J.Soil Sci. and Agric. Eng., Mansoura Univ., Vol. 9 (10): 473 – 479, 2018

Remediation of a Pb-Contaminated Soil Cultivated with Rose Geranium (*Pelargonium graveolens*) Using Nano-Zeolite

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ABSTRACT

A greenhouse experiment was carried out on a sandy clay soil cultivated with rose geranium (*Pelargonium graveolens*) which is a hyper-accumulator plant. The experiment was in a randomized complete block design (factorial) with two factors : (1) Zeolite application at seven levels: Z_0 (no zeolite addition), nZ_1 (nano zeolite 0.5 g kg^{-1} soil), nZ_2 (nano zeolite 1.0 g kg^{-1} soil), nZ_3 (nano zeolite 1.5 g kg^{-1} soil), Z_1 (ordinary zeolite 0.5 g kg^{-1} soil), Z_2 (ordinary zeolite 1.0 g kg^{-1} soil), and Z_3 (ordinary zeolite 1.5 g kg^{-1} soil) and (2) Pb pollution at two levels Pb_1 (500 mg Pb kg^{-1} soil) and Pb_2 (1000 mg Pb kg^{-1} soil). Pb uptake (by shoots, roots, plant) and residual Pb in soil significantly decreased due to zeolite application. The average decrease was in the following descending order: $nZ_3 > nZ_2 > nZ_1 > Z_3 > Z_2 > Z_1$. Highest decrease in soil residual Pb was attributed to nZ_3 (75.7%) which also had the lowest Pb uptake by shoots (76.9%), roots (70.6%), and plant (75.5%). Nano zeolite treatments were more effective than ordinary ones in decreasing residual Pb in soil (ranging from 63.39 to 75.7%); and Pb uptake by shoots(ranging from 65.2 to 76.9%), by roots (ranging from 57.8 to 70.55%) and by plant (ranging from 63.5 to 75.5%); and increasing fresh and dry weight of shoots (ranging from 5.4 to 13.2%) and roots(ranging from 7.5 to 11.7%). The most effective treatment for plant weight (fresh and dry) was nZ_1. Pb pollution significantly increased Pb uptake (by shoots, roots, and plant). Zeolite increased Pb immobilization at end of experiment with 46.0 to 83.9% immobilized in soils polluted with the low Pb rate; and with 38.7 to 80.1% in soils polluted with the high Pb rate (comparing with initial Pb applied to soil).

Keywords: nano and ordinary zeolite, lead (Pb), rose geranium (Pelargonium graveolens)

INTRODUCTION

Increasing levels of soil pollution with heavy metals is a problem of concern, due to the wide ranges of anthropogenic activities particularly the industrial ones (Kabata-Pendias and Mukherjee, 2007 and Abdel-Salam *et al*., 2015). Deposition of solid and liquid wastes, excessive doses of agricultural inputs (sludge and fertilizers), fallouts of mining, industrial and urban emissions are different sources of soil pollution with heavy metals (Kabata-Pendias and Mukherjee, 2007and Gupta, 2009) which affect biosphere and human health severely (Wilson and Pyatt, 2007 and WHO, 2010). Excessive accumulation of heavy metals particularly in agricultural soils has severe implications on food quality and safety (Antonious and Kochhar, 2009). The grown plants in such polluted soils have different potentials to absorb and accumulate heavy metals in their tissues. Some plant species have a high sensitivity towards high levels of heavy metals; it affects plant growth, enzymes activity, stoma function and photosynthes is severely (Lone *et al*.,2008). On the other hand, tolerant plants are capable of accumulate heavy metals without toxicity symptoms as a result of damaging the metabolic functions (Lone *et al*.,2008 and Feng *et al*., 2011). These plant species could be used in phyto-remediation techniques to decontaminate the polluted soils without effects on soil structure and fertility (Ghosh and Singh, 2005). Geranium plants (*pelargonium sp*) are multi metal hyper accumulator plant which absorb and accumulate more than one metal in their tissues (Arshad *et al*., 2008; Shahid *et al*., 2011 and Manshadi *et al*., 2013). Several germanium cultivars are hyper accumulators for lead under wide range of contaminated soils from acidic to calcareous soils (Arshad *et al*., 2008 and Manshadi *et al*., 2013).The accumulation depend on plant species and soil properties such as pH, CEC, soil content of OM and $CaCO_3$ (Spinoza-Quinones *et al*., 2005 and Ahmadi *et al*., 2013) thus the absorption of heavy metals depends on the availability of heavy metals in the rhizosphere zone (Shahid *et al*., 2011). Zeolite applications decrease the mobility and availability of heavy metals (Castaldi *et al*., 2004). Natural zeolites are a crystalline hydrated alumino-silicate which has a unique structure with interconnecting channels and cavities(Joshi *et al*., 2002)in addition to different types of cationic sites (Abusafa and Yucel, 2002); hence,zeolite could be used in the chemo-remediation of contaminated soils.Natural zeolite has high efficacy in adsorption, immobilization and stabilization of solid particles, liquids, gases (Christopher *et al*., 2012), hydrocarbons, radioactive cations, ammonia in addition to the adsorption of different heavy metals particularly Pb (Ponizovsky and Tsadilas, 2003 and Castaldi *et al*., 2004) and mitigation their harmful effect (Abdel-Salam *et al*., 2015). It decreases the transferring of the heavy metals to plants such as corn, mustard and oat (Ulmanu *etal*.,2006). The finer zeolite particles the higher metal exchanges capacity; hence, the higher adsorption of heavy metal (Liu and Lal, 2012). Nano-scale particles are effective choice in chemo-remediation and clean up techniques due to their unique properties particularly the large surface activity which increase their tendency to adsorb, immobilize, react, fix and stabilize metals and ions (Zedany, 2015; Wei *et al*., 2013; Taghizadeh *et al*., 2013 and Rabbani *et al*., 2016). Furthermore, the small size of the nano-materials increases their mobility and deliverability in the contaminated sites (Rabbani *et al*., 2016).

