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Use of Zeolite to Reduce the Bioavailability of Heavy Metals in a Contaminated Soil

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ABSTRACT

Soil enrichment with heavy metals plays a significant role in soil pollution, which leads towards buildup/accumulation of heavy metals in edible crops. This situation causes severe threats to the sustainability of ecosystem and human health. The bioavailability of heavy metals can be restricted by the addition of immobilizing agents. Therefore, a pot experiment was carried out to evaluate the potential of zeolite i.e., 'clinoptilolite' as immobilizing agent to reduce the bioavailability of different heavy metals in soil. For this purpose, the pots containing soil contaminated with different heavy metals (Cd, Pb, Cu and Zn) were treated with variable concentration of zeolite i.e., 1, 3, 5, 7, 9, 15, 20, 30, 40, 50 g·kg⁻¹, as well as the pots with no addition of ZL as control treatment and incubated for 30, 60 and 90 days. The effectiveness of the applied treatments was evaluated by single metal extraction method in soil using DTPA having 7.3 pH and NH₄NO₃. The results showed that the soils treated with ZL exhibited significant increases in soil pH and cation exchange capacity as well as a reduction in the concentration of metals (Cd, Pb, Cu and Zn) as compared to the control soil. Among the different concentrations of ZL, the most promising results were achieved with ZL at 50 gkg^{-1} after 90 days of incubation. It was observed that the soil treated with zeolite at 50 g·kg⁻¹ showed significantly higher contents of immobilized DTPA and NH₄NO₅ concentrations of Cd, Cu, Pb and Zn after 90 days of incubation when compared with the control treatment. The trend of reduction in DTPA extractable concentration of heavy metals was in order of $Cd \le Pb \le Zn \le Cu$ with reduction in contents up to 5.51, 23.15, 28.41 and 35.66% respectively. In turn, the reduction of content for Cd, Cu, Pb and Zn by using NH_4NO_3 was as follows 16.09, 20.11, 23.83 and 38.37%, respectively, but the trend of reduction was Cd < Pb < $Zn \leq Cu$. Therefore, reduction in concentration of heavy metals and their accumulation in the soil improved the soil quality. Hence, the addition of zeolites can significantly reduce the concentration of heavy metals in the soil although the reduction contents are not satisfactory for the production of food.

Keywords: immobilization, zeolite, DTPA, NH₄NO₃, heavy metals

INTRODUCTION

The pollution of soil with heavy metals has become a severe problem worldwide (Aryal et al., 2016; Houben et al., 2013; Luo et al., 2011; Sultana et al., 2014). Human activities, including industrial processes and production operations, smelting and mining, automobile exhaust led towards the accumulation of heavy metals in soil at the level that threatens the ecosystem services (Cheung and Gu, 2007; Jackson et al., 2009; Kumar et al., 2012; Zhou et al., 2016). For agricultural soils, irrigation with the untreated wastewater discharged by mining activities is a common source of heavy metals pollution worldwide (Kumpiene et al., 2008). Moreover, the addition of animal manure compost and municipal solid waste compost in soil are the sources of heavy metal pollution, because these organic inputs contain large amounts of heavy metals (Toth et al., 2016: Kumar et al., 2013). Among the numerous heavy metals, the concentration of Cd and Cu is much higher in municipal solid waste compost and livestock manure (Ayari et al., 2011).

Due to the accumulating nature of heavy metals, there is an increasing interest linked with the heavy metals contaminated soils and their proximate impacts on the global agricultural production system along with the food chain (Bian et al., 2014; Derakhshan Nejad et al., 2018). Ultimately now, it is a great challenge for researchers to introduce effective measuring techniques for the reduction of heavy metals bioavailability in soil. In order to minimize heavy metal contamination risk, many researchers have tested various soil remediation techniques and some of them has attached much attention worldwide (Liu et al., 2018). There are at least two ways to recover the heavy metals contaminated soil. The first way is to change the chemical state of these metals in the soil to their mobility, bioavailability and reduce the environmental risks by stabilizing heavy metals. The other way is to remove the heavy metals from the soil and bring them in the soil close or equal to the soil background (Wauna and Okieimen, 2011). Although, the immobilization of the heavy metals does not remove them from soil, it can effectively reduce the risks associated with heavy metals regarding plant intake, water pollution and soil biological exposure (Liu et al., 2018).

