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# Effect of Kiwi Shell and Incubation Time on Mobility of Lead and Cadmium in Contaminated Clay Soil

**Bahareh Lorestani[1], Chia Arjangi[2]\*,  Hajar Merrikhpour[1]**

[1] Assistant Professor, Department of Environment, Hamedan Branch, Islamic Azad University, Hamedan, Iran
[2] MSc Student, Department of Environment, Hamedan Branch, Islamic Azad University, Hamedan, Iran

**ABSTRACT:** In this study, the effectiveness of kiwi shell was investigated to reduce the mobility of Lead and Cadmium in clay soil in different intervals. For this purpose a clay soil sample was contaminated with Lead and Cadmium in distinct dishes with 10 and 600 ppm concentrations respectively and mixed with 5% kiwi shell. Samples were placed in incubator, and then sampling of soil in incubator was performed in intervals 3 hours, 1, 3, 7, 14, 21 and 28 days. Heavy metals concentrations were determined in different fractions of soil including exchangeable, carbonate, Fe-Mn oxides, organic matter, and residual with sequential extraction procedure and atomic absorption spectrophotometry. The results showed that during incubation, Lead concentration in treatments with kiwi shell rather than control soil increased in carbonate from 19.48 to 26.18 and in organic matter from 9.06 to 18.66 percent. Exchangeable, Fe-Mn oxides and residual fractions decreased from 11.48 to 6.69, 45.72 to 39.83 and 14.21 to 7.90 percent respectively. In samples with absorbent compared with control soil, Cadmium concentration in carbonate and organic matter increased from 28.20 to 38.40 and 18.76 to 24.72, while in exchangeable, Fe-Mn oxides and residual decreased from 16.66 to 13.69, 37.25 to 19.65 and 6.24 to 3.61 percent respectively. This study revealed that kiwi shell function in decreasing Cadmium and Lead mobility in studied clay soil were increased with increasing incubation time, but Cadmium compared with Lead required additional time to transfer and mobility to constant and stable soil fractions such as, organic matter and Fe-Mn oxides.

## INTRODUCTION

Heavy metals are the most important environmental pollutants. Important affecting factors in increasing heavy metals concentration in soil are included fertilizing matters, amendents, and pesticides, municipal and industrial waste waters [1].

Cadmium (Cd) and Lead (Pb) are two most common heavy metals in the environment. Cd is not an

\*Corresponding author: post.mail1@yahoo.com(Ch.Arjangi).

essential element in metabolic processes in almost all plants and animals, including human, and it can accumulate to levels that are toxic or lethal to organisms [2]. Pb has been recognized as one of the most hazardous heavy metal among environmental pollutants. The food chain transfer of Pb is one of the major pathways for human exposure to Pb contamination in soil [3]. Therefore, it is important to predict the risk of soil Pb and Cd for human and ecological receptors. Current physical and chemical procedures to improve soils contaminated with heavy metals are very costly, and also they have detrimental effects on soil physical conditions and they damage soil biological activity. Therefore, extent range of biological matters like agricultural waste and by-products more than other procedures have been considered as cheap, available, compatible with environment absorbent due to appropriate structure to absorb heavy metals [4]. These absorbents have most and active agent groups to remove heavy metals [5]. Also, natural absorbents due to having constructive effects on physical, chemical and biological soil properties are considered as one of main factors of soil fertility [6]. Reactions related to absorb metals from liquid phase on solid surfaces or reactions adsorption cation that are known as "reactions cation exchangeable" are the most important chemical reactions effective on behavior and availability of metals for plant in soil. These reactions control metal ions concentration and complexes in soil solution, and so they have important effects on absorption by plants and mobility of these elements [7]. Residence time directly relates to the bioavailability of heavy metals in soils [8]. Although it is often assumed that residence time effect reduced metal mobility and bioavailability, only a few works have been carried out to investigate whether and how time effect influence the metal chemical forms and/or metal fractions in soils [9,11]

