

Soil cadmium stabilization using an Iranian natural zeolite

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Abstract

In recent years, natural substances such as zeolite have been used to absorb heavy metals in soil in an attempt to decrease their availability to plants. Compared to other techniques, the use of zeolite is fast, clean, and inexpensive. This research was carried out to investigate the effects of an Iranian natural zeolite (clinoptilolite) on stabilizing Cd-contaminated soil treated with 0.01 M CaCl₂ leaching solution. Zeolite from Firoozkouh (Tehran Province) was added to four soils from Gilan province, northern Iran. The stabilization of Cd in soils mixed with zeolite was measured in both column and batch experiments. The results from the batch experiment showed that application of zeolite to soil reduced Cd leaching in all the contaminated soils. When more zeolite was added to soil, lower Cd concentrations were detected in the leaching solution. When 15% zeolite was applied, Cd concentration in the leachate decreased to below 0.1 mg l⁻¹. Cadmium depth analysis showed little migration of Cd in sand and clay textures with no zeolite addition and after adding 15 and 75 pore volumes of leaching solution, the remaining Cd levels were 12% and 35% of the original Cd concentration, respectively. However, these values for 9% zeolite treatments were 97% and 99%, respectively. The higher cation exchange capacity of the zeolite/soil mixture and the higher pH levels were responsible for stabilizing Cd in these soils. The effect of preventing heavy metals from leaching was found to be more pronounced when zeolite was applied to clay soils.

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1. Introduction

Heavy metals are rarely removed by microorganisms in natural ecosystems (Faghihian and Kazemian, 1999). In spite of its toxicity, cadmium is widely used in several industrial processes including metallurgical alloying, ceramic manufacturing, electroplating, textile printing, mine drainage and in production of inorganic pigments (Shanbleh and Kharabsheh, 1996). Three major reclamation techniques can be used for metal-contaminated soils which include biological, agriculture engineering, and physicochemical treatments. The biotreatment method is carried out via planting, harvesting and eventually removing non-edible crops in contaminated soils. The problem with this method is that it is time-consuming and fails to prevent pollution expansion. Agricultural methods including earth swap

and deep plowing are other alternatives but with some risk. The most direct improved method, the earth swap, is extremely costly while the deep plowing method disturbs the field and results in the contamination of groundwater in future (Lin et al., 1998). Physicochemical technique such as the use of natural clay minerals is another method to extract, stabilize and solidify heavy metals (Colella et al., 1995).

According to traditional definition, zeolites are hydrated aluminosilicates of alkaline and alkaline-earth minerals (Akbar et al., 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; Aleksiev et al., 2000). Zeolites, as natural cation exchangers, are suitable substitutes to remove toxic cations (Ames, 1961; Arellano et al., 1995; Mondale et al., 1995; Inglezakis et al., 2002). Among the natural zeolites, clinoptilolite seems to be the most efficient ion exchanger and ion selective material (Bittell and Miller, 1974; Nava et al., 1995) for removing and stabilizing heavy metals (Echeverria et al., 1998).

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Shanbleh and Kharabsheh (1996) used a natural zeolite additive to reduce the leaching of Pb^{+2} , Cd^{+2} and Ni^{+2} from a soil contaminated with mixtures of the three metals. The additive contained approximately 35% active zeolite ingredients including clinoptilolite and phillipsite. The additive enhanced the sorption capacity of soil and reduced the amount of leaching. Lead leaching was reduced by more than 97% using a minimum of 25% additive at the lowest contamination level, 500 mg/kg of each metal, to 40% additive at the highest contamination level, 5000 mg/kg of each metal, but poorly reduced Cd and Ni concentrations. The results from the repeated leaching column experiments confirmed the selectivity of the additive and a satisfactory leaching reduction was achieved for Cd and Pb.

Oste et al. (2002a) showed that *in situ* immobilization of heavy metals in contaminated soils is a good technique to improve soil quality. Natural and synthetic zeolites are potentially useful additives to bind heavy metals. These studies selected the most effective zeolite in cadmium and zinc binding out of six synthetic zeolites and one natural zeolite (clinoptilolite). The results showed that free ionic concentration of Cd and Zn strongly decreased after the application of zeolites, which might explain the reduction in metal uptake observed in plant growth experiments. The aim of this study was to evaluate the effect of zeolite to stabilize Cd in a variety of soil textures in Gilan (northern Iran) with different pH values.