Previously, several researchers have used different amendments such as biochar, lime materials, steel slag, fly ash (FA) and zeolite (ZL) as cost effective technologies for the immobilization of heavy metals due to their chemical stabilization ability (Shaheen et al., 2014: Bolan et al., 2014). Among these amendments, zeolite (ZL) is a typical mineral modification that has been successfully used to remediate the heavy metals contaminated soils (Borowski and wasag, 2019). Because of its more surface area, high affinity for heavy metals and high alkalinity which enhances the fertility of soil and ultimately improves pH, cation exchange capacity (CEC) and the water holding capacity (WHC) of the soil (Wang et al., 2016).

Zeolites are microorous, crystalline and alkaline earth metals or hydrated aluminoslicate alkali metals with negatively charged positions that can remove metals very efficiently (Radziemska and Mazur, 2016: Shahbaz et al., 2018b).

MATERIAL AND METHODS

Sampling site description

The surface soil was collected from 0-15 cm depth by the following the random sampling method at agricultural land of Gujiao in Taiyuan City, Shanxi Province, China. Its geographical area lies between $37^{\circ}40' - 38^{\circ}8'$ north latitude and 111°43' - 112°21' east longitude. Gujiao has a lot of minerals, especially coal. The area of the coal mine covers about 754 square kilometers, and coal reserves represent about 8.04 billion tons. The iron ore reserves are about 30 million tons. The bauxite reserves are approximately 65.9 million tons. The limestone reserves are about 5.6 Million tons. The dolomite reserves are about 2.65 billion tons. The CBM's reserves represent nearly 5.66 billion cubic meters. The Surface soil samples were collected from different point from the fields and mixed thoroughly to obtain a homogenized sample which was used for further analysis and studies.

Characterization of soil samples

The soil samples were collected to examine different soil properties (Table 1). For the physical and chemical analyses, the soil samples were sieved through 2 mm mesh, while the soil samples used to determine heavy metal concentrations were sieved through a mesh having size of 1 mm. The soil texture was determined using the hydrometer method. In order to determine the pH of soil, a potentiometric method was used, followed by a soil paste saturated with distilled water with 1:5 (w:v). In order to assess the organic matter contents of soil, the tiurin method was used (Sumner and Miller, 1996). For the determination of particle size distribution of soil, the pipette method was applied. The NH₄Cl-NH₄COOH method was employed for assessing the cation exchange capacity (CEC) of soil. An elemental analyzer identified the total soil nitrogen, available phosphorus, and available potassium of the control soil following the combustion method (Nelson and Sommers, 1996; Rhoades, 1982). The soil organic matter contents (SOM) were calculated using the Walkley-Black method recommended by Jackson (1962).

Soil	pН	CECª	OMÞ	N	P available	K available	Cd	Cu	Pb	Zn
	-	cmol·kg ⁻¹	%	%	mg∙kg⁻¹	mg∙kg⁻¹	mg∙kg⁻¹	mg∙kg⁻¹	mg∙kg⁻¹	mg∙kg⁻¹
	7.65	10.14	2.21	0.11	15.6	107.3	4.83	249.3	416	316
& Cation Exchange Conseity										

Table 1. The main properties of soil of the sampling site before application of amendment

^a Cation Exchange Capacity.

^b Organic Matter.

