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Original Research

Effect of Modified Polyacrylamide on Plant-Availability of Cd and Pb to Corn in Polluted Soils

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Abstract

We studied the effects of modified polyacrylamide (MPAM) on plant-uptake of Cd and Pb in two agricultural soils of different textures that had been contaminated simultaneously with Cd and Pb. In a pot experiment under greenhouse conditions different doses of modified polyacrylamide (0, 0.1, 0.2, and 0.3%) were added to artificially polluted soils (sandy and sandy loam). Results indicated that soil pH gradually increased with the application of modified polyacrylamide in both soils. Soil EC significantly increased due to the addition of modified polyacrylamide in the sandy loam soil as compared to the control. The concentrations of Cd and Pb in plants grown in sandy loam soils were less than those planted in sandy soils. The addition of modified polyacrylamide to both soils significantly decreased Pb concentrations in corn roots and shoots. On the contrary, uptake of Cd by shoots was increased in pots containing 0.1% MPAM in both soils compared to those in the unamended soils. While Cd uptake by shoots was not affected by MPAM in soils as compared to those in the unamended soils. The transfer factor (TF) values of Pb were much less than those of Cd in the same treatments.

Keywords: Cd, corn, Pb, polyacrylamide

Introduction

Soil pollution by heavy metals is a crucial environmental problem that threatens aquatic ecosystems, agriculture, and human health. Among heavy metals, Cd and Pb are very critical because of toxicity and their long half-lives in humans and animals [1]. The average concentrations of Cd in soils is between 0.06 and 1.1 mg kg^{-1} and for Pb between 10 and 67 mg kg^{-1} [2]. The average total concentrations of Cd and Pb in central Iran are 1.67 and 25.6 mg kg^{-1}, respectively [3].

In recent years, the efficiency of different natural and synthetic materials such as lime, phosphates, apatite, ferrous salt, zeolite, oyster shells, manure, humic acid, chitosan, and biochar have been studied in order to use them for on-site remediation of metal-contaminated soils [4-11]. Since bio-availability is a key factor for immobilization technologies, immobilized heavy metal ions may become mobile and plant-available with time, thus the role of the plant rhizosphere on the efficiency of the additives on immobilization of heavy metal ions needs to

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be investigated [12]. A few familiar methods for removing heavy metals are chemical precipitation, immobilization technologies, ion exchange, solvent extraction, reverse osmosis, adsorption, etc. [2]. Current technologies for soil remediation are time-consuming or too expensive. Therefore, it is imperative to develop techniques that can treat and stabilize contaminants in-situ in an efficient and cost-effective manner [13]. Chemical stabilization was evaluated as one of the most cost-effective remediation techniques for heavy metal-contaminated sites, reducing the heavy metal pool for root uptake in soil by naturally occurring or artificial additives [14].

In the last decade, polymeric materials have been used as soil conditioners on farmland and construction sites for erosion control [15]. In recent years, it was reported that cross-linked polymeric materials like polyacrylamide (PAM) gels containing functional groups such as carboxylic acid, amine, hydroxyl, and sulfonic acid groups could be used as complex agents for the removal of metal ions from aqueous solutions [16-17].

Although there are a large number of different studies on the removal of heavy metal ions from aqueous solutions using polyacrylamide, no information regarding immobilization and plant-availability of heavy metals in polyacrylamide-amended soils is available. Therefore, in this survey during a greenhouse test, the potential of modified polyacrylamide was investigated for immobilization of Cd and Pb in two different artificially polluted soils.

Materials and Methods

Materials

The reagents were of extra pure analytical grades: polyacrylamide (Sigma, Germany), $Pb(NO_3)_2$ (Fluka, Switzerland), and $Cd(NO_3)_2.4H_2O$ (Merck, Germany).

Modification of Polyacrylamide

We modified the polyacrylamide with hydrazine monohydrate as follows: 50 g polyacrylamide and 0.3 g glacial acetic acid were added to a 250 mL round-bottomed flask containing 100 mL ethanol. The suspension was mixed by a magnetic stirrer at 100ºC for 20 min. After that, hydrazine monohydrate (10 g) was added to the reaction mixture and allowed to reflux at 90ºC for 24 h. The mixture was then cooled before filtration. The solid was washed with absolute ethanol to remove all the organic impurities and then kept at 50ºC for 60 min [17]. Modification of polyacrylamide with hydrazine monohydrate is depicted in Fig. 1.

