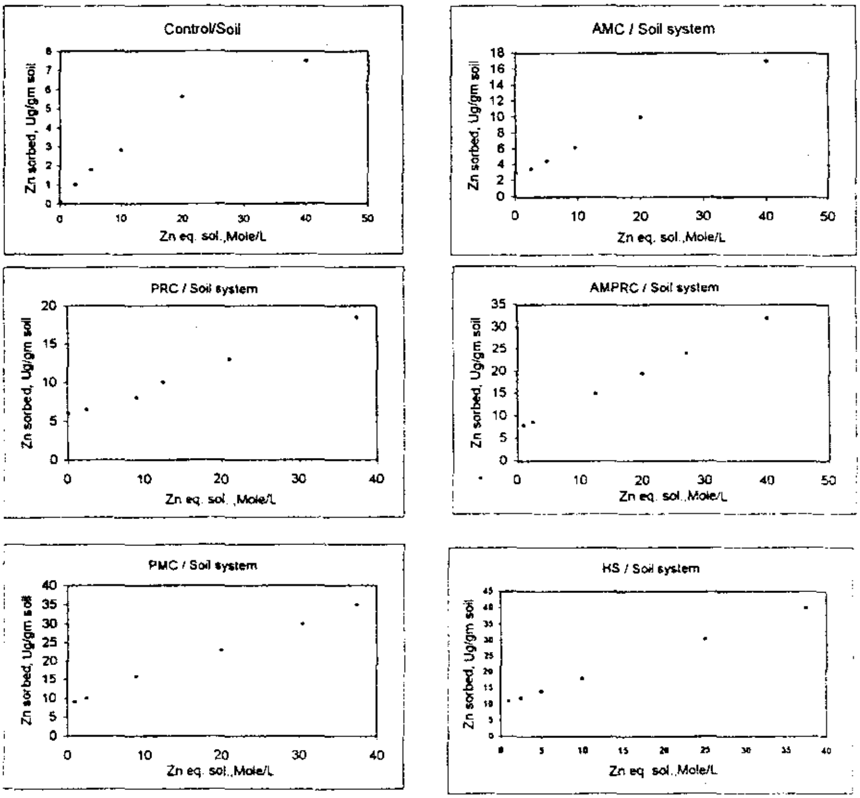

Fig. 3. Znic sorbed by the different organic materials/soils system of soil No.1 in relation to Zn in the equilibrium solution.