Zeolite properties

The 'clinoptilolite' zeolite used in the experiment was purchased from a company in Taiyuan, China. It was characterized by the following physiochemical properties EC ($2.1\pm0.1 \text{ dSm}^{-1}$), pH (8.1 ± 0.2), CEC ($127\pm5.3 \text{ cmol}\cdot\text{kg}^{-1}$, $0.052 \text{ mg}\cdot\text{kg}^{-1}$ Cd, 10.42 mg $\cdot\text{kg}^{-1}$ Pb, 10.25 mg $\cdot\text{kg}^{-1}$ Cu and 7.2 mg $\cdot\text{kg}^{-1}$ Zn). The zeolite was finely mixed. Before use, the zeolite was passed through the 0.2 mm sieve before conditioning and measuring capacity.

Pot experiment

In this study, a pot experiment was carried out in the experimental laboratory of College of Environmental Science and Engineering, Taiyuan University of Technology, China. This pot experiment was comprised of total 11 treatments with five replicates. All the pots were filled with 1000 g of dry sifted soil taken from the sampling points. The treatments applied were the addition of zeolite at different concentrations i.e., 1, 3, 5, 7, 9, 13, 15, 20, 40, and 50 g kg⁻¹ as well as a control treatment where no ZL was added. All the treatments were arranged according to completely randomized design (CRD). The zeolite was uniformly mixed in all the pots. All samples were incubated under controlled conditions where a temperature of 25°C and 40% relative humidity were maintained. Moreover, water holding capacity (WHC) of the pot was maintained at 65% by adding the required amount of water after every two days. The soil samples were incubated for three different periods i.e., 30 days, 60 days and 90 days. The treatments and incubation conditions were the same during the whole experimental period. After each incubation period, the required amount of soil sample was taken and dried at room temperature for further analysis.

Soil analysis

Soil organic carbon contents (SOC) was measured using 0.2 mm of fine blended soil treated with dichromate and was titrated with ammonium ferrous sulfate (Walkely and Black, 1934). However, extraction of heavy metals was performed using 20 grams of finely mixed soil followed by the addition of 40 ml of extracts solution (DTPA-CaCl₂-TEA having pH 7.3 and NH₄NO₃). All the soil samples were centrifuged at 5000 rpm for 1 hour and then filtered through 0.2 μ m Whatman filter. All the transparent solutions obtained after extraction were analyzed by atomic absorption spectrophotometer to determine the heavy metals contents in the soil.

Statistical analysis

In order to obtain the importance of all variables present between treatments, one-way analysis of variance was performed. However, significant difference (p > 0.05) between all the variables with in treatments was achieved through the Tukey's HSD test. All the data was analyzed using SPSS version 1.8 (released SPS. Inc.).

RESULTS AND DISCUSSION

In this study, the efficiency of in situ immobilization of heavy metals in soil was assessed by adding zeolite and using a chemical extraction test of DTPA and NH_4NO_3 . The objectives of this experiment was not to eliminate the heavy metals from the soil but to minimize the useful amount of heavy metals by altering some basic soil characteristics, including soil pH and CEC.

Effect of amendment on the soil pH

Soil pH is a fundamental and essential factor that significantly influences the metal behavior in soil and affects the effectiveness and toxicity to the soil and plants, both directly or indirectly (Radziemska, 2018). As shown in Figure 1, the soil taken from experimental field was moderately alkaline, and recorded average soil pH of the controlled pot was 7.65. Due to the strong alkaline pH, application of zeolite increased the pH of soil

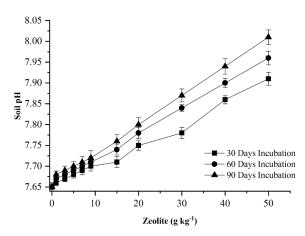


Fig. 1. Effect of amendments on the change in soil pH over control treatment

(p > 0.05) (Querol et al., 2006). All other treatments also significantly increased the pH of soil as compared to the control treatment. Radziemska (2018) observed that the addition of zeolite resulted in a significant increase in the soil pH and promoted carbonate precipitation and oxide formation, thereby reducing the quantity of heavy metals in the soil. The content of amendments added and the incubation time have a substantial effect on the immobilization of heavy metals and the increase in pH of soil (Dang et al., 2019).

