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ZINC AND MANGANESE SORPTION BEHAVIOR BY NATURAL ZEOLITE AND BENTONITE

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Iskander[1] A.L.; E.M. Khald[2] and A.S. Sheta[2]
1- Central Lab., Fac. Agric., Ain Shams Univ., Shoubra El-Khema, Cairo, Egypt
2- Soil Sci. Dept., Fac. Agric., Ain Shams Univ., Shoubra El-Khema, Cairo, Egypt

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ABSTRACT

Understanding the sorption process in natural zeolite and bentonite is necessary for effective utilization of these minerals as nutrient adsorbents and on the other side for controlling release of plant nutrients. This research was undertaken to characterize the ability of natural zeolite and bentonite minerals to adsorb and release zinc and manganese. The potentials for sorption of these ions were evaluated by applying the Langmuir and Freundlich equations. The results showed that Langmuir constant [maximum adsorption (b mmol kg^{-1})] of both Zn and Mn were for bentonite > zeolite While the [binding strength values (k in L.mmol^{-1})] for zeolite > bentonite

Zn in case of zeolite showed the lowest desorbed percentage particularly at high levels of sorbed Zn. Only, 74.7 % is readily extractable by DTPA after three successive extractions leaving, 25.3 % Zn retained by the mineral. In case of bentonite, 82.26 % of sorbed Zn is readily extractable by DTPA after three successive extractions leaving, 17.74 % Zn retained by the mineral. In case of Mn, 84.63% of Mn sorbed by zeolite is readily extractable by DTPA after three successive extractions leaving, 15.37% Mn retained by the mineral. In case of bentonite, 89.79 % of adsorbed Mn is readily extractable by DTPA after three successive extractions leaving, 10.21 % Mn retained by the mineral.

This finding may reflect clearly the possibility of using natural zeolite and bentonite as a slow release fertilizer for Zn and Mn and on the other hand preventing soil pollution with heavy metals.

INTRODUCTION

Zeolites and bentonite are naturally occurring structured and phyllosilicate minerals respectively, with high cation exchange and ion adsorption capacity. In particular, zeolites are hydrated aluminosilicates of alkaline and alkaline-earth minerals **(Mumpton, 1999)**.Their structure is made up of a framework of $[SiO4]^{4-}$ and $[AlO4]^{5-}$ tetrahedron linked to each other's corners by sharing oxygen atoms. The substitution of Si^{4+} by Al^{3+} in tetrahedral sites results in more negative charges and a high cation exchange capacity **(Akbar *et al* 1999).**

On account of higher surface area and cation exchange capacity, bentonite is a 2:1 mineral with one octahedral sheet and two silica sheets, which forms a layer. Layers are held together by Vander Waals forces. Because of these weak forces and some charge deficiencies in the structure, water can easily penetrate between layers and cations balance the deficiencies **(Mitchell, 1993)**.

Erdem *et al* (2004) reported that natural zeolites hold great potential for the sorption of several metal cations, e.g.Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+}.

Agricultural applications related to ion exchange, adsorption and desorption of ions by zeolites have been reported by many investigators **(Allen *et al* 1996)**. Natural zeolites are suitable carriers for fertilizers of various kinds **(Hershey *et al* 1980; Lai and Eberl, 1986; Chiesworth *et al* 1987; Barbarick *et al* 1990; Allen *et al* 1993; Allen *et al* 1996; McGilloway, 2003; Li, 2003; Alelishvili *et al* 2003 and Janjgava, 2003).**

Furthermore, **Sheta *et al* (2003)** suggested that natural zeolite and bentonite minerals have a high potential for Zn and Fe retention. The availability of the retained Zn was higher than for Fe, and chabazite seems to have the highest ability for Zn sorption and extractability by DTPA. Bentonite has in-

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termediate characteristics for Zn and Fe sorption among the studied zeolite mineral species.

Coarse texture arid land soils are low to very low in extractable micronutrients and many are regarded as potentially deficient. However, some micronutrient compounds have been added to the soils either directly or as an incidental component of other fertilizers.