It is important immobilizing heavy metals in contaminated soils in order to prevent transferring them to plant and at last transferring them to human food chain. For this reason, we can add different organic compounds to soil which depositing and stabilizing heavy metals decreased their absorbability by plant [7]. This organic matter can re-distribute heavy metals from soluble and exchangeable forms to fractions associated with organic matter or Fe-Mn oxides and the residual fraction [12]. This process could reduce the solubility of some metals in the soil [13]. Contradictory results were found about the effect of organic matter on bioavailability and mobility of heavy metals in soils. Studies show that Cd in the mobile fractions decreased significantly in the soil treated with organic matter [14]. The some research results indicate that an increase in dissolved organic matter (DOM), can contribute to the enhancement of metal concentration in soil solution [13, 15]. The researchers investigated Kiwi shell function in removing contamination of heavy metals as Cu, Ni, and Pb in aquatic environments in Iran. Results showed that amount absorption of these 3 metals by kiwi shell compared to experimental absorbents as active granule is very important [16]. Several investigations have revealed that the soluble organics are able to raise the trace metal carrying capacity of soil solution [17, 18]. Sequential extraction is like a fingerprint of metals, giving information about their potential for leaching, availability [19], the association of heavy metals with geochemical phases of soil, hence helps to reveal the distribution of heavy metals in fractions and to assess the actual and potential mobility of metals in soils [20]. Kiwi shell is considered as one of relevant natural absorbent, because it is disregarded after use. The purpose of this study was to investigate kiwi shell function on Cd and Pb heavy metals mobility in different fractions contaminated clay soil by

sequential extraction procedure in during incubation periods.

## MATERIALS AND METHODS

*Soil preparation and studying its physical and chemical properties*

For sampling, we pulled over 5cm from soil surface, then, we took soil of 30cm depth. For 24 hours, the soil was dried in closed environment in room temperature and far from direct radiation of sun, then after transferring to laboratory, it was screened by 2mm screen [21]. Physical and chemical soil properties like texture, amount of clay, silt and sand were determined by hydrometer. Then, using Salbu sequential extraction method, Sample was analyzed for metals Pb and Cd. pH and EC (electricity conductivity) were determined by pH meter and electricity conductivity meter respectively. Other properties like anion's and cations's studied soil, like sodium ($Na^+$), and potassium ($K^+$) solution were considered by flame photometry, phosphate ($PO_4^{3-}$), sulfate ($SO_4^{2-}$) and nitrate ($NO_3^-$) by spectrophotometry, calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) and chloride ($Cl^-$) by titration respectively [22, 23].

*Contaminating soil and adding absorbent*

10 and 600 ppm concentrations of Cd and Pb solution were added to the soil sample in the separate dishes respectively. For absorbent preparation, kiwi was washed, and then peeled, and dried in 60°C in oven (Unb 400) during 24 hours and then it was grinded. Then, 5% of absorbent namely kiwi shell was added to contaminated soil samples. Thus, 2 samples of contaminated soil with absorbent and without absorbent (control soil) were prepared [21, 24].

*Incubation, extraction and determining studied elements concentration*

Samples were placed in incubator (memert, Inb 400) in 28°C [21]. Then it was sampled in interval 3 hours, 1, 3, 7, 14, 21, and 28 days from soil in incubator. Then, using Salbu sequential extraction technique, extraction of samples 3 hours to 28 days was conducted separately to determine Cd and Pb heavy metals concentration in different fractions of soil including exchangeable, bound to carbonate, bound to Fe-Mn oxides, bound to organic matter, and residual. At last, providing standards related to studied elements, Cd and Pb heavy metals concentrations in different fractions of clay soil in intervals 3 hours to 28 days incubation using atomic absorption spectrophotometry (GBC-Aavante) was read and evaluated [23]. The steps and the operationally defined metal fractions are summarized in Table 1.

Table 1. Sequential extraction schemes for soil [24]

| Step | Fraction | Extraction Procedure |
|------|----------|----------------------|
| **1** | Exchangeable (EXC) | 2 g of soil sample, 20 mlAmmonium Acetate, pH 7, shake 2h, centrifuging (4 min, 100 rpm), Filtering, room temperature. |
| **2** | Bound to carbonate (CA) | 20ml Ammonium Acetate, pH 5, shake 2 h, centrifuging (4 min, 100 rpm), Filtering, room temperature. |
| **3** | Bound to Fe-Mn oxides (Fe-Mn) | 20 ml 0.04 mol/l $NH_2OH$ d HCl in 25% $CH_3COOH$, pH 2.0, water bath, 60C, 6 h, centrifuging (4 min, 100 rpm), Filtering, room temperature. |
| **4** | Bound to Organic Matter (OM) | 15 ml 30% $H_2O_2$, water bath, 80 C, 5.5 h, centrifuging (4 min, 100 rpm), Filtering, room temperature. |
| **5** | Residual (RES) | 5 ml, 3.2 mol/l Ammonium Acetate in 20% $HNO_3$, shake 0.5 h +15 ml dionized water, centrifuging (4 min, 100 rpm), Filtering, room temperature. |

## STATISTICAL ANALYSIS

All data were processed by Microsoft EXCEL 2007 and SPSS (PASW) 18.

## RESULTS AND DISCUSSION

*Physical and Chemical properties*

Some of physical and chemical properties of studied soil have been showed in Table2. The results showed that no element (Pb and Cd) was detected in theprimary soil.

