

Efficiency of Fe-zeolite and Fe-bentonite on Co-stabilization of As, Cd and Pb in Contaminated Soil

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Abstract: Lead (Pb), Cadmium (Cd) and Arsenic (As) have been known as a malicious environment and their toxic effects for plants, animals and humans has been demonstrated. This metals in soil have a different behaviours. The normal concentrations of Cd, As and Pb in agricultural soil were 1.1, 20 and 67 mg.kg⁻¹ respectively. In situ immobilization of Lead and Cadmium (by zeolite and bentonite) and Arsenic (by iron) in soil is well recognized. However, studies on soils that are simultaneously contaminated with lead, cadmium and arsenic are fewer, and assessment of the sorbents effectiveness on co-stabilization of As, Cd and Pb is also necessary. In this study, local bentonite and zeolite were converted to Fe-zeolite and Fe-bentonite. A Pb-, Cd- and As-contaminated soil has been treated with modified bentonite and zeolite separately in 1 and 6 wt% rate. After one month of incubation in at 80% of field capacity moisture, Sunflower (*Helianthus annuus*. L) plant was transplanted into each pot. The result showed that Fe-zeolite and Fe-bentonite decreased concentration of Pb and Cd extractable with DTPA-TEA; however, Fe-bentonite in the soil reduced water-soluble arsenate, but Fe-zeolite increased it. Finally application of Fe-bentonite can be an effective approach to co-stabilize Pb, Cd and As, in contaminated soils.

Keyword: Fe-Bentonite, Fe-Zeolite, Lead, Cadmium, Arsenic

1. Introduction

Lead (Pb), Cadmium (Cd) and Arsenic (As) have been known as a malicious environment and their toxic effects for plants, animals and humans has been demonstrated. Input sources of these elements to agricultural land include industrial production, pesticides and mining waste. [1]. The normal concentrations of Cd, As and Pb in agricultural soil were 1.1, 20 and 67 mg.kg⁻¹ respectively [1, 2].

Chemical behavior of Pb and Cd in the soil was similar while As chemical behavior are very different in comparison of these two elements. So in soils thate contaminated with Pb, Cd and As at the same time, stabilization strategies of heavy metals is different from other contaminated soils [3].

In situ stabilization is a low cost method to clean up and reduce the toxic effects of heavy metals in the contaminated soil [4-6]. Generally soil amendments have been used to stabilize of Pb and Cd include phosphate compounds [7], zero-valent iron [8], ferrous sulfate [9], metal oxides [10] and clay minerals [11]. These agents prevent the entry of lead and

cadmium into the food chain (plant uptake and leaching to subsurface water) in the long-term [12]. Keller et al. (2005) founded that the addition of 1% zeolite significantly decreased the Cd content of tobacco leaves [13]. In pot experiment it was shown that applying of bentonite to soil, reduced the significant percentage of exchangeable Cd and Pb was converted into unavailable forms [14]. Also in contaminated soils with As have been done many studies for stabilize of As [4, 15]. Other studies founded that in situ fixation of As can be achieved by addition of iron amendments, which can also reduce bioaccessibility of As [10, 16]. Reaserchers demonstrated that clay minerals with negative surface charges are not efficient for remediation of metalloids such as anionic pollutants. So they by change of surface properties of clays improved absorption of As [17] and anionic pollutants [18-23]. Further studies are needed to application of sorbents that co-stabilize metals with different chemical behavior such as Pb, Cd and As in contaminated soil. It seems that if iron is loaded on the zeolite, and bentonite (half a cation exchange capacity), at the same time

lead and cadmium absorbed by negative charges of surface clays and arsenic stabilized by iron. Therefore, the objectives of the present experiment were to investigate, i) the Fe loading on the zeolite and bentonite at 50% of their cation exchange capacity, ii) the application of Fe-bentonite and Fe-zeolite in contaminated soil and co-stabilization of As, Pb and Cd.

2. Materials and Methods

2.1. Materials

Soil was collected from agricultural site in a gold mine (Takab Town, West Azarbaijan province, NW Iran). Soil properties were determined according to standard methods [24]. The bentonite and zeolite were obtained from Anarak and Firouzkoh mines in central and northern Iran, respectively. Natural bentonite and zeolite were separately



Figure 1. Photo of (a) natural bentonite (b) Fe-bentonite (c) natural zeolite (d) Fe-zeolite.