The results presented in Figure 1 illustrate that variable addition of zeolite ranging from 1 $g \cdot kg^{-1}$ to 50 $g \cdot kg^{-1}$ and incubation time (30, 60, 90 days) influences the soil pH. The incubation period exhibited significant differences in the soil pH and these differences were more prominent in treatments where higher doses of zeolite were used i.e., 50 g·kg⁻¹. The soil pH of the samples up to 1-9 g·kg⁻¹ of the zeolite with minimum incubation time of 30 days differ from the controlled treatment with the same incubation time 7.65-7.70, while only a slight increment was observed from 7.65-7.71 when the incubation time was enhanced to 60 days with same amount of amendment, but the difference in soil pH between the 30 and 60 days of incubation was very close. The pH of the soil samples incubated for 90 days increased significantly by 7.65-7.72. Therefore, positive increments occurred in the 90 day as compared to 30 and 60 days incubation results. Similarly, as the quantity of amendment and incubation time were increased, as a significant effect of both the factors simultaneously, the highest soil pH recorded was 8.01 at incubation with 50 g·kg⁻¹ zeolite for 90 days, which was constantly significant compared to the control and all

other treatments. Therefore, it can be concluded that Zeolite has a significant effect of increasing the pH of soil and the addition of zeolite has increased 5.29% pH of the soil as compared to the control treatment.

The beet lime and biosolids compost were used for 2 years under field conditions as amendments, which changed the pH of the soil (Madejón et al., 2009). Since most heavy metals have very low mobility under alkaline conditions, increasing the soil pH can often remediate the contamination in soil by heavy metals (Teng et al., 2015). There are different processes including selective adsorption, metal precipitation with oxides, hydroxides, phosphates and carbonates to reduce the mobility of metals in soil solution which increase the soil fertility and promote the plant growth by providing the best conditions (Cárcamo et al., 2012).

Effect of amendments on the soil cation exchange capacity

Figure 2 shows the effects of addition of zeolite on CEC of soil samples during different incubation times. The results showed that the soil CEC increased significantly after the application of the zeolite in the soil samples compared to the non-amended soil samples. CEC is a significant factor in the immobilization of heavy metals (Sneddon et al., 2006). When the dose of up to 9 g kg⁻¹ zeolite was added, the soil CEC did not change significantly. However, the incubation time had a significant effect, and the soil CEC increased from 10.14–10.25 cmol·kg⁻¹ when the soil was treated with 9 g kg⁻¹ zeolite and incubated for 90 days, which was a considerable difference

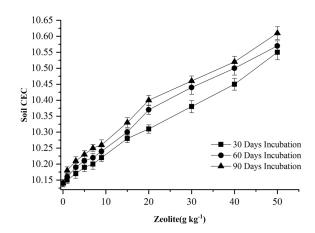


Fig. 2. Effect of amendments on the change in soil CEC over control treatment

compared to the control treatment. When 50 g·kg⁻¹ zeolite was added for 90 days incubation, the maximum CEC reached 10.61 cmol·kg⁻¹. On the basis of the results, it can be concluded that there is a positive significant effect of zeolite on the soil CEC, and the addition of zeolite in the amount of 50 g·kg⁻¹ has increased the soil CEC up to 4.31%, as compared to the control treatment.

As the amount of zeolite added increased from 10 $g \cdot kg^{-1}$ to 20 $g \cdot kg^{-1}$, the soil CEC increased significantly (Li et al., 2009). Due to its high specific surface area and high CEC, zeolite plays an essential role in surface complexation and significantly increases soil CEC also (Querol et al., 2006).