2. Materials and methods

2.1. Zeolite sampling

The clinoptilolite used in this research was collected from the Firoozkough mine, northeast of Firoozkooch township. The CEC value of this sample was 1.44 meq g^{-1} and its pH was approximately 9.1 (1:10 water:solid). Table 1 summarizes the chemical composition of the zeolite sample used in the experiments.

2.2. Soil samples

Uncontaminated soil samples with different textures were taken from the Gilan Province, northern Iran. The basic

Table 1
Chemical composition of Firoozkough zeolite used in the experiment (Faghihian and Kazemian, 1999)

	%
SiO ₂	67.24
Al ₂ O ₃	11.7
Fe ₂ O ₃	0.58
TiO ₂	0.42
CaO	3.04
MgO	1.16
Na ₂ O	1.19
K ₂ O	1.48
P ₂ O ₅	No
LOI ^a	13.47
Total	100.43

^a Loss on ignition.

Table 2

Some physical and chemical characteristics of soils prior to use in the experiment

Soil texture	Particle size fraction (%)			pH	CEC	OM	Cd (mg/kg)
	Sand	Silt	Clay				
Clay	17.55	39.04	43.05	6.8	13.82	2.15	nd ^a
Loam	42.4	33.6	24	3.9	10.65	2.04	nd
Loamy sand	76.60	11.80	11.60	5.4	8.10	2.0	nd
Sand	93.9	3.5	2.6	7.7	5.6	1.8	nd

^a nd: Less than detection limit.

chemical and physical properties of soils are presented in Table 2. Contaminated soil samples were prepared by adding 1000 mg l^{-1} CdCl₂ solution to obtain approximately 70 mg kg^{-1} of Cd content (Shanbleh and Kharabsheh, 1996). The mixture was stirred up and placed at 25 °C to dry. The samples were ground and water was added until the moisture reached the field capacity level. The wetting and air dry cycle procedure was repeated five times to allow sufficient mixing of cadmium and soil to simulate actual field conditions (Shanbleh and Kharabsheh, 1996; Lin et al., 1998).

2.3. Experimental methods

Different portions of zeolite ranging from 1 to 15 g/100 g soil (1, 3, 5, 7, 9 and 15 g/100 g) were added to contaminated soil samples. The mixtures were subjected to three cycles of the same air dry/rewetting procedure in order to achieve equilibrium. Two different experiments, namely a batch and a column experiment, were carried out.

For the batch extraction experiment, soil mixtures were placed in 150 ml flasks and 100 ml of 0.01 M CaCl₂ solution with a pH value of 6 was added. The solution was then shaken for 4 h at a constant temperature of 25 °C and centrifuged at 200 rpm. The solution was then filtered and the filtrate was used for pH and cadmium measurements (Shanbleh and Kharabsheh, 1996; Lin et al., 1998).

The purpose of the column experiment was to simulate and study the Cd migration in columns filled with a mixture of soil and zeolite. To simulate contaminated soil samples, a height of 20 cm of uncontaminated soil was initially placed at the bottom of a column of 40 cm in diameter, with another 10 cm of Cd-contaminated soil (with or without zeolite) on top of the column. The columns were saturated with a counter flow of deionized water and drained several times in order to release air bubbles in the columns. The soil columns were then submerged in water for a week for saturation. During the experiment, the column was leached using 0.01 M CaCl₂ solution at a constant head of 5 cm. The resulting leachate was collected and analyzed for cadmium concentrations and pH values. At the end of the experiment, columns were allowed to drain naturally to determine the water content and soil sample height which were then used to obtain the overall density and pore volume of the columns. After draining, the soil in the column was separated at 2 cm intervals and air dried at room temperature. Cadmium in all soil samples were extracted using aqua regia