The aim of this research is to assess the capability of nano and ordinary zeolite for remediating lead polluted soil cultivated with rose geranium (*Pelargonium graveolens*).

MATERIALS AND METHODS

A greenhouse pot experiment was carried out on rose geranium (*Pelargonium graveolens*), a hyper-accumulator plant, grown on artificially lead-polluted soil in absence and presence of ordinary and nano zeolite to evaluate ordinary and nano zeolite ability to remediate Pb polluted soil. The soil was a sandy clay, (sand 59.2% , silt 10.3% and clay 30.5%) according to the international texture triangle (Moeys ,2016), collected from the plough layer (0-15cm upper layer) of an arable field in Met-Kenana village, Toukh, Qualubia governorate. Main properties being as follows (according to Gupta, 2009): pH

= 6.5; EC = 0.74 dSm^{-1}; and saturation percent 34.7%. Available Pb was extracted using DTPA extraction (Lindsay and Norvell ,1978) while total Pb was conducted on soil using Tri acid mixture Of $HClO_4$-HNO_3-H2SO_4 (Grimshaw, 1987). Pb was measured by atomic absorption spectro-photometer 210VGP. Total Pb was 23 mg kg^{-1} and DTPA extractable-Pb was not detected. The experimental design was randomized complete block, factorial (2 factors) in 3 replicates. Factor 1: Pb pollution, involved 2 rates of 500 and 1000 mg Pb kg^{-1} soil; designated as Pb_1 and Pb_2 respectively. Pb was in the form of nitrate "$Pb(NO_3)_2$ " . The artificial Pb pollution used in the experiment involved a low rate which is very much near the critical limit reported by Chen and Harris, (1999) and a high one double such a rate. Factor 2: Zeolite addition, involved 7 treatments as follows: no zeolite (Z_0), three rates of 0.5, 1 and 1.5 g kg^{-1} soil applied as nano zeolite; designated as, nZ_1, nZ_2 and nZ_3 respectively; and three similar rates applied as ordinary zeolite; designated as Z_1, Z_2 and Z_3 respectively. Figure 1 shows an image of the nano-zeolite using a transmission electron microscope (TEM). Each pot contained one kg of air-dry soil. The contaminated soils were left for 48 hours before transplanting the hyper-accumulator plant of rose geranium (*Pelargonium graveolens*).