Table 2. Some Physical and Chemical properties of soil

| Parameter | Value | Unit |
|-----------|-------|------|
| **Textural Class** | Clay-Loam | - |
| **Sand** | 26 | % |
| **Silt** | 43 | % |
| **Clay** | 31 | % |
| **pHs** | 7.22 | - |
| **EC** | 0.15 | dS /m |
| **$Ca^{2+}$** | 32 | mg/l |
| **$Mg^{2+}$** | 9.6 | mg/l |
| **$Na^+$** | 26.2 | mg/l |
| **$K^+$** | 45.2 | mg/l |
| **$PO_4^{-3}$** | 0.63 | mg/l |
| **$NO_3^-$** | 69.4 | mg/l |
| **$SO_4^-$** | 13.3 | mg/l |
| **$Cl^-$** | 81.6 | mg/l |

*Pb concentration changes*

Table 3 and Figure 1 show the distribution of Pb in the five fractions: exchangeable (EXC), carbonate (CA), Fe–Mn oxides (Fe–Mn), organic matter (OM) and residual (RES) fractions in control soil and with absorbent soil incubated for 3 hour, 1, 3, 7, 14, 21, and 28 days. During incubation, in samples control soil, Pb concentration range in exchangeable fraction

was 0.007-25.30%, carbonate 6.45-26.37%, Fe-Mn oxides 24.36-79.41 %, organic matter 0.005-18.34 %, and in residual9.02-18.25 % respectively. In samples with absorbent, this range in exchangeable was 0.003-14.92%, carbonate 12.71-31.66 %, Fe-Mn oxides 33.17- 49.98 %, organic matter 16.17-23.26 % and in residual 2.20-14.02% respectively. Pb concentration average in intervals 3 hours to 28 days incubation in exchangeable, carbonate, Fe-Mn oxides, organic matter and residual fractions in samples control soil was 11.48 %, 19.48 %, 45.72 %, 9.06 %, 14.21 % and in samples with kiwi shell was 6.96%, 26.18%, 39.83%, 18.66%, 7.90% respectively.

*Pb absorption process in different fractions of clay soil in during incubation*

Naturally, small fraction of heavy metals was absorbable by plants. Generally, exchangeable form was considered readily mobile and easily bioavailable, while residual form was considered to incorporate into crystalline lattice of soil minerals and appeared to be the most inactive. The carbonate, Fe–Mn oxides, and organic matter bound fractions could be considered relatively active depending on the actual physical and chemical properties of soil [25]. Thus, if the metal was in the first fractions of a soil, this would exhibit a greater potential hazard when compared with other soils where the metal was mainly found in the last fractions, especially in the last, where it was available only under extreme conditions rarely found in the environment [26]. Pb concentration average in samples with absorbent compared with samples control soil in exchangeable, Fe-Mn oxides and residual fractions decreased 4.52 %, 5.89 % and 6.31 % and in carbonate and organic matter fractions increased 6.7 % and 9.6 % respectively. Pb concentration in the bound to organic matter fraction was significantly different (p < 0.05) observed between the control and with

absorbent soil samples after 28 days incubation (Table 4). In first 3hours, Pb concentration in samples with absorbent compared with samples control soil in exchangeable, carbonate and Fe-Mn oxides fractions decreased 0.009 %, 0.4 % and 16.03 % and in organic matter and residual fractions increased 13.04 % and 3.42 % respectively. Decrease of exchangeable and carbonate fractions showing a decrease in metel availability shortly after amendent addition to soil. In first day incubation, Pb concentration in samples with absorbent compared with samples control soil in exchangeable, Fe-Mn oxides, and residual fractions decreased 0.005%, 29.43 % and 0.09 %, while in carbonate and organic matter fractions increased 6.26% and 23.25% respectively. In third day, Pb concentration in samples with absorbent compared with samples control soil in exchangeable, carbonate, Fe-Mn oxides decreased 0.004%, 5.44 % and 17.57 % and in organic matter and residual fractions increased 20.14% and 2.87 % respectively. In 7th day of experiment each two Pb treatments (with absorbent and control soil), Pb distribution in different fractions of clay soil has been stability and monotonous relatively. In this time, Pb concentration in samples with absorbent compared with samples control soil in exchangeable and residual fractions decreased 6.53 % and 13.59 %, while in carbonate, Fe-Mn oxides and organic matter fractions increased 9.59%, 8.69 % and 1.83% respectively. In 14th day of incubation, Pb concentration in samples with absorbent compared with samples control soil in exchangeable, organic matter and residual fractions decreased 3.62%, 2.07% and 12.51% while in carbonate and Fe-Mn oxides fractions increased 9.39 % and 8.81 % respectively. In 21th day of experiment, Pb concentration in samples with absorbent compared with samples control soil in exchangeable and residual fractions decreased 14.37 % and 11.36 %, while in carbonate,