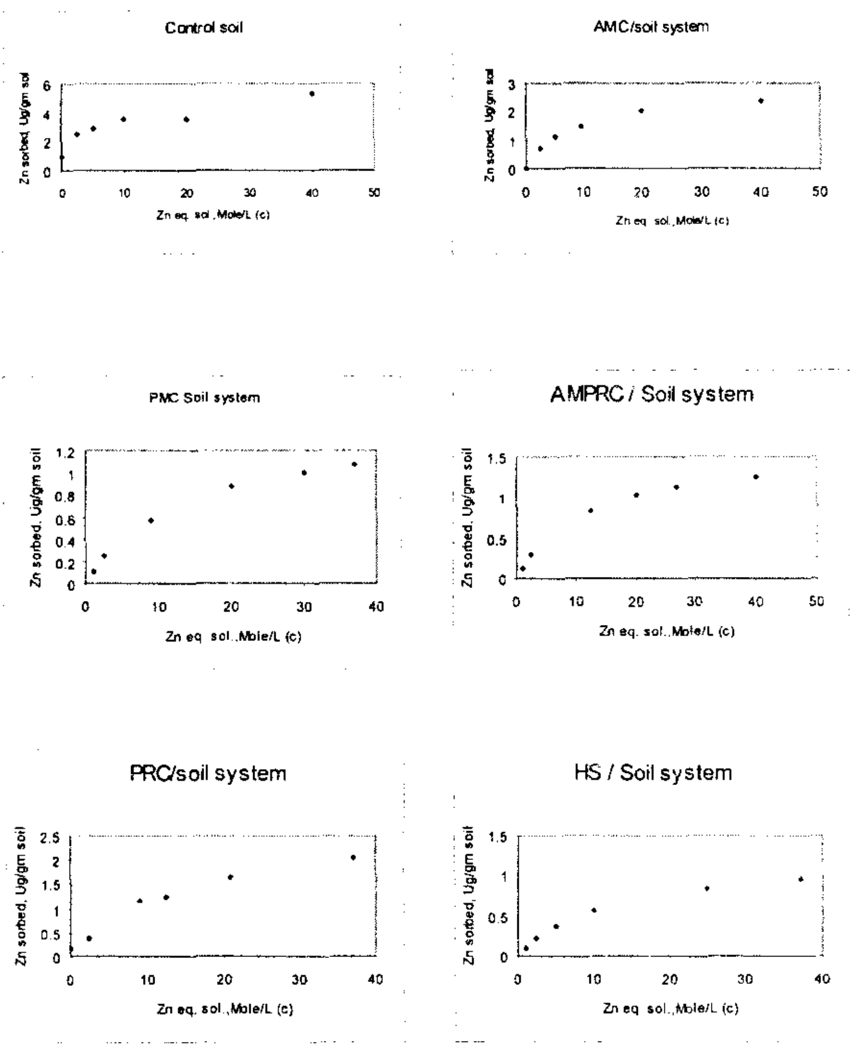

Fig. 4. Znic sorbed by the different organic materials/soils system of soil No.1 in relation to Zn in the equilibrium solution.