Effect of amendments on the availability of heavy metals in soil

All zeolite amendments significantly reduced the concentration of extractable heavy metals in the soil samples compared to the control treatment. Although the extent of the effect depends on two factors, the amount of zeolite and heavy metals. Zeolite significantly reduced the amount of DTPA and NH4NO3 extractable heavy metals in the soil samples during all three incubation times. According to Figures 3 and 4, after 90 days of incubation, up to 9 g·kg⁻¹ zeolite content reduced the DTPA extractable Cd and Pb concentration in the soil samples from 4.96 (control) to 4.89 mg·kg⁻¹ for Cd and 416 (control) to 391 mg·kg⁻¹ for Pb. The same reduction trend was noted when the amount of zeolite increased from 15–50 $g \cdot kg^{-1}$ at the same incubation time. When the soil samples were incubated for 90 days with 50 $g \cdot kg^{-1}$ zeolite, the best effect of zeolite amendment was observed and DTPA extractable concentration was up to 4.66 mg·kg⁻¹ and 316 mg·kg⁻¹ for Cd and Pb respectively, which is more significant than all other treatments.

According to some scientists, DTPA is the best extractant and suitable for calcareous soil because it is buffered at 7.3 pH, thus preventing the dissolution and release of $CaCO_3$. There is a high concentration of $CaCl_2$ in the DTPA extractant in which Ca^{+2} can be rapidly exchanged with bivalent cations; this exchange is quicker especially with the Cd contaminated soils. The greater concentration of chloride ions makes a complex of these two elements and triethanolamine (TEA) that is buffered at pH 7.3 can replace the H⁺ with cations at exchanging site. The findings of such

extraction studies can be more reliable to study the effectiveness of soil amendments (Lin and Zhou, 2009).

Our findings indicate that the soil pH significantly increased after the application of zeolite, resulting in high retention of the heavy metals at solid phase in soil, and the metal retention of zeolite may increase due to the effect of lime. The zeolite can fix heavy metals in the mineral clay layer of the soil by diffusion and increase the pH of the soil for a longer time (Lahori et al. 2017). The application of zeolite has significant effects on the immobilization of heavy metals, so the amount of metals in the soil becomes reduced and the roots of plants can make full use of heavy metals as previously explained by Trakal et al. (2011) who noticed that the willow tree's ability to absorb heavy metals decreased significantly after the zeolite application in the soil.

 $\rm NH_4NO_3$ is the mild extractant as compared to DTPA which can easily extract the fraction of exchangeable heavy metals in the soil solution. Therefore, the concentration of heavy metals is comparatively lesser in this extractant as compared to the others, especially DTPA. The reason behind this low fraction is the soil pH, because the availability of metals is directly dependent on the soil pH, and the concentration of $\rm NH_4NO_3$ extractable concentration reflects the effect of amendments of soil pH.

All zeolite amendments reduced the content of heavy metals in the soil, compared to the non-amended soil samples extracted with 1M NH₄NO₃. According to Figures 5 and 6, after 30 days of incubation, up to 9 g·kg⁻¹ zeolite content reduced the NH₄NO₂ extractable Cd and Pb concentration in the soil samples from 4.76 (controlled) to 4.59 mg·kg⁻¹ for Cd and 416 mg·kg⁻¹ (control) to 401 mg \cdot kg⁻¹ for Pb, which was not much different from controlled treatment. The addition of 15–50 mg \cdot kg⁻¹ (ZL) with the same incubation time and the result was 4.02 mg·kg⁻¹ and 319 mg kg⁻¹ for Cd and Pb at addition of 50 g·kg⁻¹ zeolite. The values of the Cd and Pb (extracted with 1M NH₄NO₃) contents in the soil without any change in amendment (ZL) level also decreased 4.68-3.91 mg·kg⁻¹ and 416-332 mg·kg⁻¹ as the incubation time was increased to 60 days.

The best result was achieved when the samples with 50 $g \cdot kg^{-1}$ zeolite were incubated for 90 days and the values reached up to 3.86 mg $\cdot kg^{-1}$ Cd and 346 mg $\cdot kg^{-1}$. According to the results, the content of reduction in NH₄NO₃ extractable Cd is

significantly greater than the results of the DTPA extraction. In turn, the reduction in the Pb content in lesser by NH_4NO_3 than DTPA.