$$\text{CEC of zeolite} = \frac{94\text{meq}}{100\text{gr zeolite}}$$

$$50\% \text{ of CEC} = \frac{47\text{meq}}{100\text{gr zeolite}} = \frac{47\text{meq Fe}^{3+}}{100\text{gr zeolite}} = \frac{15.66 \text{ mmol Fe}^{3+}}{100\text{gr zeolite}} \times \frac{1 \text{ gr zeolite}}{6.5\text{ml}} \times \frac{1\text{mmolFeCl}_3}{1\text{mmol Fe}^{3+}} = \frac{0.024 \text{ mmolFeCl}_3}{1\text{ml}} = 0.024\text{M}$$

$$\text{CEC of bentonite} = \frac{76\text{meq}}{100\text{gr bentonite}}$$

$$50\% \text{ of CEC} = \frac{38\text{meq}}{100\text{gr bentonite}} = \frac{38\text{meq Fe}^{3+}}{100\text{gr bentonite}} = \frac{12.66 \text{ mmol Fe}^{3+}}{100\text{gr bentonite}} \times \frac{1 \text{ gr bentonite}}{6.5\text{ml}} \times \frac{1\text{mmolFeCl}_3}{1\text{mmol Fe}^{3+}} = \frac{0.019 \text{ mmolFeCl}_3}{1\text{ml}} = 0.019\text{M}$$

Characterization of modified clays were investigated by X-ray diffraction (XRD) and standard methods, respectively (Figure. 2 and Table 2).

2.2. Pot Experiments

The modified bentonite and zeolite separately were added to the soil (1kg) in 1 and 6 wt% rate (in three replicate). After one month of incubation at 80% of field capacity moisture, two healthy Sunflower (*Helianthus annuus*. L) plants were transplanted into each pot. Plants were allowed to grow for 10 weeks in the greenhouse (temperature range 16–30°C; average photosynthetically active radiation was 825 $\mu\text{mol m}^{-2}\text{s}^{-1}$) and watered daily or as needed. At the end of experiment, shoot, root and soil sample from each pot were collected. Soil pH was determined with a pH meter in a 1:2

put in contact with 0.3 M NaCl solution (1:6.5 solid-liquid ratio) under reflux for 12 h. This process was repeated one more time changing the NaCl solution. The phases were separated by centrifugation and the solid phases were washed until Cl^- elimination was achieved using the AgNO_3 test. Then bentonite and zeolite were dried at 333 K for 24 h. After modification by Na, the clays were treated by (0.024M FeCl_3 for zeolite, 0.019 M for bentonite) under agitation for 24 h to prepare Fe-bentonite and Fe-zeolite (equivalent to 50% of their CEC). The solid phases were separated by centrifugation and washed by distilled water. This step was repeated so many times until amount of iron in the suspension supernatant was no detected. The solid phases dried at 323 K for 17 h. Then each sample was thermally treated at 373 K for 24 h. In final Fe-bentonite and Fe-zeolite were prepared (Figure 1) [25].

(w:w). Water-soluble arsenic [26] as well as Cd and Pb extractable with Diethylenetriaminepentaacetic acid-Triethanolamine (DTPA-TEA) 0.05 M [27] of soil samples were measured by Graphite Furnace Atomic Absorption Spectrometry (GF-AAS). As, Cd and Pb in plant samples (root and shoot) were determined by GF-AAS following $\text{HNO}_3\text{-HClO}_4$ digestion (0.25g dried and ground plant material was digested with 6 mL conc. HNO_3 plus 2 mL conc. HClO_4) [28].

2.3. Data Processing

The pot experiment was set up in a randomized complete block design with three replications. The ANOVA (SAS program., version 9.2) was employed for statistical analysis of data.

3. Results and Discussion

3.1. Characteristics of the Soil, Bentonite and Zeolite

Physical and chemical characteristics of soil were presented in Table 1. The pH value of the soil (7.8) was close to neutral. Soil texture was loamy. Comparing of concentration of As, Pb and Cd in soil from Zarshuran area and tolerable levels of metals (20 mg/kg As, 100 mg/kg Pb, and 3 mg/kg Cd) [2] indicated that total As, Pb, and Cd concentration in Zarshuran soil were extremely high.

Table 1. Physical and chemical characteristics of Zarshuran soil.

Clay %	Silt %	Sand %	CEC (cmol(+)/kg)	OM %	EC _e (dS/m)	pH	As (mg,kg ⁻¹)	Pb (mg, kg ⁻¹)	Cd (mg, kg ⁻¹)
25.7	45	29.3	15.3	1.5	1.7	7.8	2569	800	21

CEC: cation exchange capacity

OM: organic matter

EC: electrical conductivity

According to chemical properties of natural and modified zeolite and bentonite (Table 2) the cation exchange capacity (CEC) of zeolite and bentonite were 94 and 76 meq/100gr respectively. The natural zeolite and bentonite had alkaline properties (pH about 8.3 and 8 respectively). After

modification of clays by iron, their properties became acidic. Existence alkali and alkaline earth metals on the bentonite bedrock, Due to of high electrical conductivity in bentonite. By removing lime and minerals in raw bentonite, electrical conductivity decreased.