Zinc sorption is an important factor governing Zn concentration in soils and is influenced by several factors, such as pH, clay mineral content, surface area, soil organic matter, hydrous oxides, and soil type. Clay-bound Zn was characterized as dominantly reversible in association with clay surface groups, while the rest exists in an irreversible non exchangeable form associated with lattice entrapment **(Tiller and Hodgson, 1962).** Zn concentration and physicochemical forms in surface soil directly influence the movement of Zn, especially in sandy soils **(Cezary and Singh, 2001).** Appreciable fractions of total soluble zinc may be in equilibrium with specially adsorbed forms associated with insoluble organic matter **(Bourg, 1995).** 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).**

Adsorption of Mn has been shown to conform to the Langmuir or Freundlich isotherm **(Willett and Bond, 1995).** Adsorption in the Ao horizon near the surface (0 to 4 cm) has been found to be increased due to the higher CEC, higher soil organic matter, and higher content of amorphous Fe oxide. Adsorption enhances with increasing pH, due to the increased hydrolysis species of Mn^{2+} that is preferably adsorbed and increased negative charge on the exchange complex **(Reddy and Perkins, 1976).** The bioavailability of Mn in soils is generally adequate at pH< 6.5 but it becomes significantly lower in soils with higher pH values **(Ducic and Polle, 2005).** In general, sorption of Mn onto soils can be facilitated by several mechanisms. First, the oxidation of Mn to higher-valence oxides and/or precipitation of insoluble compounds in soils are subjected to wetting and drying. Second, absorption into the crystal lattice of clay minerals and adsorption on exchange sites may occur **(Evans, 1989).** Presence of chelating agents is not able to form stable Mn complexes in soils because Fe or Ca can substitute for Mn **(Norvell and Lindsay, 1972).**

Sorption and desorption characteristics of micronutrients (Fe, Zn, Mn, Cu and B) by natural zeolite minerals is almost scarce in literature, despite the relative importance of zeolite as natural carrier for nutrients. The objectives of this research included (1) the evaluation of Zn and Mn sorption characteristics by natural zeolite and bentonite minerals, and (2) the determination of retained Zn and Mn forms through the extraction using diethylene triamine pentaacetic acid (DTPA) and selective dissolution methods.

MATERIALS AND METHODS

The naturally occurring zeolite and bentonite minerals used in this study were supplied by International Company for Mining and Investments (ICMI) and Delta Biotech Company, respectively. The mineralogical properties, cation exchange capacity CEC (cmol kg^{-1}), surface area (m^2g^{-1}), of these compounds are given in **Table (1).**

Cation Exchange Capacity (CEC) for the clay adsorbents were estimated by the ammonium acetate method at (pH=7.0) **(Tan, 1996).**

The surface areas for the used adsorbents were estimated utilizing Sears' method **(Sears, 1956).** Representative zeolite and bentonite samples were used without any chemical pretreatment. In preparation for sorption and extraction experiments, the samples were grounded in an agate mortar and passed through a 1.0 mm sieve.

Zn^{2+} as $ZnSO_4$ and Mn^{2+} as $MnCl_2.2H_2O$ were used in the current experiment as adsorbates. Stock solutions containing 1000 mgL^{-1} from Zn^{2+} and Mn^{2+} were prepared using the above mentioned analytical chemical reagents and different concentration were prepared by dilution to give : 0, 50, 100, 200, 400, 600 and 1000 mgL^{-1}

Adsorption experimental work

Sorption experiment were carried out using the batch equilibrium by weighing duplicate 1.0 g samples in 50 mL centrifuge tubes and 20 ml of the initial concentrations were added to each sample, then suspensions were shaken for 2 h at constant room temperature (20 °C) followed by centrifugation for 15 min on 5000 rpm / min. Zn and Mn concentrations in equilibrium solutions were measured by Atomic Absorption Spectrophotometer (AAS) according to **(Barker and Suthr, 1982).** The amount of adsorbed ions (mmol.kg^{-1}) were calculated by the difference between ion added and that remained in the equilibrium solutions. The obtained results of adsorption experiments are interpreted in the light of Langmuir and Freundlich adsorption isotherms as follows:

The Langmuir equation model used is

$$C/x/m=l/kb + C/b$$

Table 1. Selected chemical analyses of zeolite and bentonite minerals used in the study

Materials	CEC (cmol kg^{-1})	Surface area (m^2 g^{-1})	Si/Al ratio	Total oxides(g.kg^{-1})			
				SiO_2	Al_2O_3	Fe_2O_3	MgO
Zeolite	122.5	800	5.30	710.0	118.0	17.0	14.0
Bentonite	80.1	1000	3.10	563.0	160.1	53.1	22.1