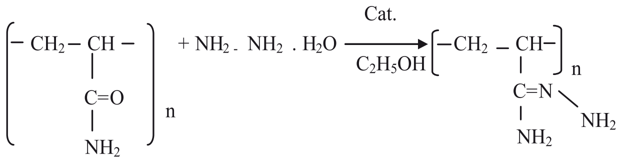

Fig. 1. Modification of polyacrylamide with hydrazine monohydrate.

Soil

Two types of soils – sandy loam and sandy – were collected from pistachio fields in Rafsanjan, Iran. Fresh soil samples were taken at a depth of 0-25 cm, air dried, and sieved (<4 mm) before analysis and potting. Prior to artificial contamination, soil texture, cation exchange capacity (CEC), and organic carbon of the bulk soil was determined using a hydrometer, sodium acetate, and wet oxidation, respectively [18]. Total Cd and Pb concentrations in soils were determined using flame atomic absorption spectrophotometry (AAS) after digesting 0.5 g of soil with concentrated acids (6 mL of HNO_3+6 ml of HF). Prior to undertaking the pot experiments, the feasibility of modified polyacrylamide to support plant growth was assessed in a plant growth screening test. Corn seeds were sown on soils treated with modified polyacrylamide at different weight ratios, namely 0%, 0.1%, 0.2%, and 0.3% (w/w). Plants were observed to grow well on modified polyacrylamide-treated soils. Some chemical and physical properties of investigated soils are presented in Table 1.

Table 1. Some chemical and physical properties of soils.

Characteristics	Sandy loam	Sand
Clay (%)	14.5	4.8
Silt (%)	11	3.6
Sand (%)	74.5	91.6
Bulk density (g cm^{-3})	1.3	1.46
θ_{FC} %	17	10.98
P (mg kg^{-1})	7.9	9.1
K (mg kg^{-1})	265.43	247.77
Fe (mg kg^{-1})	1.47	1.34
Cu (mg kg^{-1})	1.63	1.82
Zn (mg kg^{-1})	2.1	1.75
Pb (mg kg^{-1})	BDL	BDL
Cd (mg kg^{-1})	BDL	BDL
OM (%)	0.87	0.1
$CaCO_3$ (%)	4.9	4.87
$CaSO_4$ (%)	0	0
pH	7.91	7.83
EC_e (dS m^{-1})	2.69	1.04
CEC (meq 100g^{-1})	15.61	7.4

BDL: below detection limit

Table 2. Soil EC and pH after applying the polyacrylamide.

Modified polyacrylamide	Sandy soil		Sandy loam	
	pH	EC (dsm^{-1})	pH	EC (dsm^{-1})
0	7.89[a*]	0.677[c]	7.7[a]	2.209[b]
0.1%	7.95[a]	0.605[c]	7.73[a]	2.595[b]
0.2%	7.97[a]	0.653[c]	7.85[a]	2.661[b]
0.3%	8.15[a]	0.756[c]	7.99[a]	3.14[a]

*Values in the same column followed by the same letter are not significantly different at p<0.05.

Pot Experiment

The pot experiment was conducted on both soils with modified PAM at four different levels (0, 1, 2, and 3 g MPAM kg^{-1} soil). Predetermined amounts of Cd and Pb solutions were mixed concurrently with 1 kg sub-samples of soils to provide 150 mg Pb per kg soil and 2.5 mg Cd per kg soil. These soils were transferred to polyethylene pots (12 cm diameter and 15 cm depth). All treatments were replicated four times. Four control pots per soil were also set up without amendment. Pots were incubated at 25-30ºC for two weeks and maintained at 60% water-holding capacity (WHC) before sowing the corn seeds. Six seeds of corn (*Zee mayssp.*) were planted in pots and were thinned to three seedlings per pot after 12 days. The experiment was conducted in a greenhouse under 12 h sunlight at a temperature range of 25-30ºC. Plants were regularly irrigated with distilled water to maintain the soils at 60% WHC. After 45 days, all the plants were harvested and shoots and roots were separated, washed by distilled water, and oven dried at 65ºC to a constant mass. The concentrations of Cd and Pb in the plant roots and shoots were determined by atomic absorption spectroscopy (GBC, Avanta) following digestion with HCl (0.5 g of dried and ground plant material was digested with 5 ml HCl 2N) [18].