Table 2. Chemical properties of natural zeolite and bentonite and modified zeolite and bentonite.

Sorbent	CEC (cmol (+)/kg)	EC (dS/m)	pH	Fe loaded on the clay (% CEC)
Natural Zeolite	94	0.6	8.3	-
Natural Bentonite	76	10.9	8	-
Fe-Zeolite	Nd	0.8	3.3	50
Fe-Bentonite	Nd	2	2.7	50

Nd: no determinate

According to the XRD pattern (Figure. 2), the bentonite was composed of 85.5% montmorillonite, 12% quartz and 2.5% illite, the zeolite of 80.6% clinoptilolite, 9.6% quartz, 5.8% illite and 4% feldspar. Existence of a peak at 13.1 Å in natural bentonite was an indication of high amount of montmorillonite. Several peaks at 2.96, 3.94 and 9 Å in natural zeolite were indication of high amount of clinoptilolite.

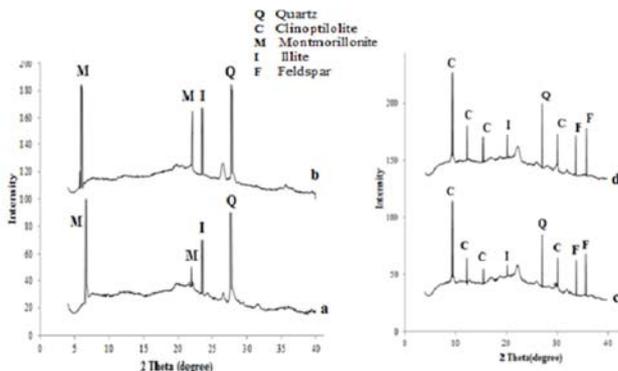
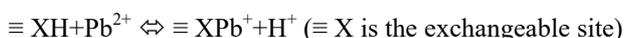


Figure 2. The XRD pattern of Natural Bentonite (a), Fe-Bentonite (b), Natural Zeolite (c) and Fe-Zeolite (d).

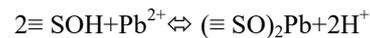
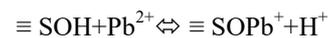
3.2. Mobility of Metals in the Soil

Table 3 presented that adding of Fe-zeolite and Fe-bentonite to soil caused a slight decrease of pH. Application of Fe-zeolite and Fe-bentonite in soil has resulted in lowering amount of Pb and Cd extractable with DTPA-TEA. Probably Pb and Cd were adsorbed on exchangeable site and complex with surface functional groups of zeolite and bentonite by following mechanisms (This mechanism occurs in the part of the CEC that is not saturated with iron):

To exchange with hydronium ion:



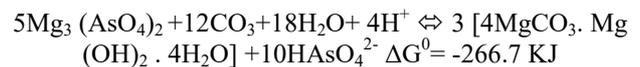
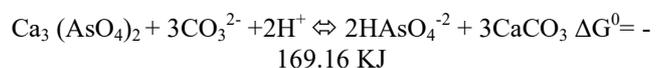
To complex with surface functional groups:



The adsorption mechanism of Cd on the clays similar to Pb.

Usman et al (2006) demonstrated that by the addition of zeolite at 1% (w/w) to a contaminated-soil, the labile Pb and Cd fractions were significantly reduced [29]. Iron bonded to the zeolite and bentonite was affected to the lower mobility of Cd. Mench et al. (1998) reported that the soluble and exchangeable fractions of Cd in two contaminated soils were decreased by the application of hydrous Fe oxide [30]. In this study, Fe-zeolite had a strong effect on reducing of DTPA-TEA extractable Cd compared to the Fe-bentonite.

With application of Fe-bentonite in the soil, reduced water-soluble arsenate, but Fe-zeolite increased water-soluble arsenate. Probably Fe-zeolite even with slight decreasing of soil pH, increased solubility of magnesium and calcium arsenate and arsenate is increased in the solution phase by the following reactions [31]:



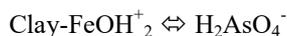
Due to low external cation exchange capacity and non-expandable structure of zeolite, little amount of arsenate could enter to the zeolite pit (Iron connected into the zeolite pits). Arsenate has been linked to the iron by following mechanisms (This mechanism occurs in the part of the CEC that is saturated with iron):

1) Bidentate Inner sphere complex:

(Columbic and Lewis acid-base interactions)



2) Monodentite Inner sphere complex:
(Columbic and Lewis acid-base interactions)



In bidentite and monodentite inner sphere complex, arsenic species such as HAsO_4^{2-} and H_2AsO_4^- , are connected with iron (by electrostatic bonding). Sherman and Randall (2003) explained the exact mechanism of the adsorption of As (V) onto iron compounds such as goethite, lepidocrocite, hematite and ferrihydrite to be the formation of inner-sphere surface complexes resulting from bidentate corner-sharing between AsO_4^{3-} and FeO_6 polyhedra [32].