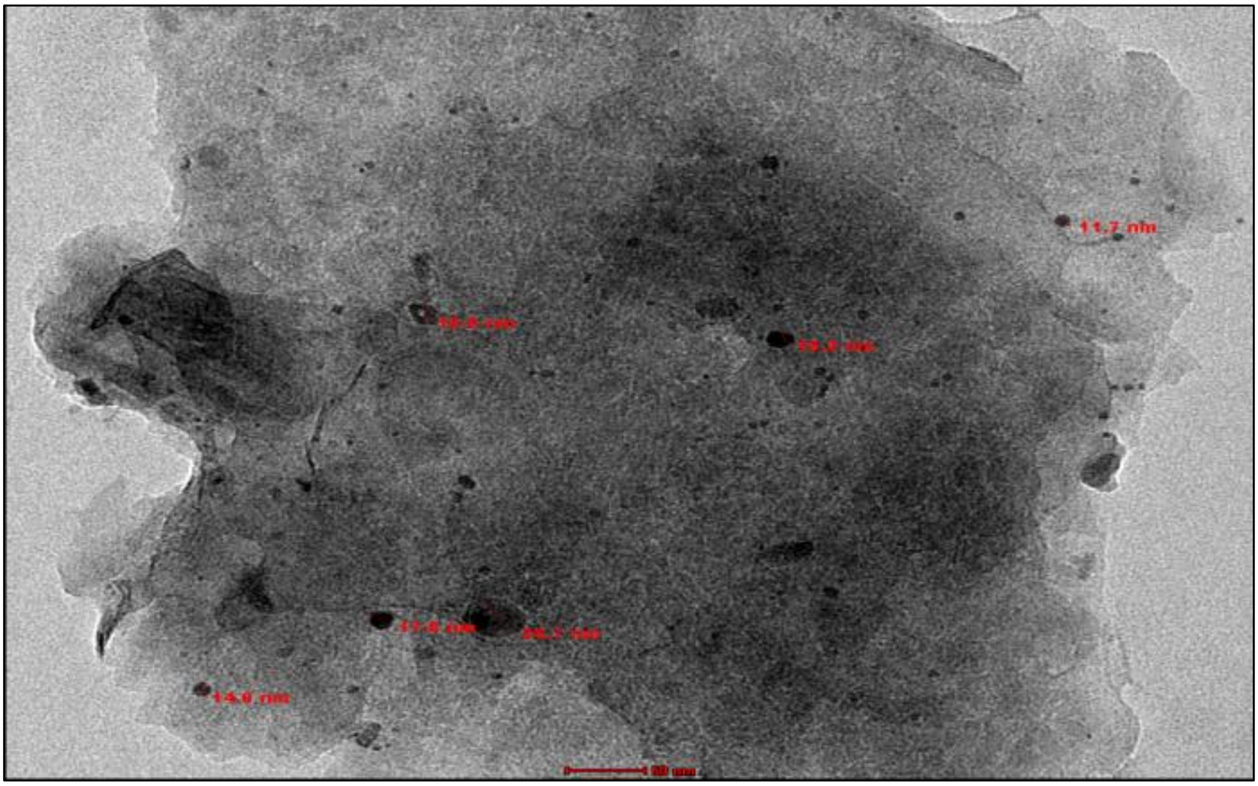

Fig. 1. Transmission Electron Microscope (TEM) Image of nano zeolite particles.

Pots were watered as required using tap water (no soluble lead was detected in water), keeping the moisture at about 75% of the water-holding capacity. Nutrients were added through foliar spray once a week, using nutrient solution prepared according to Douglas (1985). The experiment lasted 3 months at the end of which, plants were removed from pots, rinsed with distilled water, separated into shoots and roots then dried at 70 ºC for 24h and analyzed for Pb (digested by conc. sulphuric-perchloric acid mixture) (Chapman and Pratt, 1961). Pb was measured by atomic absorption spectro-photometer 210VGP. At the end of experiment soil was analyzed for DTPA-extractable Pb (Lindsay and Norvell ,1978) and apparent immobilization of Pb was calculated.

The apparent immobilization of Pb by soil constitutes the difference between "the sum of Pb element taken up by whole plant plus the amount of Pb extracted by DTPA" and the rate of Pb application. All expressed in terms of mg per pot. The calculation is as follows:

X = (Pb uptake in plant + Pb residual in soil) – Pb applied to soil.

Since the soil had practically no DTPA-extractable at start of experiment, the Pb applied is the source of Pb found in plant and soil of the experiment. As the weight of soil per pot is one kilogram, therefore contents of element per kg is the same as amount of element per pot.

RESULTS AND DISCUSSION

Weight of fresh and dry shoots and roots (Tables 1 to 4):

The high rate of Pb pollution showed greater plant growth than the low rate since the element was added as lead nitrate $Pb(NO_3)_2$ hence increasing its rate was associated with an increase in the vital nutrient of nitrogen which in turn caused increased growth of shoots and roots(Tables 1 to 4). The plant is a hyper-accumulator for heavy metals and could withstand high concentration of Pb with no negative effects (Manshadi *et al*., 2013). Ruley *et al. (*2006) reported that growth of *Sesban iadrummondii*, a hyper-accumulator plant, thrived in soils polluted with high doses of Pb added as $Pb(NO_3)_2$with no negative effect on photosynthesis activity.