It was noticed that zeolite decreased the concentration of Cd by 5.51%, 16.09% and of Pb by 23.5%, 20.11%, as compared to the controlled treatment extracted with DTPA and NH₄NO₃ solution. The DTPA extractable concentration of Cu and Zn is shown in Figures 7 and 8. The concentration of Cu and Zn in the soil samples amended with zeolite is significantly different from that of control, which indicates the effects of zeolite on the Cu and Zn concentration. On the contrary, it can be seen from Figure 7 and 8 that the

a)

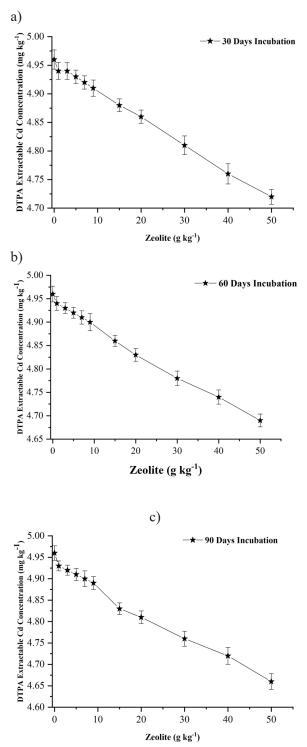


Fig. 3. Effect of amendments on the change in the concentration of Cd extracted with DTPA solution over control treatment

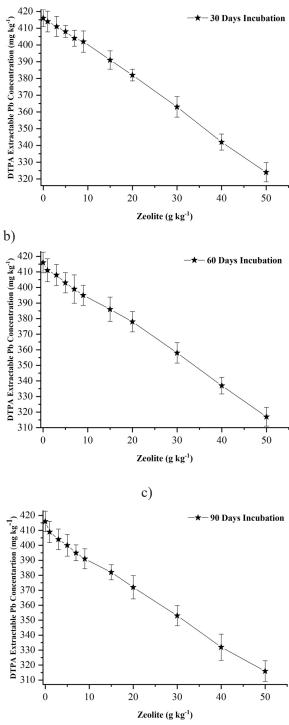


Fig. 4. Effect of amendments on the change in the concentration of Pb extracted with DTPA solution over control treatment

incubation time also has positive influence on the mobility of Cu and Zn. Both the incubation time and amount of zeolite decreased the Cu and Zn concentration with the following order (highest to lowest) control > $1-50 \text{ g} \cdot \text{kg}^{-1}$ simultaneously.

According to our results, the effect of zeolite with a minimum concentration and a minimum incubation time of 30 days is not obvious,

a)

4.8

4.'

4.6

4.5

4.4

4.3

4.2

have a significant impact, and with increasing incubation time and amount of zeolite added, after 50 g·kg⁻¹ of zeolite and 90-day incubation and the concentration of DTPA extractable Cu decreases to 168 mg·kg⁻¹, while the DTPA extractable a) 420 **30 Days Incubation** (mg kg⁻¹) 410 400 ation 390 380 NH₄NO₃ Extractable Pb Concen 370 360 350 340 330 320 40 50 0 10 20 30 Zeolite (g kg⁻¹) b)

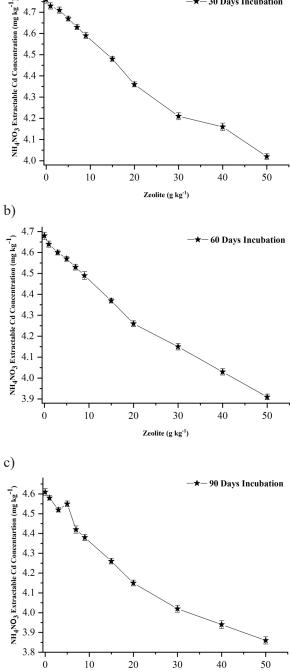
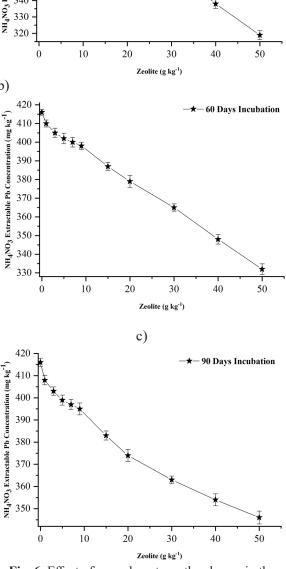