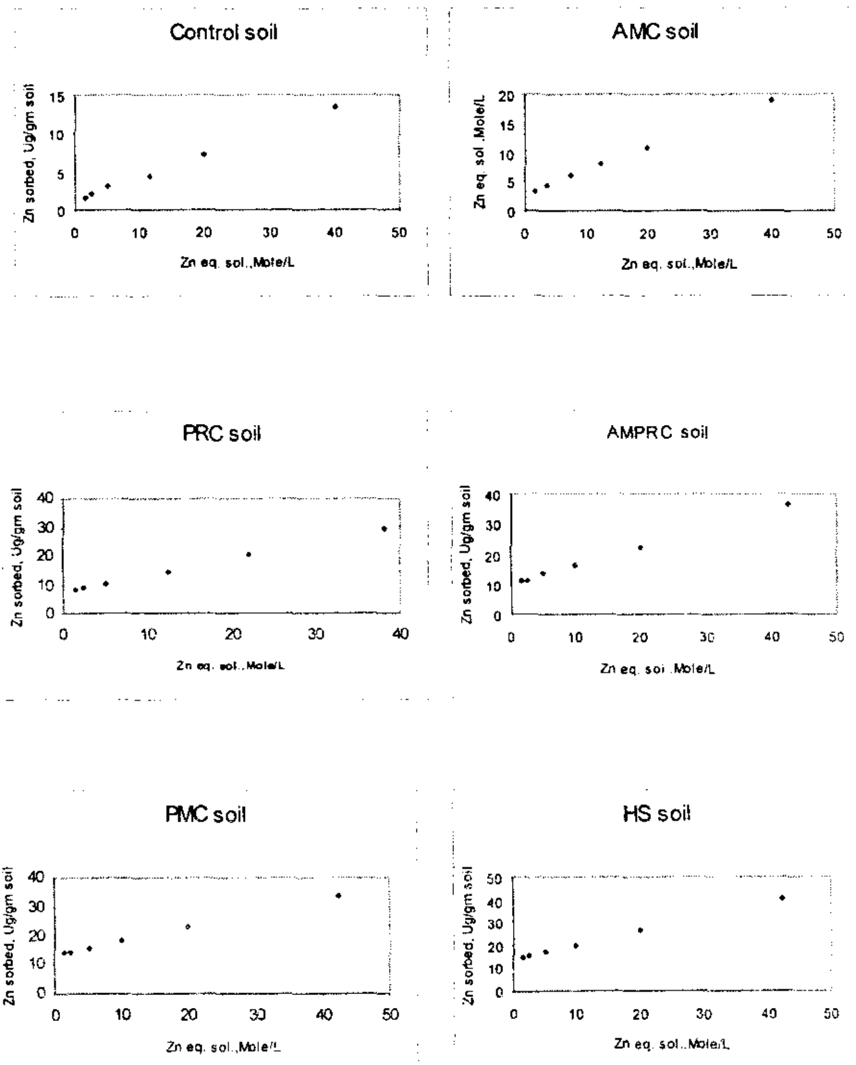

Fig. 5. Znic sorbed by the different organic materials/soils system of soil No.2 in relation to Zn in the equilibrium solution.

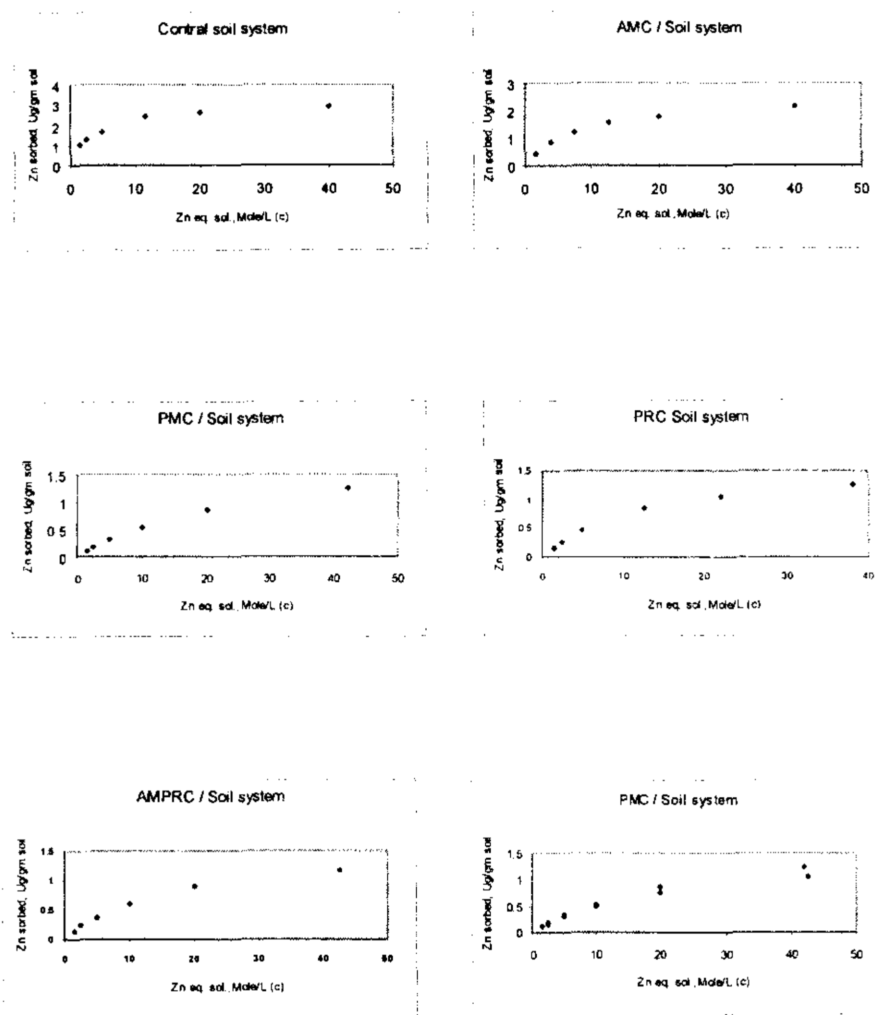

Fig. 6. Znic sorbed by the different organic materials/soils system of soil No.2 in relation to Zn in the equilibrium solution.