Fe-Mn oxides and organic matter fractions increased 15.2 %, 2.95 % and 7.59 % respectively. In 28th day , Pb concentration in samples with absorbent compared with samples control soil in exchangeable and residual fractions decreased 7.1% and 12.96% and the other fractions namely in carbonate, Fe-Mn oxides and organic matter fractions increased about 12.34%, 1.34 % and 3.37 % respectively (Table 3). In general, Pb absorption sequential in different fractions of control soil in during incubation follows the order: Fe-Mn oxides > carbonate > residual > exchangeable > organic matter. This process in different fractions of soil with absorbent in during incubation follows the order: Fe-Mn oxides > carbonate > organic matter > residual > exchangeable. In each two samples with absorbent and control soil was found maximum Pb concentration in third fraction of soil or Fe-Mn oxides fraction. Its one possible cause that studied soil in this investigation had high amount of Fe-Mn oxides and it was made which high Pb amount was absorbed by Fe-Mn oxides soil. Also, in this study pH soil was neutral and relatively alkaline. Under condition alkaline pH and about neutral which it is often found in soils, cationic metals could be adsorbed by Fe, Al and Mn hydroxides which they are available in soil [27]. There are different results. Studies results indicate that without application of calcined egg shell, Pb was found mainly in the organically bound fraction (31.7%) [28]. Some researchers in assess the influence of sewage sludge amendment on metal mobility in Chilean soils found that as can be seen from the extraction before the amending process, the highest content of the Pb was found in the residual fraction in all soil [26]. Researchers found that among the non-residual, organic fractions contain the highest amount of Pb in the samples and the oxide fraction contains the lowest [29]. Spanish researchers found that most Pb

was associated with the oxide fraction in their study of polluted Spanish soils, with only very low amount in exchangeable fraction [30]. Similar findings have been reported by other researchers [31]. Increasing incubation time (from third day of incubation to forward), Pb concentration distribution in different fractions of clay soil was more stability and monotonous and from first week incubation to last incubation, maximum Pb concentration was decreased in third fraction or Fe-Mn oxides. In soil contaminated with Pb which has amending matter of kiwi shell compared with control soil, increasing incubation time especially from 7th day to 28th incubation, exchangeable and residual fractions decreased and carbonate, Fe-Mn oxides and organic fractions increased. The dissolution and consequently the mobility and bioavailability of metals were controlled by organic matter and oxides that acted as principal adsorbents and can prevent excessive mobilization of heavy metals [32]. These results are according to researchers results. They in own investigation found that the concentration of Cu, Pb and Fe in the soil solution and present in exchangeable forms (extracted with $CaCl_2$) were very low (< 0.5mg/kg) [33]. Studies also show that application of calcined eggshell decreased particularly the mobile fraction of Pb from 4.8 to 1.4 %. Instead, fraction organically bound fraction of Pb was increased. The ratios of Pb uptake from soils to roots (total contents) decreased from 0.01 to < 0.001 for Pb [28].

In general, concentration of heavy metals were controlled in different fractions of soil, including exchangeable fraction and as a result their bioavailability and mobility by soil properties such as pH, soil clay content, capacity cation exchangeable, redox potential, organic matter and time. Increasing incubation time, Pb concentration in exchangeable fraction of the samples controlled soil from 25.30

percent in 21th day to 16.48 percent decreased in 28th day incubation. There were several reasons for this: The first possible cause was the effect of time. Time caused to reduce the Pb concentration in mobile phases of soil such as exchangeable phase and increased concentration in less mobility phases of soil such as carbonate, Fe-Mn oxides, organic and residual. Metallic elements decreased their mobility and their forms of the more soluble changes to forms of low soluble, because created a balance between metal and soil over time, and due to reactions such as adsorption, exchange, sediment, oxidation-reduction, reaction with Fe-Mn hydroxides and inputing to minerals lattice. Perhaps could be said that if the incubation period of experiment was increased, the process of reducing the Pb concentration in the exchangeable fraction of control soil would increase. The decreasing the concentration of exchangeable form and increasing Pb concentrations of the other fractions were not unexpected, because changing soluble and exchangeable forms of metals over time and converting them to forms with lower solubility have been reported by other researchers [34]. Lim found that although the increase shaking time in soil treated with Cd from 1 to 7, 15, 30, 50, 65 days had no significant effect on the adsorption of Cd, but it was caused to convert more soluble forms of the metal to less solubility forms [9]. Misraina studied to determine the effect of time on the extract ability of six metals Zn, Cu, Ni, Cd, Pb and Cr in four different soils under saturated situation, observed that With adding the 50 mg/kg soil of the metals and extraction using DTPA induring120 days incubation, in spite of metals extractability was depended on metal nature and soil properties, but increasing incubation time caused to decrease extractable metals amounts [35]. The second possible cause was the studied soil's pH. Availability of heavy metals, particularly Pb and Cd in the soil was influenced by pH and decreased with the increasing pH. The association between metal adsorption on exchangeable surfaces of soil and pH was partly due to the competition of $H^+$ for adsorption sites at low pH resulting in decreased metal adsorption [36]. Lim investigated the changes of speciation of Pb and Cd in soil at various pH values with different times and found that the changes of Pb and Cd in exchangeable fraction were pH dependent [9]. Sauve reported that the concentration of dissolved Pb and activity of free $Pb^{2+}$ ions were highly significantly correlated to soil pH and total Pb content [37]. Janssen reported that soil pH affected the proportion of Pb bound to soil oxides and highly significantly (P < 0.001), the exchangeable Pb and Zn. More than 95% of the variability of Pb and Zn in the exchangeable fraction was explained by the variability of soil pH [38].