Where C and x/m are the equilibrium ion concentration (mmol.L^{-1}) and the amount of ion sorbed (mmol.kg^{-1}), respectively. The empirical constants b and k are related to the adsorption maximum (mmol.kg^{-1}) and bonding strength of the adsorbent (L.mmol^{-1}), respectively. This equation will be used to compare the adsorption maximum (b) between zeolite and bentonite since these adsorbents and the experimental conditions are identical as proposed by **Veith and Sposito (1977)**. From linear form of Langmuir equation, b = 1 / slope and k = slope / intercept.

The linear form of Freundlich equation is

log x/m = log k + 1 /n log C

Where: x/m = the amount of ion sorbed (mmol.kg^{-1}), C = concentration of the considered ion in the equilibrium solution (mmol.L^{-1}), K and n are Freundlich isotherm constants.

Desorption experiments

Sorbed Zn and Mn were extracted sequentially three times with 20 ml DTPA extract according to the method described by **Lindsay and Norvell (1978).** In each case suspensions were shaken thoroughly in a mechanical shaker for 2 hours, and then centrifuged at 5000 rpm / min. The clear supernatant obtained after centrifugation was analyzed for the respective cations by Atomic Absorption Spectrophotometer (AAS) according to **Veith and Sposito (1977).**

RESULTS AND DISCUSSION

Zn and Mn sorption isotherms were executed by plotting sorbed amount of the considered ion per unit weight of adsorbent i.e. x/m (mmol kg^{-1}) against the equilibrium Zn and Mn concentrations C mmol l^{-1} **Fig. (1)**. The pattern of the isotherms are quite similar with a slight difference between zeolite and bentonite. At lower initial concentrations, the isotherms have a relatively high slope whereas at higher concentrations the slope was relatively low with a defined plateau for the adsorption maximum in the two studied minerals. Sorption isotherms follow L-shaped type similar to that described by **Sposito, (1984).** Such sorption behavior could be explained by the high affinity of zeolites and bentonite for Zn and Mn at low concentrations, which decrease as Zn and Mn concentration increases. Langmuir and Freundlish constants for Zn and Mn sorption were calculated from the best fitting straight line between C/x/m and C & log x/m and log c, respectively **Tables (2 and 3)** & **Figs. (2 and 3).**

Data of maximum adsorption (b mmol kg^{-1}) indicated the following decreasing order: bentonite Mn > zeolite Mn > bentonite Zn > zeolite Zn. The binding strength values (k in L.mmol^{-1}) were in the order: zeolite Mn > zeolite Zn > bentonite Mn > bentonite Zn. Results also show that, the amount of Zn sorbed by Bentonite ranged between 5.90 and 18.88 % from the added Zn while it ranged from 4.21 to 16.18% for Zeolite. The amount of Mn sorbed by bentonite ranges between 9.83 and 33.24 % from the added Mn while it ranged from 6.74 – 28.3 % for zeolite.

These data reflect differences between zeolite and bentonite minerals for Zn and Mn sorption, particularly in the case of Mn sorption. Differences in the mineralogical structure of zeolite and bentonite surface characteristics could play an important role in the sorption behavior of Mn ions. **Sheta *et al* (2003)** investigated the adsorption characteristics of natural zeolite and bentonite via zinc and iron and concluded that heavy metal adsorption substantially depends on the mineralogical compositions of materials and kinds of heavy metal used in the tests.

Data of the native Zn and Mn extracted by successive DTPA extractions **Table (4)** reveal that their concentrations decreased drastically after the successive extractions and were almost negligible after the third one in both mineral.