Zeolite application with the exception of Z_1 (which only gave a significant increase with dry weight of shoots) significantly increased the weight of fresh and dry shoots as well as fresh and dry roots. All nano forms surpassed the ordinary forms. Increases in shoots fresh weight averaged 5.4, 8.31, 10.35, 2.73, 7.12, and 6.79% due to nZ_1(nano zeolite at 0.5 g kg^{-1} soil),nZ_2 (nano zeolite at 1.0 g kg^{-1} soil), nZ_3 (nano zeolite at 1.5 g kg^{-1} soil),Z_1(zeolite at 0.5 g kg^{-1} soil), Z_2(zeolite at 1.0 g kg^{-1} soil), and Z_3(zeolite at 1.5 g kg^{-1} soil) respectively. Respective increases in weight of dry shoots were 9.47, 11.89, 13.24, 5.77, 7.89 and 8.23%. Also respective increases in weight of dry roots were 7.46, 10.26, 11.66, 2.56, 5.36, and 7.23%. The slight effect of Z_1treatment indicates that this low rate of ordinary zeolite was not enough to decrease the movement and mobility of Pb. This particular treatment absorbed considerable Pb (highest uptake among zeolite treated treatments), see Tables 5 to 7, as well as the highest Pb in soil after termination of experiment, residual Pb (Table 8).

Table 1.Effect of zeolite application to Pb polluted soil cultivated with rose geranium (*Pelargonium graveolens)* plant on fresh weight of shoots (g pot^{-1}).

Lead pollution (Pb)	Zeolite application (Z)							Mean
	Z_0	nZ_1	nZ_2	nZ_3	Z_1	Z_2	Z_3	
Pb_1	62.64	66.14	67.81	69.85	63.66	68.36	68.21	66.67
Pb_2	72.79	76.63	78.89	79.61	75.47	76.72	76.42	76.65
Mean	67.72	71.38	73.35	74.73	69.57	72.54	72.32	
$LSD_{(0.05)}$			Pb =1.41	Z = 2.63	Pb Z = ns			

Notes: Z_0: no zeolite , nZ_1, nZ_2, nZ_3, are nano zeolite at 0.5, 1.0 and 1.5 g kg^{-1} soil respectively; Z_1, Z_2, Z_3 are ordinary zeolite at same aforementioned respective rates. Pb_1 ,and Pb_2 are 500 and 1000 mg Pb kg^{-1} soil respectively. ns: not significant

Table 2. Effect of zeolite application to Pb polluted soil cultivated with rose geranium (*Pelargonium graveolens)* plant on dry weight of shoots (g pot^{-1}).

Lead pollution (Pb)	Zeolite application (Z)							Mean
	Z_0	nZ_1	nZ_2	nZ_3	Z_1	Z_2	Z_3	
Pb_1	24.09	26.14	26.46	27.22	25.42	26.33	26.52	26.02
Pb_2	27.88	30.75	31.71	31.65	29.57	29.76	29.73	30.15
Mean	25.99	28.45	29.08	29.43	27.49	28.04	28.13	
$LSD_{(0.05)}$			Pb = 0.55	Z= 1.02	Pb Z = ns			

***See footnotes of Table 1 for treatment designations.**

Table 3. Effect of zeolite application to Pb polluted soil cultivated with rose geranium (*Pelargonium graveolens)* plant on fresh weight of roots (g pot^{-1}).

Lead pollution (Pb)	Zeolite application (Z)							Mean
	Z_0	nZ_1	nZ_2	nZ_3	Z_1	Z_2	Z_3	
Pb_1	9.16	9.90	10.07	10.23	9.45	9.78	9.74	9.76
Pb_2	10.66	11.06	11.87	11.39	10.76	11.09	11.16	11.14
Mean	9.91	10.48	10.97	10.81	10.10	10.43	10.45	
$LSD_{(0.05)}$			Pb = 0.34	Z = 0.63	Pb Z = ns			

***See footnotes of Table 1 for treatment designations.**

Table 4. Effect of zeolite application to Pb polluted soil cultivated with rose geranium (*Pelargonium graveolens)* plant on dry weight of roots (g $plant^{-1}$).

Lead pollution (Pb)	Zeolite application (Z)							Mean
	Z_0	nZ_1	nZ_2	nZ_3	Z_1	Z_2	Z_3	
Pb_1	4.01	4.32	4.31	4.59	4.16	4.22	4.25	4.27
Pb_2	4.57	4.91	5.14	4.99	4.64	4.82	4.94	4.86
Mean	4.29	4.61	4.73	4.79	4.40	4.52	4.60	
$LSD_{(0.05)}$			Pb = 0.11	Z = 0.21	Pb Z = ns			

***See footnotes of Table 1 for treatment designations.**

Increased growth of plant was associated with application of zeolite, and a progressive increase occurred with application rate, particularly the nano forms.This reflects the ability of zeolite to decrease movement and availability of heavy metals, hence alleviating the harmful effect on plant growth (Christopher *et al.*, 2012). A study by Panayotova and Velikov (2002) showed that addition of zeolite to solutions containing heavy metals caused a strong immobilization of Pb due to tight adsorption on zeolite particles. Wanga and Peng (2010) stated that zeolite ability to immobilize heavy metals in aqueous solutions followed a descending order of Pb > Cu > Cd ~ Zn.