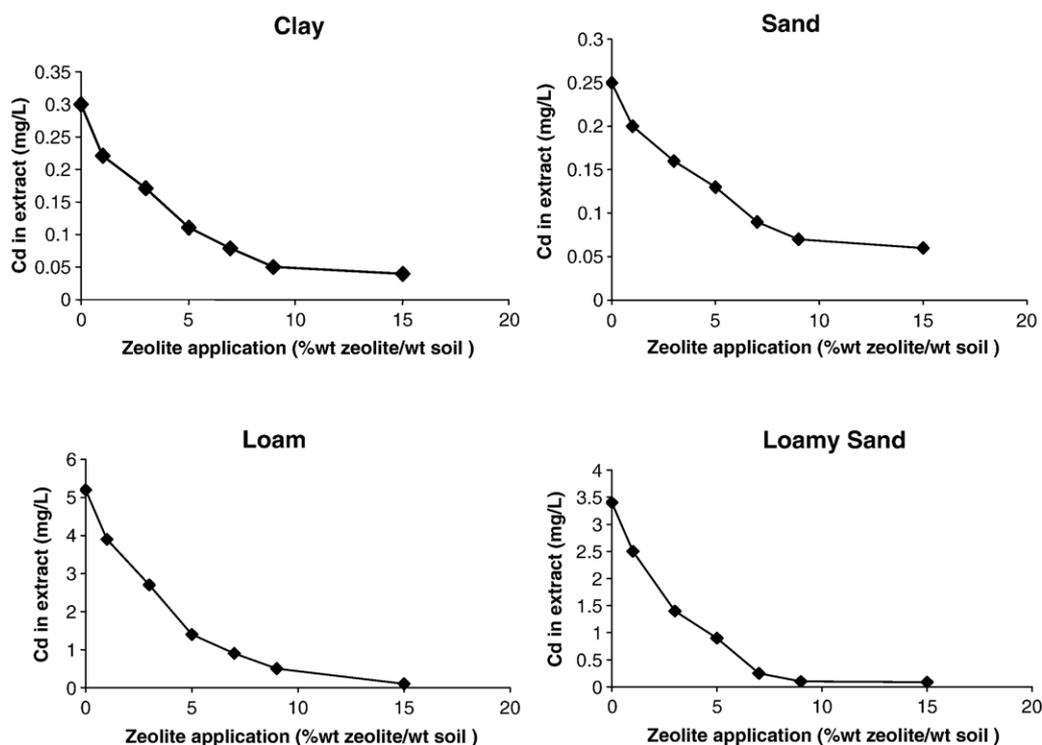


Fig. 1. Leachate Cd concentration from simulated contaminated soils as a function of the zeolite dosage.

solution. Two grams of soil and 16 ml of a concentrated HCl–HNO₃ mixture, with a ratio of 3:1 by volume, were boiled under reflux for 2 h. The methods used were those described by Potts (1993).

2.4. Analytical methods

The zeolite size distribution was measured using standard sieves (Benning et al., 2000) and its CEC value using the indirect ammonium acetate method (Cerri et al., 2002). Cadmium concentration was determined using a Perkin-Elmer Atomic Absorption Spectrometer Model 3030. Soil pH was measured using a pH meter Jenway model 3310. The hydraulic conductivity was determined in soil columns at a constant head by monitoring leaching rate with time (Shanbleh and Kharabsheh, 1996).

3. Results

Previous reports had indicated the capacity of zeolite in reducing metal concentration in contaminated soils. In this experiment, different amounts of zeolite were mixed with four Cd-contaminated soil samples. The change in Cd concentration in the leachate indicated that zeolite enhanced the sorption capacity of the soil (Fig. 1). Without zeolite addition, the leachate Cd concentration was approximately 0.3, 0.25, 5.2 and 3.4 mg l⁻¹ for clay, sand, loam and loamy sand textures, respectively. The addition of natural zeolite strongly inhibited the leaching of cadmium in all the soil samples (Fig. 1). Shanbleh and Kharabsheh (1996) showed that when natural

zeolite (approximately 35% active faujasite and phillipsite) was added to a soil contaminated with mixtures of Pb⁺², Cd⁺² and Ni⁺², the concentration of metals in leachate drastically reduced while the sorption capacity of the soil increased.