Fig. 5. Effect of amendments on the change in the concentration of Cd extracted with NH₄NO₃ solution over control treatment

Zeolite (g kg⁻¹)



and only a small amount of DTPA extractable

Cu and Zn has decreased from 258 mg·kg⁻¹ to

265 mg·kg⁻¹ and 318 to 295 mg·kg⁻¹. These results

30 Days Incubation

Fig. 6. Effect of amendments on the change in the concentration of Pb extracted with NH₄NO₃ solution over control treatment

concentration of Zn decreased to 224 mg kg⁻¹, which is very significant compared to all other treatments. This reduction is 35.66 and 28.41% for Cu and Zn, respectively, as compared to the controlled treatment.

Compared with the control by immobilization in soil samples, the heavy metal content was significantly reduced after applying natural zeolite (90 t·ha⁻¹), but this reduction in the heavy metal content was lower than that of dolomite and bentonite. These results belong to an experimental study by Szakova et al. (2007), who noticed that the extractable heavy metal concentration reached a minimum effect after applying zeolite. According to their results, the extractability was reduced by only 30% after applying natural

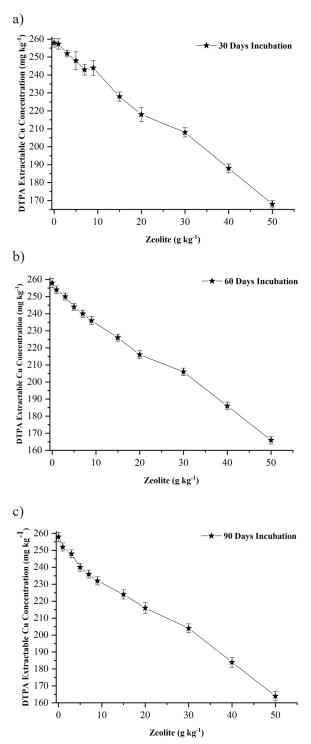


Fig. 7. Effect of amendments on the change in the concentration of Cu extracted with DTPA solution over control treatment

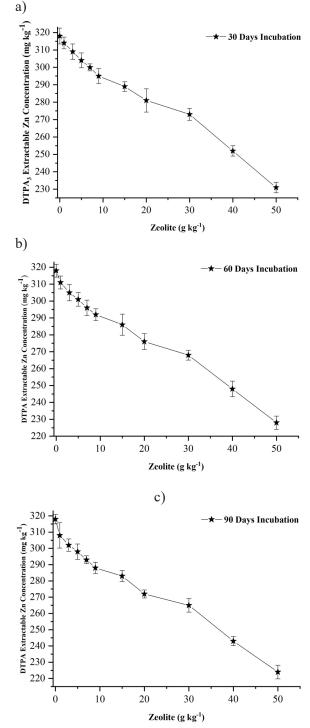


Fig. 8. Effect of amendments on the change in the concentration of Zn extracted with DTPA solution over control treatment

zeolite. Usman et al. (2005) also obtained similar results in their research, namely the use of clay minerals to fix heavy metals.

A similar reduction was noticed when the soil samples were extracted with 1M NH_4NO_3 solution, and it can be seen from Figure 9 and 10 that the zeolite (ZL) also has positive role in immobilizing Cu and Zn extraction with 1M NH_4NO_3 .