Regarding fresh weight of roots, all treatments receiving zeolite showed grater growth which was particularly significant with the nZ_2 and nZ_3, nano forms of zeolite, with increases of 10.70 and 9.08% respectively. Other treatments had no significant effect. The nZ_1treatment significantly increased weight of shoots (fresh and dry) and roots (fresh and dry). Also there was no significant difference between nZ_1 with Z_1, $Z_2$and Z_3. This indicates that nZ_1had the same effect as Z_1, Z_2andZ_3 on shoots (fresh and dry) and roots (fresh and dry) weight. Hu *et al.* (2018) assessed nano and ordinary zeolite ability to remediate Cd polluted soil where tobacco was planted and found that the most effective treatment was the nano one as it decreased available Cd in soil and Cd in all plant parts. Results show no significant differences among nZ_1, nZ_2, and nZ_3except in shoots dry weight where nZ_3surpassed nZ_1.Therefore increasing zeolite application, in its nano form, has a positive effect in the weight of shoots and roots and the most effective for shoots and roots weight is the lowest rate of nano zeolite (nZ_1).

Pb uptake in plant shoots (Table 5) :

The high rate of Pb pollution showed greater Pb uptake than the low rate considering lead nitrate $Pb(NO_3)_2$was the source , thus increasing plant growth (Tables 1 to 4). Arshad *et al.* (2008) conducted a field experiment with two soils high in their Pb content (1830 and 39250 mg Pb kg^{-1}) and six cultivars of *Pelargonium* and noted that all plants had vigorous growth with no toxicity symptoms in spite of the high Pb accumulation, indicating and asserting that they are hyper accumulators for Pb. This explains the increase of Pb uptake associated with higher growth.

Table 5. Effect of zeolite application to Pb polluted soil cultivated with rose geranium (*Pelargonium graveolens)* plant on Pb uptake in shoots (mg pot^{-1}).

Lead pollution (Pb)	Zeolite application (Z)							Mean
	Z_0	nZ_1	nZ_2	nZ_3	Z_1	Z_2	Z_3	
Pb_1	29.92	9.05	7.59	5.35	18.99	16.58	16.36	14.83
Pb_2	44.99	17.03	14.26	11.93	23.46	22.01	21.22	22.13
Mean	37.46	13.04	10.92	8.64	21.23	19.29	18.79	
$LSD_{(0.05)}$			Pb = 0.64	Z = 1.19	Pb Z = 1.68			

***See footnotes of Table 1 for treatment designations.**

Zeolite application significantly decreased Pb uptake in shoots. The decrease averaged 65.19, 70.85, 76.94, 43.33, 48.51, and 49.84% due to nZ_1,nZ_2, nZ_3, Z_1,$Z_2$and Z_3, respectively (Table 5).Such decrease indicates zeolite ability to immobilize Pb in soil (Panayotova and Velikov, 2002; Wanga and Peng, 2010; Christopher *et al.*, 2012). Nano zeolites were most certainly more efficient in immobilizing Pb than ordinary zeolites as they exhibited lower Pb uptake (Tables 5to 7) and lower residual Pb in soil at end of plant growth (Table 8) with a conclusive indication of higher immobilization of Pb in the nano-zeolite treated than the ordinary-zeolite treated soils (Table 9). Increasing zeolite application in both nano and ordinary caused a progressive decreased in Pb uptake. Regarding Pb uptake by shoots, there was no significant difference between Z_2 and Z_3. This shows that increasing ordinary zeolite application form Z_2 to Z_3 had no significant effect on Pb uptake by shoots despite significantly decreasing residual Pb. This reflects that the amount of immobilized Pb by increasing zeolite from Z_2 to Z_3 was not enough to affect Pb uptake by shoot. Hu *et al.* (2018) found that nano zeolite was more effective than ordinary zeolite in reducing Cd in all parts of tobacco plant grown in Cd polluted soil. Li *et al.*, (2009) found that Pb uptake by rape in Pb contaminated soil decreased with increasing zeolite addition, also that the reduction of Pb uptake (as percentage) reached 30% in shoot and 49% in root.

There was a significant interaction between Pb pollution and zeolite application. Under Pb_2, the ordinary zeolite increase from Z_1 to Z_2caused no significant decrease in Pb uptake by shoots. On the other hand, under Pb_1 the nano-zeolite increase from nZ_1 to nZ_2 caused no significant decrease in Pb uptake by shoots. This shows that increasing zeolite application form Z_1 to Z_2, under Pb_2, or from nZ_1 to nZ_2, under Pb_1, did not significantly affect Pb uptake by shoots.