Leachate Cd concentration of all four soil samples dropped to below 0.1 mg l⁻¹ when 15 g of zeolite was added to 100 g of soil. Adding zeolite raises soil pH, thus effectively inhibiting the leaching of cadmium from soil and uptake of cadmium by crops. The pH value of the loamy sand soil increased from 5.45 to 7.7 when 15% zeolite was applied. Fig. 1 further illustrates that the cadmium concentration reaches a plateau after a critical amount of zeolite is applied. The optimum level of zeolite for clay, sand and loamy sand soils was approximately 9 g/100 g soil whereas for the loam texture, it was about 15 g/100 g soil. Cd concentrations in the leachate prior to zeolite application

Table 3

Effect of different zeolite dosages on pH levels of different soil textures used in the experiment

Zeolite dosage (g/100 g soil)	Soil texture			
	C	L	SL	S
0	6.8	3.9	5.4	7.7
1	7.1	4.4	5.8	7.9
3	7.4	4.7	6.2	8.0
5	7.6	4.9	6.4	8.2
7	7.0	5.2	6.7	8.5
9	7.3	5.5	6.9	8.8
15	7.6	5.8	7.1	9.0

C: Clay, L: Loam, SL: Sandy Loam, S: Sand.

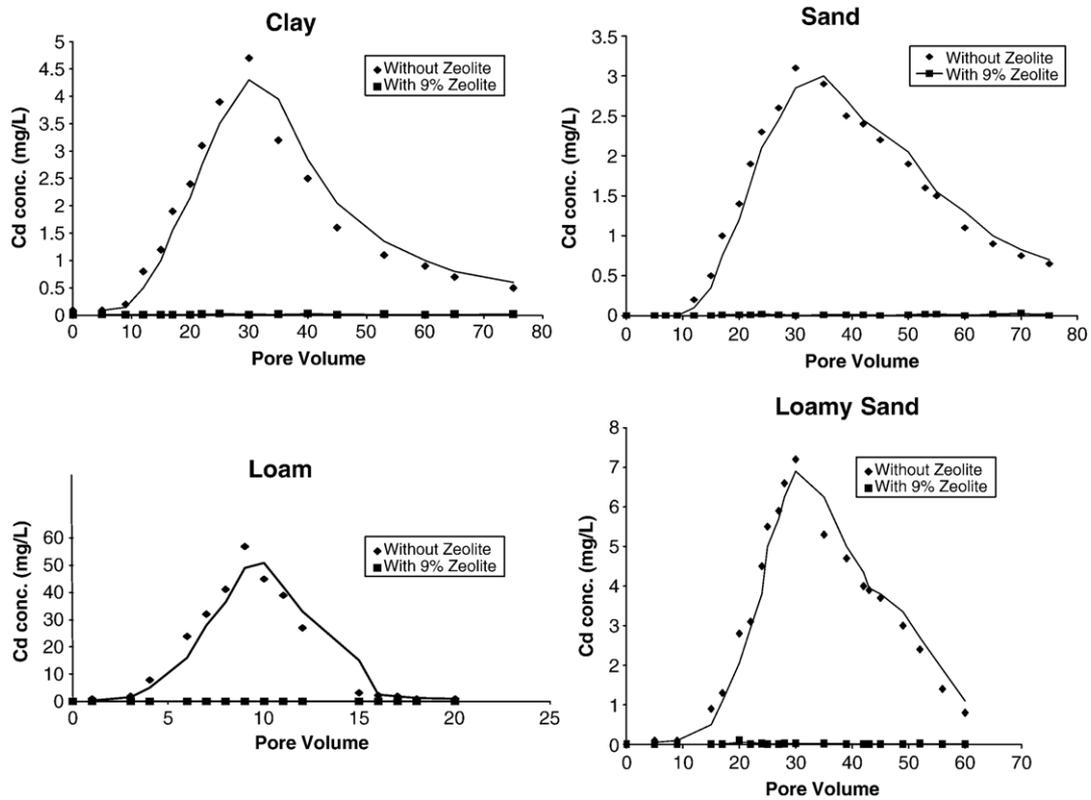


Fig. 2. Cd concentration in effluent as a function of leachate pore volume (results of simulated contaminated soil column leaching).

were 0.3 and 3.4 mg l⁻¹ for clay and loamy sand soils, respectively. Applying 15% zeolite decreased Cd concentration in the leachate to below 0.1 mg l⁻¹.