According to our results, the effects of zeolite with a maximum concentration of 50 g·kg⁻¹ and a minimum incubation time of 30 days were obvious, and only a significant amount of NH₄NO₃ extractable Cu has decreased from 255 mg·kg⁻¹ to 161 mg·kg⁻¹, while the NH₄NO₃ extractable concentration of Zn reduced from 316 mg·kg⁻¹ to 244 mg·kg⁻¹ which is highly effective than

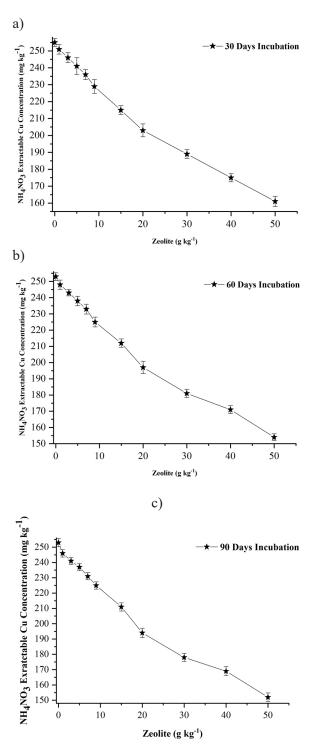


Fig. 9. Effect of amendments on the change in the concentration of Cu extracted with NH₄NO₃ solution over control treatment

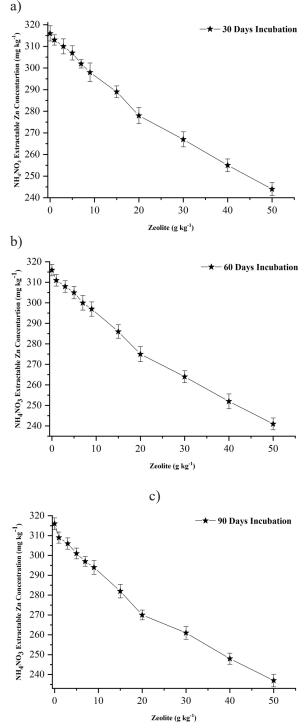


Fig. 10. Effect of amendments on the change in the concentration of Zn extracted with NH_4NO_3 solution over control treatment

control and all other treatments. The results of other minimum concentrations did not differ much than the control treatment. The results of the samples incubated for 60 days without any alteration the content of amendment (ZL) had a significant effect on the decrease in the Cu and Zn concentration. The highest level of decrease was noticed 154 mg·kg⁻¹ and 237 mg·kg⁻¹ for Cu and Zn respectively, when the samples were amended with 50 g·kg⁻¹ (ZL) and incubated for 90 days. The addition of zeolite reduced NH-4NO₃ extractable by 35.66, 38.37% and 28.41, 23.81% for Cu and Zn extracted with DTPA and 1M NH₄NO₃ solution, respectively as compared to the controlled treatment.

CONCLUSION

The main purpose of this study was to compare the effectiveness of zeolite aiming at the reduction behavior of negative effects of soil pollutants. The proposed results suggest that zeolite is highly beneficial for the decontamination of polluted soil.

- Zeolite can increase the pH and CEC of soil and immobilize the heavy metals in soil, thus it can reduce its availability and reduce the toxicity of pollutants in the soil.
- Zeolite amendments were effective for reducing the mobility of heavy metals due to binding of metals and forming the complexes.
- Although these amendments reduced the concentration of heavy metals in the soil, the best results achieved at dose of 50 g·kg⁻¹.
- According to the results, the retention time also influenced the performance of zeolite.
- The extraction behavior of both extractants (DTPA and HN₄NO₃) is different and both have a positive effect on the magnitude of extraction, and are efficient for the experimental studies.
- Despite encouraging finding, the tested amendment will be applied under the field conditions for the further evaluation in the future, specifically in historically polluted areas; as time goes by, more pay attention to metals, as our results show that the application of amendments reduces the environmental risks.

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