Pb uptake in plant roots (Table 6) :

As occurred with shoots, high Pb pollution showed greater Pb uptake than the low one. As in Pb uptake by shoots, zeolite application significantly decreased Pb uptake by rose geranium roots. The decrease in Pb uptake caused by the zeolite treatments averaged 57.81, 62.42, 70.55, 33.79, 39.93 and 42.82% due to nZ_1,nZ_2, nZ_3, Z_1, Z_2, and Z_3 respectively (Table 6).The decrease was in the following descending order :nZ_3>nZ_2>nZ_1>Z_3>Z_2>Z_1, as in Pb uptake by shoots. Regarding Pb uptake by roots as in its uptake by shoots, there was no significant difference between Z_2 and Z_3. Castaldi *et al*, (2005) grew lupin on soil contaminated with heavy metals, Pb (19.663 g kg^{-1}), Cd (0.196 g kg^{-}) and Zn (14.667 g kg^{-1}), and found that heavy metal uptake by plant decreased due to zeolite application, with Pb and other heavy metals uptake by roots being higher than by shoots.

There was a significant interaction between Pb pollution and zeolite application. Under Pb_2 lead uptake by roots showed no significant difference between Z_1 and Z_2, and nZ_1 and nZ_2 while under $Pb_1$the uptake by roots showed no significant difference between nZ_1 and nZ_2. This indicates that increasing zeolite application form Z_1 to Z_2, under Pb_2, and from nZ_1 to nZ_2under $Pb_1$and Pb_2, did not significantly affect Pb uptake by roots.

Table 6. Effect of zeolite application to Pb polluted soil cultivated with rose geranium (*Pelargonium graveolens)* plant on Pb uptake in roots (mg pot^{-1}).

Lead pollution (Pb)	Zeolite application (Z)							Mean
	Z_0	nZ_1	nZ_2	nZ_3	Z_1	Z_2	Z_3	
Pb_1	9.07	3.75	3.21	2.37	6.41	5.49	5.23	5.08
Pb_2	13.07	5.59	5.12	4.14	8.25	7.82	7.42	7.35
Mean	11.07	4.67	4.16	3.26	7.33	6.65	6.33	
$LSD_{(0.05)}$			Pb = 0.21	Z = 0.40	Pb Z = 0.57			

***See footnotes of Table 1 for treatment designations.**

Pb uptake by whole Plant (Table 7):

Pb pollution on Pb uptake by rose geranium plant was the same as on Pb uptake by its shoots and roots. Increasing Pb pollution in soil significantly increased Pb uptake by roots. As in Pb uptake by shoots and roots, zeolite significantly decreased Pb uptake by plant. The decrease in Pb uptake averaged 63.51, 68.91, 75.50, 41.15, 46.53, and 48.26% due to nZ_1, nZ_2, nZ_3, Z_1, Z_2, and Z_3 respectively (Table 7). The decrease was in the following descending order: $nZ3>nZ_2>nZ_1>Z_3>Z_2>Z_1$, as in Pb uptake by shoots and roots. Regarding Pb uptake by plant as in its uptake by roots and shoots, there was no significant difference between Z_2 and Z_3. Lead uptake by plant had a significant interaction between Pb pollution and zeolite application, as occurred in Pb uptake by shoots. Under Pb_2, lead uptake by plant had no significant difference between Z_1 and Z_2 while under Pb_1 the uptake by plant had no significant difference between nZ_1 and nZ_2.

Ulmanu *et al.* (2006) stated that uptake of Pb, Cu, Zn, Cd and Mn by corn, mustard and oat was decreased progressively as zeolite application to soil increased.

Table 7. Effect of zeolite application to Pb polluted soil cultivated with rose geranium (*Pelargonium graveolens)* plant on Pb uptake in whole plant (mg pot^{-1}).

Lead pollution (Pb)	Zeolite application (Z)							Mean
	Z_0	nZ_1	nZ_2	nZ_3	Z_1	Z_2	Z_3	
Pb_1	38.99	12.80	10.79	7.72	25.39	22.07	21.59	19.91
Pb_2	58.06	22.62	19.37	16.08	31.72	29.84	28.63	29.48
Mean	48.53	17.71	15.08	11.89	28.56	25.95	25.11	
$LSD_{(0.05)}$	Pb = 0.79 Z = 1.47 Pb Z = 2.08							

***See footnotes of Table 1 for treatment designations.**

DTPA-extractable Pb in soil at end of plant growth "residual Pb" (Table 8):