Transfer Factor

The Root concentration factor (RCF) and shoot concentration factor (SCF) were calculated as follows [16]:

$$RCF = \frac{C_{root}}{C_{soil}} \qquad (1)$$

$$SCF = \frac{C_{shoot}}{C_{soil}} \qquad (2)$$

…where, C_{root}, C_{shoot}, and C_{soil} represent the total metal concentrations in roots, shoots, and soil on a dry mass basis, respectively.

Statistical Analysis

Analyses of variance (ANOVA) were performed using MINITAB and MSTATC programs to test Cd and Pb concentrations in plant shoots and roots. The effect of a given factor was considered signification when the P-value was <0.05.

Results

Soil Properties

Effects of the modified polyacrylamide on soil pH and electrical conductivity (EC) are shown in Table 2. At the end of the experiment (after 45 days), soil pH gradually increased with the application of modified polyacrylamide in both soils, but this change was not significant. Soil EC significantly increased due to the addition of modified polyacrylamide in the sandy loam soil as compared to the control. The highest value of soil EC was observed in sandy loam soil, which contains 0.3% modified polyacrylamide (3.14 dS m^{-1}).

Plant Biomass

Plant biomass significantly did not change with the application of the modified polyacrylamide (Table 3).

Pb Concentration

For both soils, the Pb content of roots was significantly decreased by modified polyacrylamide at levels of 0.2

Table 3. Plant biomass.

Modified polyacrylamide	Sandy soil		Sandy loam soil	
	Root biomass (g pot^{-1})	Shoot biomass (g pot^{-1})	Root biomass (g pot^{-1})	Shoot biomass (g pot^{-1})
0	0.82[a*]	0.88[a]	0.62[a]	0.79[b]
0.1%	0.82[a]	0.94[a]	0.81[a]	0.65[b]
0.2%	0.75[a]	0.89[a]	0.84[a]	0.67[b]
0.3%	0.76[a]	0.85[a]	0.69[a]	0.55[b]

*Values at the same column followed by the same letter are not significantly different at p < 0.05.

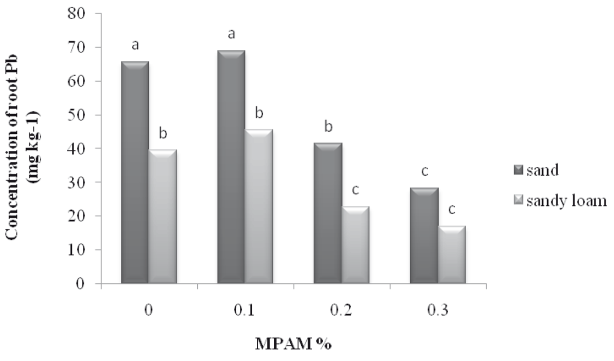

Fig. 2. Pb concentrations in corn roots in sand and sandy loam soil.

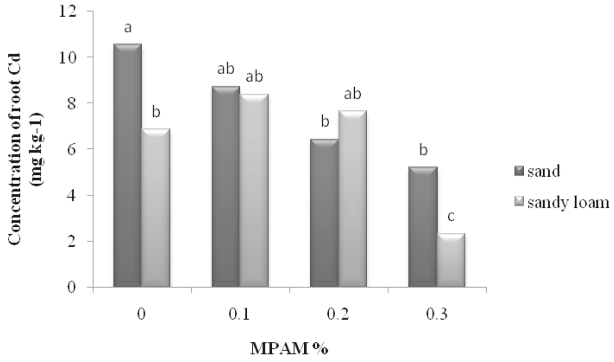

Fig. 4. Cd concentrations in corn roots in sand and sandy loam soils.