"b" (adsorption maximum) as compared with the other systems .Thus , the values of " b'' can be arranged in the order : AMPRC>HS>AMC >PMC>PRC. However, the bonding energy or affinity for Zn by the different organic materials/soil systems can be arranged in the order: PRC>PMC>AMC>HS >AMPRC.

TABLE 4. Langmiur isotherm for Zn adsorption maximum (b) and bonding energy (affinity) constant (a)for the different systems for soil No.1 and soil No.2.

Organic material	Langmiur equation	b, ug Zn /g soil	a
Soil No.1			
Control	Y=0.011+0.304x	32.88	2.55
AMC	Y=0.019+0236x	42.25	1.99
PRC	Y=0.010+0.0377x	26.50	3.45
AMPRC	Y=0.025+0.0213x	46.75	0.85
PMC	Y=0.012+0.0306x	32.60	2.55
HA	Y=0.022+0.0277x	43.95	0.99
Soil No.2			
Control	Y=0.011+0.0221x	30.20	2.85
AMC	Y=0.011+0.0316x	31.60	2.70
PRC	Y=0.012+0.0456x	22.22	3.75
AMPRC	Y=0.017+0.0258x	36.75	1.50
PMC	Y=0.012+0.0332x	30.11	2.85
HA	Y=0.015+0.0286x	34.90	1.80

References

Anderson, P.R. and Christensen, T.H. (1988) Distribution coefficients of Cd,Co, Ni, and Zn. in soils. *J. Soil Sci.* **39**, 15.

Alvarez, J.M.; Rico, M.I. and Obrador, A. (1997) Leachability and distribution of zinc applied to an acid soil as controlled- release zinc chelates. *Common. Soil Sci. Plant Anal.* **28**, 1579.

Betran, K. and Andreas (1994) *"Methods for Analysis of Compost"*, Publisher: Federal Compost Quality Assurance Organization (FCQAO).

El-Kouny, H.M. (1999) Evaluation of compost production and its properties with special reference to compost extract. *Ph. D. Thesis.* Faculty of Agriculture. Alexandria University. Alex. Egypt.

Elsokkary, I.H. (1974) Leaf analysis as a guide to the nutrition status of orange trees in some alluvial and desert calcareous soils of Egypt .Beitrage trop. Landwirtsch, *Veterinarmed* **12**, 249.

Elsokkary, I.H. (1980) Reaction of Labeled 65 ZnCl, 65 Zn EDTA &65 Zn DTPA with different clay-systems and alluvial Egyptian soils. *Plant and Soil* **54**, 383.

Fitch, A. and Du, J. (1996) Solute transport in clay media : effect of humic acid. *Environ. Sci. Technol.* 30, 12 .

Goh, T.B.; Violante, A. and Huang, P.M. (1986) Influence of tannic acid on retention of copper and zinc by aluminum products. *Soil Sci. Soc. Am. J.* **50**, 820.

Harter, R.D. (1983) Effect of soil pH on adsorption of lead, capper.Zinc and nickel. *Soil Sci. Soc. Am. J.* **47**, 47.

Harter , R.D. and Naidu (1995) Role of metal organic complication in metal sorption by soils. *Adv. Agron.* **55**, 219.

Inbar,Y.Y.; Chen,Y.; Hadar and Hotink, A.J. (1990) New approaches to compost maturity. *Biocycle.* **31**, 64 .

Jurinak, J.J. and Bauer, N. (1956) Thermodynamics of zinc adsorption on calcite, and magnetite- type minerals. *Soil Sci. Soc. Am. Proc.* **20**, 466.

Kabata–Pendias, A. and Pendias, H. (1992) *"Trace Elements in Soils and Plants"*, 2[nd] ed., CRC Press, Inc, Boca Raton, FL.

Kaloosh, A.A.M. (1995) Characteristics of organic fertilizers in Dubai, *U.E.J. Agric. Sci. Mansoura Univ.* **18**, 1562.

Li, Z. and Shuman, L.M. (1997) Mobility of Zn, Cd and Pb in soils as affected by poultry litter extract and leaching in soils columns. *Environ. Pollut.* **95**, 219.