The high Pb pollution treatment showed higher extractable Pb in soil compared with the low pollution treatment. All soils showed contents below the initial Pb added to soils at start of experiment. Soils receiving no zeolite showed a decrease of about 30% of applied Pb. Decreases caused by the nano zeolite were greater than by the ordinary zeolite. The decrease ranged from 41.9% (of the initially applied Pb) caused by the low ordinary zeolite of the high Pb pollution (Z_1Pb_2) to a considerable 85.5% caused by the high nano zeolite of the low Pb pollution (nZ_3Pb_1) .The decrease was progressive with the increase in the rate of zeolite (nano - or ordinary). Percent decrease for the nano treatments of nZ_1, nZ_2, and nZ_3 at the low Pb pollution (Pb_1) amounted to 73.7, 76.7 and 85.5% (of the initial Pb rate) respectively. Comparable decreases at the high Pb pollution rate (Pb_2) were 74.7, 79.6, and 81.8 % respectively. Percent decreases for the ordinary zeolite treatments of Z_1, Z_2, and Z_3 at the low Pb were 51.1, 55.7, and 71.2% respectively. Comparable decreases for the high Pb treatments were 41.9, 48.7 and 53.1%respectively. Average decreases over the two Pb rates followed the order of $nZ_3> nZ_2> nZ_1> Z_3> Z_2> Z_1$with average decreases of 75.73, 69.50, 63.39, 41.65, 30.10 and 21.38% (in relation to the no zeolite treatment) respectively. Such pattern of decrease is in line with the pattern of Pb uptake by shoots and roots and whole plant. Therefore nano zeolite was more effective in immobilizing Pb than ordinary zeolite. Addition of zeolite to soil (in nano as well as ordinary forms) decreased residual Pb in soil and Pb uptake by plant. The decrease was progressive with the increase in the rate of zeolite addition. Despite residual Pb of Z_3 failing behind Z_2 significantly, such significant differences were not observed regarding Pb uptake in shoots, roots, and plant.

These results demonstrate the ability of zeolite to fix and immobilize Pb in soils. Misaelides (2011) stated that heavy metals, especially lead, in soils can be stabilized and/or removed by zeolite. Mozgawa (2000) noted that heavy metals in polluted soils became inactive by addition of zeolites and Mozgawa *et al.*(2009) attributed Pb immobilization by zeolite to the mineralogical structure of the mineral. Decreased availability of heavy metals including Pb by addition of zeolite was reported by Damian *et al.* (2013) using for different soils.

Table 8. Effect of zeolite application to Pb polluted soil cultivated with rose geranium (*Pelargonium graveolens)* plant on DTPA- extractable Pb at end of experiment (mg kg^{-1}).

Lead pollution (Pb)	Zeolite application							Mean
	Z_0	nZ_1	nZ_2	nZ_3	Z_1	Z_2	Z_3	
Pb_1	349.7	131.7	116.3	72.7	244.7	221.3	144.0	182.9
Pb_2	701.0	253.0	204.0	182.3	581.3	513.0	469.0	414.8
Mean	525.3	192.3	160.2	127.5	413.0	367.2	306.5	
$LSD_{(0.05)}$	Pb = 3.61 Z = 6.76 Pb Z = 9.56							

***See footnotes of Table 1 for treatment designations.**

Apparent immobilization of Pb in soil (Table 9)

The apparent immobilization in the high Pb treatment showed double the amount of immobilized Pb compared with the low Pb treatment. Nearly about more than one fifth of Pb applied to soils receiving no zeolite was subject to immobilization by the soil. Addition of zeolite increased such immobilization. The immobilized Pb ranged from 46.0 to 83.9% of the initially applied Pb for soils polluted with the low Pb rate; and from 38.7 to 80.2% for soils polluted with the high Pb rate. The nano forms were far more effective than the ordinary forms. Immobilization and tight fixation of soluble Pb were reported by Mozgawa (2000), Panayotova and Velikov, (2002), Wanga and Peng (2010), Misaelides (2011), Christopher *et al*., (2012) and Damian *et al*., (2013).

Table 9. Effect of zeolite application to Pb polluted soil cultivated with rose geranium (*Pelargonium graveolens)* plant on Pb apparently immobilized by the soil(mg pot^{-1})*.

Lead pollution (Pb)	Zeolite application							Mean
	Z_0	nZ_1	nZ_2	nZ_3	Z_1	Z_2	Z_3	
Pb_1	111.31	355.5	372.91	419.58	229.91	256.63	334.41	297.18
Pb_2	240.94	724.38	776.63	801.62	386.98	457.16	502.37	555.73
Mean	176.13	539.94	574.77	610.60	308.45	356.90	418.39	
$LSD_{(0.05)}$			Pb = 4.0	Z =7.4	Pb Z = ns			

(1) See footnotes of Table1 for treatment designations. (2) Immobilized Pb is calculated as the difference between the sum of "Pb-uptake by plant + soil DTPA–extractable Pb" and total Pb applied; all expressed in terms of mg pot^{-1}; noting that the amount of soil per pot is 1 kg.