In general, Pb changes process in treatments control soil in all studied clay soil fractions and more incubation times has no consistency, regular and anticipated pattern and it always had ascendant-descend process and vice versa. These changes in treatments with natural matter of kiwi shell in many incubation times had increasing-decreasing process, so that first, Pb concentration in early fractions increased and then it decreased. While, Pb changes pattern in quintuple fractions of clay soil in treatments with absorbent had not identical and constancy process as in soil without absorbent.

*Cd concentration changes*

Table 3 and Figure 2 show the distribution of Cd in the five fractions: exchangeable (EXC), carbonate (CA), Fe–Mn oxides (Fe–Mn), organic matter (OM) and residual (RES) fractions in control soil and with absorbent soil incubated for 3 hour, 1, 3, 7, 14, 21, and 28 days. During incubation, in samples control soil, Cd concentration range in exchangeable was 17.01-0.28 %, carbonate19.83-38.43 %, Fe-Mn oxides 20.46-60.33 %, organic matter 0.33-48.21 %

and in residual 0.28-11.48 % respectively. In samples with absorbent, this range in exchangeable was 1.82-21.05%, carbonate 12.26-93.15 %, Fe-Mn oxides 1.27-41.90%, organic matter 1.91-68.91% and in residual 0.10-21.05 % respectively. Cd concentration average in intervals 3 hours to 28 days incubation in exchangeable, carbonate, Fe-Mg oxides, organic matter and residual fractions in samples control soil was 9.50 %, 28.20 %, 37.25 %, 18.76 %, 6.24 % and in treatments with kiwi shell was 12.29 %, 38.40 %, 72.65%, 24.19%, 3.61% respectively.

*Cd absorption process in different fractions of clay soil in during incubation*

Cd concentration average in samples with absorbent compared with samples control soil in exchangeable, carbonate and organic matter fractions increased 2.79%, 10.2 % and 5.96% and in Fe-Mn oxides and residual fractions decreased 17.6% and 2.63% respectively. The sum of Cd in the exchangeable and carbonate fractions in clay soil of investigated ranged from 2 to 12 percent on average, which indicates that the Cd in these soils may be highly available for plant.

In first 3 hours of incubation, Cd concentration in samples with absorbent compared with samples control soil in Fe-Mn oxides and organic matter fractions decreased 19.19% and 40.94% and in exchangeable, carbonate and residual fractions increased 1.54%, 57.05% and 1.54 % respectively. In first day, Cd concentration in samples with absorbent compared with samples control soil in carbonate and Fe-Mn oxides fractions decreased 12.69 % and 58.95 %, and in exchangeable, organic matter and residual fractions increased 1.54%, 68.58% and 1.54% respectively. In third day, Cd concentration in samples with absorbent compared with samples control soil in Fe-Mn oxides and organic matter fractions decreased 15.98% and 26.11% and in exchangeable, carbonate and residual fractions