Table 3 shows the basic properties of soil column used in this study under different conditions. The results of the batch experiment indicate that zeolite application reduces Cd leaching from all types of contaminated soils. The more the zeolite applied, the lower the Cd concentration detected in the leaching solution. This is in line with the results reported by Lin et al. (1998).

The results obtained from the column experiments of two loamy soils demonstrated that column A with no zeolite began to have Cd leachates after 2.1 pore volumes of the CaCl₂ solution was reached (Fig. 2) while Cd was not detected in the leachate from column B with 9 g/100 g soil of zeolite added

until 12.3 pore volumes was reached; the concentration levels never got beyond 0.27 mg l⁻¹. After passing 8.7 pore volumes of leaching solution, the Cd concentration in the leachate reached its peak of 57 mg l⁻¹. For the sandy soil, cadmium migration was slower than that in all the other soil textures. It took more than 11.7 pore volumes of the leaching solution for Cd to be detected in the column effluent.

Analysis of different depths within the soil columns treated with zeolite also confirmed that contaminated soils were stabilized in the upper layer (top 10 cm), resulting in negligible Cd migration (Fig. 3). Decreasing hydraulic conductivity in soils treated with zeolite (Table 4) is responsible for slow Cd migration. Furthermore, Cd moves easily downward in soil with high hydraulic conductivity. The zeolite particle size distribution (0.05–0.1 mm) has its own effects as well. For sandy and loamy

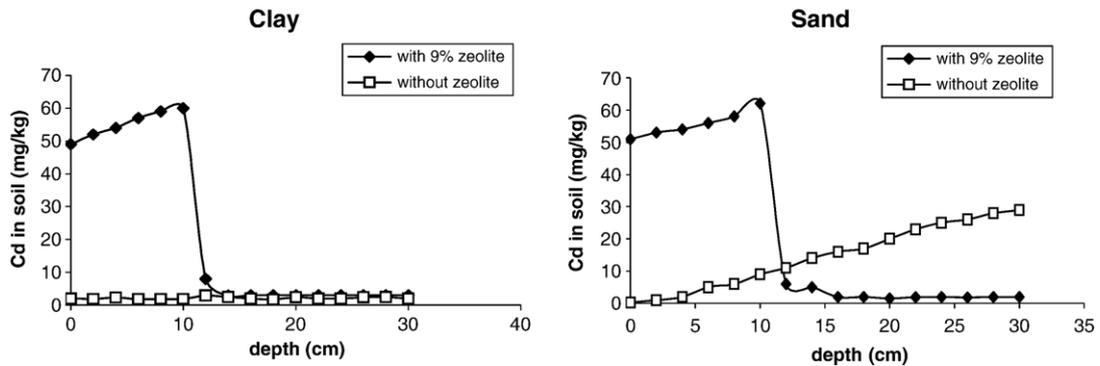


Fig. 3. Cd content variation as a function of soil column depth.

Table 4
Effect of zeolite dosage on hydraulic conductivity of different soil textures used in the experiment

Zeolite dosage (g/100 g soil)	Soil texture			
	C	L	SL	S
0	0.12	0.29	19.1	20.4
1	0.17	0.12	7.4	9.3
3	0.19	0.15	5.7	5.6
5	0.21	0.12	4.2	3.4
7	0.22	0.09	2.6	1.5

C: Clay, L: Loam, SL: Sandy Loam, S: Sand.

soils, application of zeolite effectively reduces soil hydraulic conductivity. In the case of clay soils, on the contrary, zeolite would slightly increase its hydraulic conductivity. The findings of the present study can be used in determining possible applications of Iranian natural zeolites for cadmium stabilization in soils.

4. Discussion and conclusions

Application of zeolite to soil changes a number of parameters such as surface area, pH and hydraulic conductivity. Cd leachate in soil reduces as surface area and pH increase and hydraulic conductivity decreases. In batch experiments, application of 15% zeolite reduced Cd leaching by 91%, 93%, 98% and 97% in clay, sand, loam and loamy sand textures, respectively (Table 5).