Page, A.L.,Miller, R.H. and Kenny, D.R. (1982) *"Methods of Soil Analysis"*, Amer. Soc. Agron., Madison, Wisconsin.

Pulford, I.D. (1986) Mechanisms controlling zinc solubility in soils. *J. Soil Sci.* **37**, 427

Schnitzer, M.L.; Lowe, E.; Dormaar, J.Fe. and Martel, Y. (1981) A procedure for the characterization of soil organic matter. *Can. J. Soil Sci.* **61**, 517.

Shuman, L.M. (1975) The effect of soil properties on zinc adsorption by soils. *Soil Sci. Soc. Am. Proc.* **39**, 454 .

Shuman, L.M. and Li, Z. (1997) Ameliorator of Zn Toxicity in cotton using Lime or Mushroom compost. *J. Soil Contam.* **6**, 425 .

Shuman, L .M. (1980) Zinc in soils. In "Nriagu, *Zinc in The Environment*", Part 1, *Ecological Cycling*, pp 39-69, John Wiley and Sons, New York.

Stevenson, F.J. and Fich, A. (1981) Reactions with organic matter. In *"Copper in Soils and Plants"*, J.F. Loneragan *et al.* (Ed.), pp 69-95, Academic Press, Sydney, Australia.

Waller, P.A. and Pickring, W.F. (1992) Effect of time and pH on the lability of copper and znic sorbed on humic acid particles. *Chem. Speciat.Bioavailab.***4**, 29 .

(*Received* 10/2002)

امتصاص الزنك على أراضى معاملة بالمادة العضوية

حامد مبروك القونى

قسم بحوث الأراضى الملحية والقلوية – الأسكندرية – معهد بحوث الأراضى والمياه والبيئة– مركز البحوث الزراعية– القاهرة – مصر.

استخدم فى هذة الدراسة خمس مواد عضوية مكمورة (كمبوست) هى : كمبوست سماد حيوانى (AMC) ، كمبوست مخلفات نباتية مختلفة ، كمبوست خليط من AMC ، PRC و كمبوست سبلة دواجن PMC و مواد دبالية (HS) ونوعين من الأرض رسوبية (١) وجيرية (٢) .

حضرت نظم المادة العضوية مع الأرض ، لتقييم امتصاص الزنك بواسطة النظم المختلفة من المادة العضوية مع الأرض من محلول كلوريد الزنك.

أوضحت النتائج أن امتصاص الزنك بواسطة هذه النظم من المادة العضوية مع الأرض قد زاد بزيادة pH حتى pH=8 كما أظهرت النظم المختلفة اختلافات فى سعتها لامتصاص الزنك .

وكانت الزيادة أو النقص النسبى لامتصاص الزنك عند pH = 8 هى ٤٥.٥ ٪ ، ٣٦.٤ ، ١٨.٢ ، -٩.١ ، ٥٤.٥ ٪ لكل من نظم AMC ، AMPRC مع الأرض والمواد الدبالية HS مع الأرض على التوالى للأرض رقم (١).

أما فى حالة الأرض رقم (٢) كانت هذه القيم -٧.٦ ، -٦.٧٠ ، -٤٧.١٨ ، -٨.٧٢ ، ٦٥ ، ٤٥ ٪ على التوالى .

كذلك أوضحت النتائج أن إدمصاص الزنك يتبع معادلة لانجموير وخاصة عند التركيزات المنخفضة للزنك . وقد وجدت القيم الاعلى للحد الأقصى للأدمصاص (b) مع نظام AMPRC الأرض و أما الأصغر كانت مع PMC مع الأرض , PRC مع الأرض لكل من الأرض الرسوبية والجيرية .

وعلى الرغم من ذلك ، كانت طاقة الربط (a) لنظم المادة العضوية مع الأرض للزنك الأعلى مع نظم PRC مع الأرض عن نظم AMPRC مع الأرض لكل من الأرض الرسوبية والجيرية .