increased 20.7%, 0.7% and 20.7% respectively. In 7th day of incubation, Cd concentration in samples with absorbent compared with samples control soil in carbonate and residual fractions decreased 18.31% and 10.73%, while in exchangeable, Fe-Mn oxides and organic matter fractions increased 4.62%, 7.79 % and 16.63% respectively. In second week of incubation, Cd concentration in samples with absorbent compared with samples control soil in exchangeable, carbonate and residual fractions decreased 1.06 %, 4.15 % and 10.02 %, and in Fe-Mn oxides and organic matter fractions increased 6.13% and 9.09% respectively. In 21th day of incubation, Cd concentration in samples with absorbent compared with samples control soil in exchangeable, Fe-Mn oxides and residual fraction decreased 2.85 %, 22.02 % and 11.37 %, while in carbonate and organic matter fractions increased 31.57% and 4.67% respectively. In last time of incubation, namely in 28th day, Cd concentration in samples with absorbent compared with samples control soil in exchangeable, Fe-Mn oxides and residual fractions decreased 5%, 20.95% and 10.04% and in carbonate and organic matter fractions increased 17.25% and 9.74% respectively (Table 3). In most incubation intervals, Cd concentration average in organic matter fraction with absorbent increased, but no significant differences ($p > 0.05$) in the concentrations of Cd the bound to organic matter fraction were observed between the control and with absorbent soil samples after 28 days incubation (Table 4). It's one possible cause that, Cd bound and connection to soil organic phase occurred in longer and higher period, therefore increasing Cd concentration in organic fraction of clay soil related to increasing incubation time.

Cd absorption sequential in different fractions of control soil during incubation follows the order: Fe-Mn oxides > carbonate > organic matter > exchangeable > residual.

This process in different fractions of clay soil with absorbent during incubation follows the order: carbonate > organic matter > Fe-Mn oxides > exchangeable > residual.

In samples control soil Cd concentration in the first 3 periods of incubation of exchangeable fraction was very low and then with increasing incubation time increased. It's a possible cause that some of soil fractions, such as carbonate, Fe-Mn oxides, organic and residual fractions compared with exchangeable fraction have higher capacity for maintain of heavy metals such as Cd in the soil and are able to stabilize large quantities of these metals quickly and convert to less mobility forms [34]. High percentage of the total concentration of Cd (respectively: Fe-Mn oxides: 260.75, carbonate: 197.44, organic: 131.38 and residual: 43.7) in the control soil has been entered to second to fifth soil fractions (Table 3).

A decrease in exchangeable Cd in samples with absorbent in first day incubation may be attributed to the formation of soluble Cd-organic associations over the time of incubation. Neal and Sposito found that soil sorption of Cd were reduced by the formation of soluble-organic associations in the aqueous solution [39]. From first 3 hours to first 7 days incubation, in samples with kiwi shell compared with samples control soil, Cd concentration increased in exchangeable soil, indicating that in first 3 periods of incubation most of Cd entered the mobile fraction. Researches in own investigation observed that after 30 days incubation PM4 (poultry manure 4%) and PM2 (poultry manure 2%) increased Cd in soil by 130 and 38%, respectively, compared with that of control. After 60 days incubation, PM4 increased Cd by 22-fold followed by PM2 (14-fold) and FM2 (farm yard manure 2%) (12-fold) compared with that of control [40]. Cd concentration in soil available fractions namely exchangeable and carbonate fractions began to decrease from 14th incubation.

Increasing incubation time (from second week to the last incubation time) in samples with absorbent compared with samples of control soil, Cd had decreasing process in exchangeable, carbonate and residual and increasing process in organic matter. Cd has more mobility than the other heavy metals in soil [41]. Therefore, Cd as a mobile element requires more time to move and transfer from unstable fractions like exchangeable fraction to stable soil fractions like bound to Fe-Mn oxides and organic matter fractions [25]. Decrease of Cd could be due to high capacity cation exchangeable of organic matter and its ability to complex Cd in the soil because organic matters caused to decrease bioavailability due to increasing capacity cation exchangeable of soil [26, 42]. It's another possible cause is that Cd has been absorbed by clay soil. Considering the relatively large amount of clay mineral present in these soils (31%,) (Table 2), adsorption to clay can be an important mechanism that controls Cd concentration. The observed decrease of Cd concentration with time can be attributed to the "ageing effects" of metal ion adsorption to clay. The ageing effects are stronger for Cd than for Pb, probably because that more Cd is adsorbed to clay minerals than Pb does. The most significant Cd adsorption to clay is predicted for soil which has a relatively low pH. But the calculation shows that soil organic matter is far more important in the adsorption of Cd than clay minerals [43]. Studies show that application of calcined eggshell decreased particularly the mobile fraction of Cd from 43.3 % to 0.2%, the ratios of Cd, uptake from soils to roots lettuce (total contents) decreased from 0.25 to < 0.01 [28]. Researchers in own investigation observed that the concentration of free $Cd^{2+}$ and also the concentration of soluble Cd were reduced by rice straw addition, with the incubation time, but changed with time for Cd is not always consistent [43]. Some studies results indicated that there was a significant

decrease in AB-DTPA extractable Cd due to application of amendments after 30 days incubation except PM4 (poultry manure 4%) and PM2 (poultry manure 2%).Organic matter increased significantly ($P < 0.05$) with amendments after 30 days incubation [33].