Table 3. Concentrations of water-soluble arsenate, cadmium and lead extractable with DTPA-TEA (mg/kg) and pH in soil enriched with different sorbents, analysis of variance by ANOVA.

Treatment	Water-Soluble arsenate	Cadmium extractable with DTPA-TEA	Lead extractable with DTPA-TEA	pH
Control	9.25 b	1.48 a	6.55 a	7.7 a
Fe-Zeolite 1%	14.12 a	1.14 d	4.54 b	7.6 ab
Fe-Zeolite 6%	14.73 a	1.31 b	5.28 b	7.5 b
Fe-Bentonite 1%	7.55 c	1.24 c	5.19 b	7.65 a
Fe-Bentonite 6%	4.29 d	1.34 b	4.27 b	7.25 c

The different letters in the same line indicated the results of comparisons according to LSD test; data are means, n=3.
DTPA-TEA: Diethylenetriaminepentaacetic acid- Triethanolamine

3.3. As, Cd and Pb Uptake by Sunflower

Adding of Fe-zeolite to the contaminated soil, As concentrations in plant (roots and shoots) increased, whereas Cd and Pb concentration decreased. In soils enriched with Fe-bentonite concentration of As, Cd and Pb in plant (roots and shoots) reduced, (Table 4). The calculation of the shoot/root ratio shows a slight penetration of arsenic in the

3) Ligand exchange



In ligand exchange processes, arsenic species such as HAsO_4^{2-} and H_2AsO_4^- , were exchanged by OH^- .

Thus, the As released from dissolution of magnesium and calcium arsenate is more than As stabilized on the Fe-zeolite. In case of Fe-bentonite, the amount of arsenate stabilized by iron, is more than the As released from magnesium and calcium arsenate. Probably the lamellar structure, expandable layer and high interlayer space of bentonite allowed that the As easily bonded with iron.

shoot (0.01-0.03) and significantly higher values for Pb (0.08-0.15). The highest values of the shoot/root ratios are observed for Cd (0.69-0.80) (Table 4). With application of sorbents, this index decreased for As, Pb and Cd. Results obtained in Table 3 and 4 indicated that Fe-bentonite was the most effective treatment rather than Fe-zeolite.

Table 4. Concentrations of As, Cd and Pb in sunflower grown on soil enriched with different of sorbents, analysis of variance by ANOVA.

Treatments	As (mg. kg ⁻¹)			Cd (mg. kg ⁻¹)			Pb (mg. kg ⁻¹)		
	Root	Shoot	Sh/R	Root	Shoot	Sh/R	Root	Shoot	Sh/R
Control	365 a	8.2 b	0.02	18.32 a	13.88 a	0.75	133.56 a	21 a	0.15
Fe-Zeolite 1%	368 a	11.2 a	0.03	14.43 b	11.66 b	0.8	95.4 bc	9.61 c	0.1
Fe-Zeolite 6%	344 ab	10.5 a	0.03	13.88 b	9.99 bc	0.71	89.64 c	7.88 c	0.08
Fe-Bentonite 1%	340 ab	6 c	0.01	16.66 ab	11.64 b	0.69	89.62 c	7.8 c	0.08
Fe-Bentonite 6%	288 c	5.1 d	0.01	15.21 b	10.54 b	0.69	111.43 b	14.4 b	0.12

The different letters in the same line indicated the results of comparisons according to LSD test; data are means, n=3.
Sh/R: values of shoot-to-root ratios

4. Conclusion

In a contaminated soil, efficiency of two sorbents for reducing of bioavailability of Cd, As and Pb were evaluated. Application of Fe-zeolite and Fe-bentonite decreased bioavailability of Pb and Cd in soil. Fe-bentonite stabilized water-soluble As, but Fe-zeolite increased water-soluble As in soil. In final, the additions of 6% (w/w) Fe-bentonite have a most effective treatment as indicated by the reductions of water-soluble As, and DTPA-TEA extractable Cd and Pb (53.6, 9 and 34.8% respectively) in the soil.

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