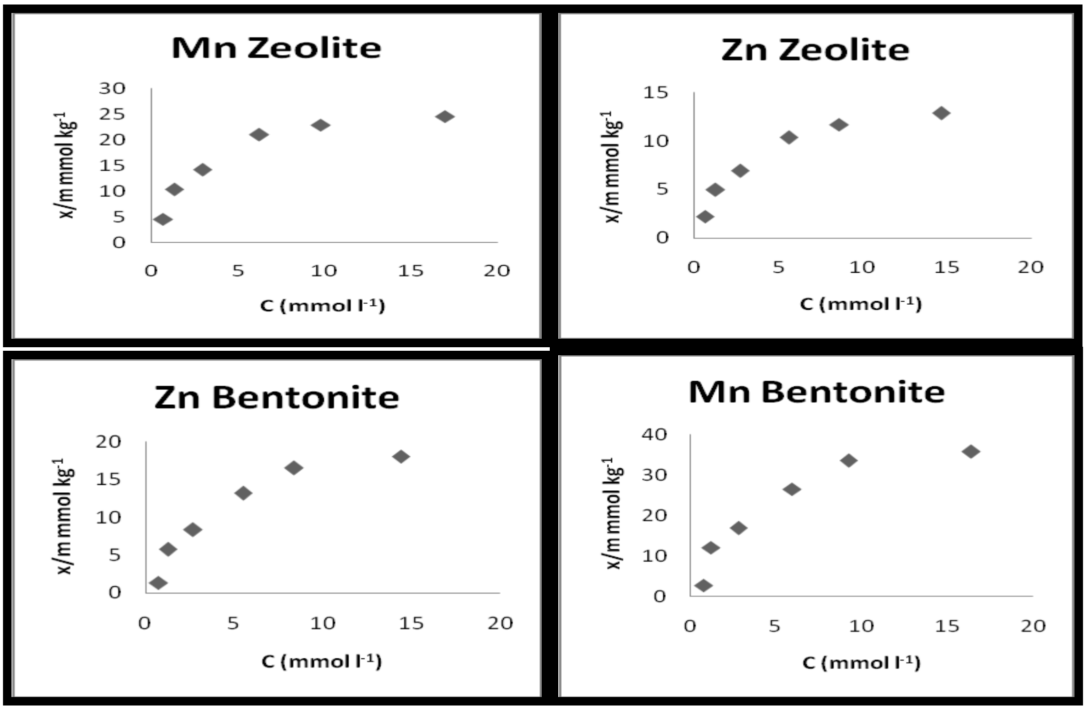

Fig.1. Sorption isotherms of Zn and Mn by zeolite and bentonite

Table 2. Linear forms of Langmuir equations and constants (b and k) for Zn and Mn adsorption by zeolite and bentonite

Sample	Equation	K* $mmol.L^{-1}$	b* $mmol.kg^{-1}$	R^2
Zeolite / Zn	y = 0.0643x + 0.190	0.338	15.55	0.9977
Bentonite / Zn	y = 0.0424x + 0.177	0.239	23.58	0.9916
Zeolite / Mn	y = 0.0354x + 0.086	0.410	28.24	0.9977
Bentonite / Mn	y = 0.0224x + 0.084	0.264	44.64	0.9894

K*= slope / intercept b*= 1 / slope

Table 3. Freundlich equations and constants for Zn and Mn sorption by zeolites and bentonite

Sample	Equation	n($kg.l^{-1}$)	log k ($mmol.kg^{-1}$)	R^2
Zeolite / Zn	y = 0.4113x + 0.6664	2.43	4.638	0.9713
Bentonite / Zn	y = 0.4936x + 0.7266	2.02	5.328	0.9765
Zeolite / Mn	y = 0.3575x + 0.9901	2.79	9.774	0.9569
Bentonite / Mn	y = 0.4496x + 1.0498	2.22	11.215	0.9708