Also decrease in DTPA-extractable Cd with incubation was also recorded by some researchers with the application of mushroom compost and grape marc [44].Researchers suggest that Cd in the mobile fractions decreased significantly in the soil treated with organic matter [14].

In general, Cd changes in all clay soil fractions were investigated and in more incubation in treatments with absorbent and treatments control soil had not stable, regular and anticipated pattern and it always had ascendant-descent process and vice versa.

Table 3. Pb and Cd distribution percentage (%) in different fractions of clay soil   with kiwi shell absorbent and control soil in during incubation

| Incubation period | Fraction | | | | | Treatment |
|---|---|---|---|---|---|---|
| | Exchangeable | Carbonate | Fe-Mn Oxides | Organic Matter | Residual | |
| 3 hour | 0.001 | 26.09 | 59.05 | 5.40 | 9.42 | |
| 1 day | 0.008 | 6.45 | 79.41 | 0.006 | 14.11 | |
| 3 day | 0.007 | 26.37 | 64.58 | 0.005 | 9.02 | clay soil |
| 7 day | 21.45 | 20.48 | 25.40 | 14.85 | 17.79 | contaminated with Pb |
| 14 day | 17.11 | 22.02 | 24.36 | 18.24 | 18.25 | without  kiwi shell |
| 21 day | 25.30 | 15.64 | 32.72 | 10.53 | 15.78 | (control soil) |
| 28 day | 16.48 | 19.32 | 34.58 | 14.44 | 15.16 | |
| Sum | 80.35 | 136.37 | 320.1 | 63.47 | 99.53 | |
| 3 hour | 0.003 | 25.69 | 43.02 | 18.44 | 12.84 | |
| 1 day | 0.003 | 12.71 | 49.98 | 23.26 | 14.02 | clay soil |
| 3 day | 0.003 | 20.93 | 47.01 | 20.15 | 11.89 | contaminated with Pb |
| 7 day | 14.92 | 30.07 | 34.09 | 16.68 | 4.20 | with kiwi shell |
| 14 day | 13.49 | 31.48 | 33.17 | 16.17 | 5.74 | |
| 21 day | 10.93 | 30.84 | 35.67 | 18.12 | 4.42 | |
| 28 day | 9.38 | 31.66 | 35.92 | 17.81 | 2.20 | |
| Sum | 48.72 | 183.38 | 278.86 | 130.63 | 55.31 | |

Continue of table 3

| | | | | | | |
|---|---|---|---|---|---|---|
| **3 hour** | 0.28 | 36.10 | 20.46 | 42.85 | 0.28 | |
| **1 day** | 0.44 | 38.43 | 60.32 | 0.33 | 0.44 | |
| **3 day** | 0.35 | 20.35 | 30.71 | 48.21 | 0.35 | |
| **7 day** | 15.49 | 30.57 | 34.11 | 8.96 | 10.85 | clay soil |
| **14 day** | 16.71 | 29.32 | 32.56 | 11.27 | 10.12 | contaminated with |
| **21 day** | 17.01 | 22.84 | 40.74 | 7.91 | 11.48 | Cd without kiwi |
| **28 day** | 16.27 | 19.83 | 41.85 | 11.85 | 10.18 | shell |
| | | | | | | (control soil) |
| **Sum** | 66.55 | 197.44 | 260.75 | 131.38 | 43.7 | |
| **3 hour** | 18.26 | 93.15 | 1.27 | 1.91 | 1.82 | clay soil |
| **1 day** | 1.98 | 25.74 | 1.38 | 68.91 | 1.98 | contaminated with |
| **3 day** | 21.05 | 21.05 | 14.73 | 22.10 | 21.05 | Cd with kiwi shell |
| **7 day** | 20.11 | 12.26 | 41.90 | 25.59 | 0.12 | absorbent |
| **14 day** | 15.65 | 25.17 | 38.69 | 20.36 | 0.10 | |
| **21 day** | 14.16 | 54.41 | 18.72 | 12.58 | 0.11 | |
| **28 day** | 11.27 | 37.08 | 20.90 | 21.59 | 0.14 | |
| **Sum** | 102.48 | 268.86 | 137.59 | 173.04 | 25.32 | |