CONCLUSION

Remediating Pb polluted soils can be achieved using zeolite particularly in its nano form (nZ) rather than its ordinary one (Z). Rates were 0.5, 1.0 and 1.5 g kg^{-1}. Growing a hyper-accumulator plant such as rose geranium (*Pelargonium graveolens*) can be practical preposition in phyto remediation. Nano zeolite (nZ) was more effective giving lower residual Pb in soil as well as Pb uptake in plant shoots, roots, of rose geranium. It gave higher immobilization of Pb in soil than ordinary zeolite (Z). Immobilization of added Pb ranged between 46.0 to 83.9% in soils polluted with 500 mg Pb kg^{-1}; and 38.7 to 80.1% in soils polluted with 1000 mg Pb kg^{-1} (comparing with initial Pb applied to soil). The most effective treatment was nZ_1. Pb uptake in shoots, roots, and whole plant and residual Pb significantly decreased in the following descending order: $nZ_3>nZ_2>nZ_1>Z_3>Z_2>Z_1$. Highest decrease in residual Pb was caused by nZ_3 which had the lowest Pb uptake by plant.

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علاج ارض ملوثة بالرصاص و مزروعة بنبات ابرة الراعى (*Pelargonium graveolens*) باستخدام النانو زيوليت

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تمت زراعة نبات ابرة الراعى، نبات عالى التجميع للعناصر الثقيلة، في صوبة في ارض قوامها sandy clay. كان تصميم التجربة عاملية في قطاعات تامةالعشوائية و كان هناك عاملين للتجربة العامل الأول إضافة الزيوليت تم على سبع مستويات كالتالى: Z_0 (لم يتم إضافة زيوليت)، nZ_1 (اضيف نانو زيوليت بمعدل ٠.٥ جم كجم$^{-1}$ ارض)، nZ_2 (اضيف نانو زيوليت بمعدل ١.٠ جم كجم$^{-1}$ ارض)، nZ_3 (اضيف نانو زيوليت بمعدل ١.٥ جم كجم$^{-1}$ ارض)، Z_1 (اضيف زيوليت عادى بمعدل ٠.٥ جم كجم$^{-1}$ ارض)، Z_2 (اضيف زيوليت عادى بمعدل ١.٠ جم كجم$^{-1}$ ارض)، Z_3 (اضيف زيوليت عادى بمعدل ١.٥ جم كجم$^{-1}$ ارض) و العامل الثانى التلوث بالرصاص تم على مستويين كالتالى: Pb_1 (٥٠٠ مللجرام رصاص كجم$^{-1}$ ارض)، Pb_2 (١٠٠٠ مللجرام رصاص كجم$^{-1}$ ارض). انخفض امتصاص الرصاص (بواسطة مجموع خضرى او جذرى او للنبات) و الرصاص المتبقى في التربة انخفاضا معنويا نتيجة لاضافات الزيوليت. متوسط الانخفاض كان طبقا للترتيب التنازلى التالى : $Z_1< Z_2< Z_3< nZ_1< nZ_2<nZ_3$. اعلى انخفاض في الرصاص المتبقى في التربة كان عند المعاملة nZ_3 (٧٥.٧%) التي أيضا عندها كان اعلى انخفاض في الرصاص الممتص بواسطة المجموع الخضرى (٧٦.٩%)، المجموع الجذرى (٧٠.٦%)، النبات (٧٥.٥%). المعاملات التي تلقت نانو زيوليت كانت اكثر فاعلية في خفض الرصاص المتبقى في التربة (تراوحت بين ٦٣.٣٩ الى ٧٥.٧%)، امتصاص الرصاص بواسطة المجموع الخضرى (تراوحت بين ٦٥.٢ الى ٧٦.٩%)، امتصاص الرصاص بواسطة المجموع الجذرى (تراوحت بين ٥٧.٨ الى ٧٠.٥٥%)، امتصاص الرصاص بواسطة النبات (تراوحت بين ٦٣.٥ الى ٧٥.٥%)، و كان النانو زيوليت اكثر فاعلية من الزيوليت العادى في زيادة وزن المجموع الخضرى سواء جاف او طازج (ترواح بين ٥.٤ الى ١٣.٢%) ، و زيادة وزن المجموع الجذرى سواء جاف او طازج (ترواح بين ٧.٥ الى ١١.٧%). اكثر المعاملات تاثيرا على وزن النبات (سواء طازج او جاف) كانت nZ_1. معاملات الزيوليت زادت من الرصاص المثبت في نهاية التجربة و كانت الزيادة تتراوح بين ٤٦.٠ الى ٨٣.٩% في الاراضى الملوثة بإضافة الرصاص المنخفضة (Pb_1) اما في الاراضى الملوثة بإضافة الرصاص المرتفعة (Pb_2) فكانت تتراوح بين ٣٨.٧ الى ٨٠.١%(بالمقارنة مع الرصاص المضاف الى التربة).