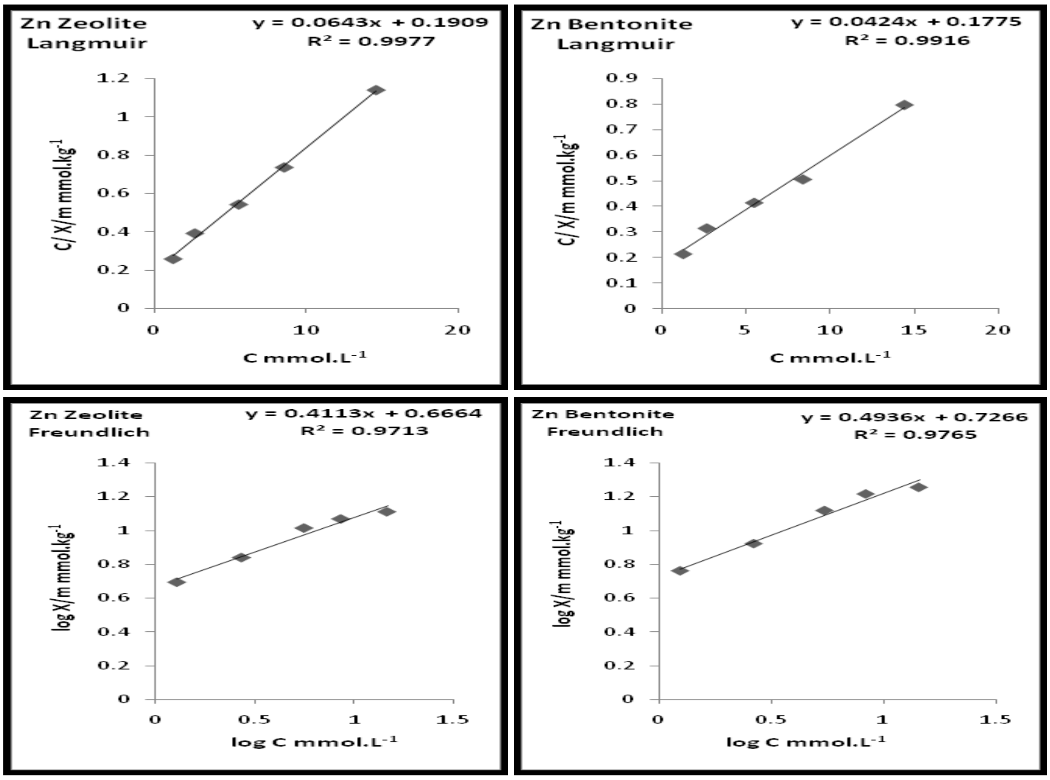

Fig. 2. Linear forms of Langmuir and Frendlich equations for Zn adsorbed by zeolite and bentonite

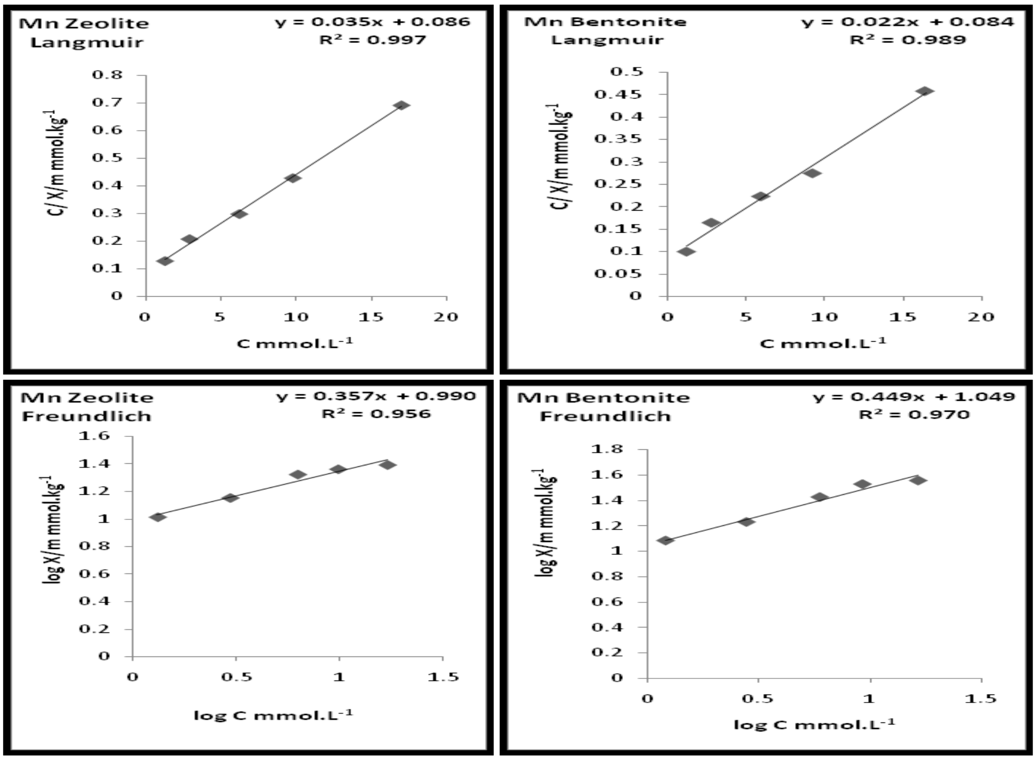

Fig. 3. Linear forms of Langmuir and Frendlich equations for Mn adsorbed by zeolite and bentonite