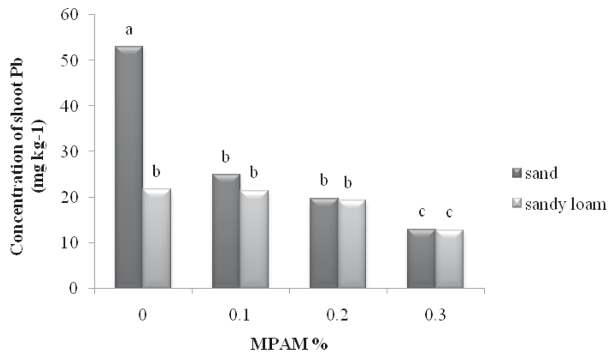

Fig. 3. Pb concentrations in corn shoots in sand and sandy loam soils.

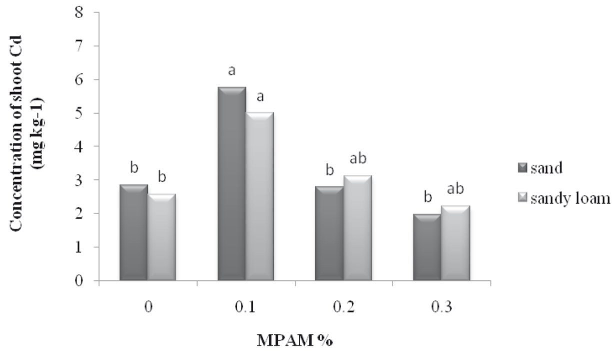

Fig. 5. Cd concentrations in corn shoots in sand and sandy loam soils.

and 0.3% (Fig. 2). In sandy soil, the Pb concentrations of roots of corn grown in pots containing 0.2 and 0.3% modified polyacrylamide were 27.3% and 58.6% lower than those planted in control, respectively. In sandy loam soil, the corresponding values were 41% and 56% lower than those of control, respectively. In the sandy soil, Pb concentrations in corn shoots was decreased significantly by modified polyacrylamide at all levels (Fig. 3), while polyacrylamide only at level 0.3% decreased Pb concentration of corn shoots in sandy loam soil.

In sandy soil, the Pb concentrations of roots of corn grown in pots containing 0.1, 0.2, and 0.3% modified polyacrylamide were 50%, 60.9%, and 76.1% lower than those planted in control, respectively. In sandy loam soil, applying 0.3% polyacrylamide decreased Pb concentration of corn shoot 43.6% lower than the control.

Cd Concentration

In sandy soil, the application of 0.2 and 0.3% PAM significantly ($p<0.05$) decreased the concentrations of Cd in corn roots as compared to the control (Fig. 4). The Cd concentrations of roots of corn grown in pots containing 0.2 and 0.3% modified polyacrylamide were 39% and 57.1% lower than those planted in control, respectively.

In sandy loam soil, the addition of PAM didn't have a significant effect on the uptake of Cd by roots of corn, except for 0.3% PAM (Fig. 4). Cadmium concentrations of roots grown in amended soil with 0.3% PAM were 66.2% lower than those of control.

Compared to the control soil, the PAM applications at a level of 0.1% significantly ($p<0.05$) increased the concentrations of Cd in shoots of corn grown in both sandy and sandy loam soils (Fig. 5). Whereas 0.2 and 0.3% PAM had no significant effects on ($p<0.05$) the concentrations of Cd in corn shoots (Fig. 5).

Transfer Factors

Transfer factors (TFs) of Cd and Pb from soil to root and to shoot showed in Tables 4 and 5. In both soils, transfer factors of Pb from soil to roots and to shoots, and Cd from soil to roots were decreased significantly by the addition of PAM, but the PAM application didn't have a significant effect on the transfer factor of Cd from soil to shoot.

TF values were higher for Cd than for Pb in the corresponding treatments. TF values calculated by metals concentrations of roots were higher than by those of corresponding shoots.

Table 4. Soil-to-root transfer factor (RCF) and soil-to-shoot transfer factor (SCF) for Pb.

Modified polyacrylamide	Sandy soil		Sandy loam soil	
	RCF	SCF	RCF	SCF
0	0.539[a*]	0.348[a]	0.419[a]	0.145[b]
0.1%	0.56[a]	0.163[b]	0.372[a]	0.139[b]
0.2%	0.43[ab]	0.135[b]	0.182[b]	0.124[b]
0.3%	0.245 [b]	0.086[c]	0.163[b]	0.074[a]

*Values at the same column followed by the same letter are not significantly different at $p<0.05$.