An optimum quantity of zeolite for reducing Cd leaching in clay, sand and loamy sand soils was found to be 9% while it was 15% for loamy soil.

The column experiment showed that with 9% zeolite, the Cd leaching rates in clay and sand soils were less than those in loam and loamy sand soils. Thus, zeolite, as a soil amendment material, is highly beneficial and suitable especially in both fine- and coarse-textured soils. The pH values of loam and loamy sand soils were lower but cadmium concentration in the

Table 5
Properties of soil columns used for the leaching experiments

Soil column								
	A	B	C	D	E	F	G	H
Soil texture ^a	C	C	L	L	SL	SL	S	S
Particle density (g cm ⁻³)	2.53	2.53	2.61	2.61	2.64	2.64	2.69	2.69
Bulk density (g cm ⁻³)	1.2	1.2	1.3	1.3	1.5	1.5	1.6	1.6
Pore volume (cm ³)	147	138	133	133	150	156	154	162
Zeolite dosage (% wt/wt)	None	9/100	None	9/100	None	9/100	None	9/100
Soil weight (g)	560	565	543	545	550	554	548	540
Cd conc. (mg kg ⁻¹)	61	58.2	6.1	5.8	7.3	7.8	9.7	9.1
Total volume of influent (l)	1.4	1.6	7.1	7.4	11.2	10.8	18.5	17.4

^a C: Clay, L: Loam, SL: Sandy Loam, S: Sand.

Table 6
Chemical properties of cadmium (Greenwood and Earnshaw, 1984)

Free energy of hydration (kcal/gr-ion)	Hydrated ionic radius (Å)	Ionic radius (Å)	Cations
-430.5	4.26	1.03	Cd ²⁺

leachate from these soils was higher. It may, therefore, be concluded that pH value is one of the primary factors affecting Cd leachability (Shanbleh and Kharabsheh, 1996). Although the application of zeolite effectively reduced the average particle size in sand and loamy soils, thus lowering their hydraulic conductivity, it increased hydraulic conductivity in clay soils. This indicates that texture is an important parameter when applying zeolite to soil for reclamation purposes. Lin et al. (1998) also reported that application of zeolite to sandy and loamy soils effectively reduced average particle size, and consequently, lowered hydraulic conductivity (Table 6).

The results also confirmed the capability of Firoozkouh zeolite to stabilize cadmium in soil. There are major factors, other than CEC, such as pH and hydraulic conductivity in soil that affect the ability of zeolite to stabilize Cd in soil. In addition to binding sites on the surface of the immobilizing material, an increase in soil pH contributes to the immobilization of heavy metals in soil by making the exchange sites in soil more reactive to metal binding due to a lower proton competition (Oste et al., 2002b). Since the pH of zeolite was around 9.1, introducing zeolite into soil increased its soil Cd stabilization capacity. Soil hydraulic conductivity is also affected by zeolite, and thereby, influencing Cd migration. However, the effect of hydraulic conductivity highly correlates with physical and chemical properties of soil. Deep penetration of Cd resulted from the transport of water suspension in the macropore system. This flow is mainly laminar, and therefore, mixing of the suspension is not thorough. As a result, a great portion of the particles do not react with the macropore walls and deep penetration of small particles with cadmium may occur. When zeolite is applied, the decrease in pore size is higher than that of hydraulic conductivity. Application of zeolite effectively reduces hydraulic conductivity and pore size, thereby, the leaching of Cd decreases (Lichner et al., 2006). Similarly, migration of Cd in soils, especially in sandy soils, reduces with zeolite application. Measurement of variations in Cd levels in sandy and clay soils of experimental columns showed that maximum Cd pollution occurred in the upper layer (top 10 cm) and also that Cd leachate was negligible (Fig. 3). It is evident that 15% zeolite is capable of satisfactorily reducing Cd leaching into deeper soil horizons. Therefore, groundwater and soil in the underlying layers can be safe against Cd pollution. The results from the present study can be used for predicting the efficiency of zeolite application for the remediation of contaminated soils.

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