Table 4. Amounts of sorbed Zn and Mn and DTPA extractable Zn and Mn (three successive extractions) from Zn and Mn treated and untreated zeolite and bentonite

Adsorbent	Added Zn & Mn mg.kg^{-1}	Zn sorbed mg.kg^{-1}	∑ DTPA Extractable Zn * mg .kg^{-1}	Zn Extractable /sorbed %	Mn sorbed mg.kg^{-1}	∑ DTPA Extractable Mn * mg kg^{-1}	Mn Extractable /sorbed %
Zeolite	0.00	0.00	0.60	-	0.00	1.00	-
	1000	144.60	135.00	93.36	254.20	246.00	96.77
	2000	323.60	305.00	94.20	566.00	550.00	97.17
	4000	452.20	412.80	91.28	779.80	744.00	95.40
	8000	675.20	593.80	87.94	1152.20	1076.00	93.38
	12000	764.00	639.00	83.63	1257.40	1138.00	90.50
	20000	842.00	629.00	74.70	1349.40	1142.00	84.63
Bentonite	0.00	0.00	1.22	-	0.00	1.80	-
	1000	89.40	79.20	88.59	153.40	144.00	93.87
	2000	377.60	359.60	95.23	664.80	650.00	97.77
	4000	547.60	509.20	92.98	930.20	896.00	96.32
	8000	860.20	780.80	90.76	1460.80	1388.00	95.01
	12000	1078.60	957.20	88.74	1845.00	1732.00	93.87
	20000	1180.60	971.20	82.26	1966.60	1766.00	89.79

* = Summation of DTPA extractable Zn or Mn (three successive extractions).

The cumulative amounts of native Zn ranged from 0.6 mg kg^{-1} for zeolite to 1.22 mg kg^{-1} for bentonite. While The cumulative amounts of native Mn ranged from 1 mg kg^{-1} for zeolite to 1.8 mg kg^{-1} for bentonite.

Therefore, the native available Zn to plants in zeolite or bentonite mineral was low Moreover, mixing such minerals with soils low in available Zn or Mn cannot support the plants need for Zn and Mn.

On the other hand, data in **Table (4)** indicated that more Zn and Mn was extracted after the third extraction by DTPA from both minerals treated samples where they were higher for bentonite compared with zeolite. For example, at higher initial Zn added, bentonite released 107.8 mg kg^{-1} in the third extraction while zeolite released 62.2mg kg^{-1} and at higher initial Mn added bentonite releases 197.8 mg kg^{-1} in the third extraction while zeolite released 128.2 mg kg^{-1}.

Also, the percentage of cumulative extracted Zn and Mn (% from sorbed) varied considerably with the sorbed amounts and with zeolite or bentonite. Zeolite Zn showed the lowest desorbed percentage particularly at high levels of sorbed Zn. Only 74.7 % was readily extractable by DTPA after three successive extractions leaving 25.3 % of Zn retained by the mineral. In case of bentonite 82.26 % is readily extractable by DTPA after three successive extractions leaving 17.74 % of Zn retained by the mineral.

Data also indicated that 84.63% of zeolite Mn after three successive extractions by DTPA is readily extractable leaving 15.37% of Mn retained by the mineral while in bentonit, 89.79 % is readily extractable leaving 10.21 % of Mn retained by the mineral. These results are in a good agreement with binding energy calculated from Langmuir **Table (2).** This finding may reflect clearly the potentially positive role of using zeolite and bentonite as a slow release fertilizer for Zn and Mn, in this context treated zeolite is much preferable to use as slow release for micronutrients.

It can be concluded that surface retention of heavy metals by natural zeolite and bentonite minerals can regulate the solubility of metals in the soil solution and control the distribution of these heavy metals between solid phase and solution phase. This, in turn, will help in keeping micronutrients from loss with drainage water, and hence be available for the growing plants. On other hand, heavy fertilization or the addition of materials contains trace elements can be controlled by the presence of these nature minerals and will prevent the possibility of the toxic effect of these metals in the soil or ground water system.

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