Table 5. Soil-to-root transfer factor (RCF) and soil-to-shoot transfer factor (SCF) for Cd.

Modified polyacrylamide	Sandy soil		Sandy loam soil	
	RCF	SCF	RCF	SCF
0	5.15[a*]	1.27[b]	4.38[a]	0.797[b]
0.1%	4.34[ab]	2.347[a]	4.11[a]	2.458[a]
0.2%	3.41[b]	1.265[b]	3.62[a]	1.736[ab]
0.3%	2.36[b]	0.938[b]	1.32[b]	1.318[b]

*Values at the same column followed by the same letter are not significantly different at $p<0.05$.

Discussion

Treating polyacrylamide with hydrazine hydrate modifies amide groups to hydrazine groups, which are highly reactive toward heavy metal ions. It is known that $-CO-NH_2$ is considered the adsorption site for heavy metals chelation [16].

The bioavailability and solubility of heavy metals in soils depends on several factors, especially soil pH [19]. As soil pH significantly did not change with the application of the modified polyacrylamide (Table 2), the influence of the amendment on metal availability may not be related to the changes of pH.

The decreased uptake of heavy metals ions by corn (Pb concentration of roots and shoots of corn and Cd concentration of corn roots) grown in MPAM-amended soils may be related to the high affinity of heavy metal ions to functional groups commonly found in the MPAM. These functional groups form metal complexes or chelates that immobilize Cd and Pb, which are less mobile and bioavailable. In some cases PAM had no significant effect on decreasing metal uptake by corn (e.g. Cd concentrations of shoots). This may be due to competition between Pb and Cd for adsorption sites of soil colloids and stabilization agents when they are concurrently introduced to soils. It is reported that Pb has the ability to inhibit Cd sorption onto high-affinity adsorption sites of polyacrylamide [15] and soil colloids [20]. In the study performed by [20], Pb was shown to be less exchangeable than Cd and inhibited Cd sorption. Cadmium had little effect on Pb sorption at exchange sites of soils and sediments. Pb more readily forms inner-sphere surface complexes with soil surface functional groups than Cd. Therefore, Cd was more easily taken up and transported from the roots to the aerial parts of the plants.

In general, the concentrations of Pb and Cd in the corn roots and shoots grown in the sandy soils were higher compared to those planted in the sandy loam soils. This may be due to a higher clay percentage and CEC of sandy loam soil compared to sandy soil. This is in agreement with the results of [21], who reported that heavy metals had more mobility in soils that had less clay and silt content.

The transfer factor values of Cd were much higher than those of Pb, which may be due to the differences in metal ion characteristics and the resultant affinity for adsorption sites of the clay and soil colloids [12]. Cadmium has higher solubility and mobility as compared to Pb. The hydrated Pb and Cd cations have 6.1 and 7.6 water molecules in their hydration shells, respectively. The hydration energy of Cd is -1755 kJ mol^{-1} and that of Pb is -1425 kJ mol^{-1}[21]. The higher hydration energy of Pb means that it does not lose its hydration shell as compared to Cd. This could explain the weaker affinity of Cd than Pb to the adsorption sites of the soil colloids [12]. Therefore, Cd was more easily taken up by plants as compared to Pb [12, 15].

Conclusion

Modified polyacrylamide had an important and significant inhibitory effect on the uptake of Cd and especially Pb from contaminated soils. The ability of modified polyacrylamide to immobilize heavy metals in contaminated soils depends on the amendment doses, the types of metal cations, and soil texture. The effectiveness of PAM increased with PAM application rate, and the highest rate of 0.30% PAM was most effective. For both soils, the modified polyacrylamide decreased Pb concentrations in corn roots and shoots. In both soils, Cd concentration in shoots increased in pots containing 0.1% modified polyacrylamide. The concentration of Cd and Pb in plant growing in sandy loam soils was less than sandy soils. In both soils, RCF and SCF for Pb and RCF for Cd were decreased by the modified polyacrylamide, but SCF for Cd was increased in pots containing 0.1% modified polyacrylamide in both soils. The transfer factor (TF) values of Pb were much less than those of Cd in the same treatments.

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