Table 4.Pb and Cd concentration average in organic fraction soil with absorbent and control soil in during incubation

| **Metal** | **t** | **df** | **Sig. (2tailed)** |
|---|---|---|---|
| **Pb** | -14.22 | 6.68 | 000 |
| **Cd** | 0.94 | 11.18 | 0.36 |
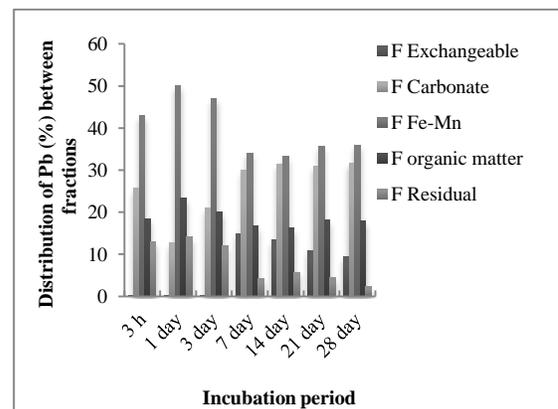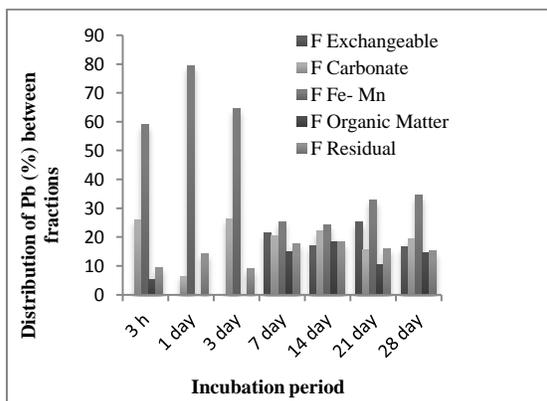


**(A)**



**(B)**

Figure 1.Pb distribution percentage in different fractions control soil (A) and soil with kiwi shell absorbent (B) in during incubation
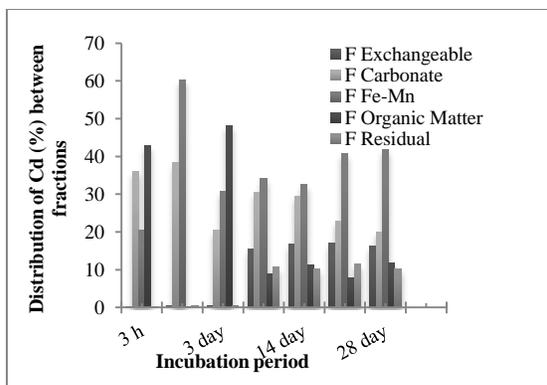
**(C)**
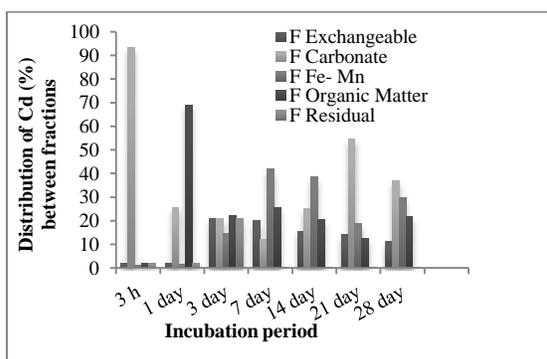


**(D)**

Figure 2. Cd distribution percentage in different fractions control soil (C) and soil with kiwi shell absorbent (D) in during incubation

## CONCLUSION

The distribution of the metals in the various fractions confirms their difference in mobility and bioavailability. With ageing, metal is generally subject to transformation or incorporation into a more stable solid phase that can lead to a decrease in metal bioavailability. In samples amended with kiwi shell compared with samples not amended, increasing incubation time, Pb and Cd concentration decreased in mobile and available fractions of soil like exchangeable fraction and it increased in low mobility and stable fractions like Fe-Mn oxides and organic matter fraction. Among the metals investigated, Pb was easily transformed from the exchangeable fraction to more stable fractions during the incubation period than Cd. In other words, in

during incubation, kiwi shell in decreasing mobility of exchangeable fraction in Pb treated more efficacy than Cd. It's one possible cause that Cd compared with Pb bound to organic matter fraction of soil loosely. It's another possible cause that organic matters decomposition in soil contaminated with Pb compared with soil contaminated with Cd was slower, as a result these matters remained in soil with Pb durably and long. It could be said that kiwi shell of absorbent capacity in Pb was more than Cd. At the end of this study, it would be resulted that organic amendent of kiwi shell may be used as efficacy factor in decreasing mobility to amend clay soil contaminated with heavy metal Cd and especially Pb.

## ACKNOWLEDGEMENT

## REFERENCES

1. Panahpour E., Efuni M., Hommaei M., Hoodji M., 2008. Cd, Cr and Co mobility in soil treated with sludge waste and salt of these metals and its adsorption by vegetables in east region of Isfahan. Journal of Water and Waste water. 3, 9-17.

2. Oliver M.A., 1997. Soil and human health, a review. European Journal of Soil Science 48, 573–592.

3. Finzgar N., Kos B., Lestan D., 2006. Bio availability and mobility of Pb after soil treatment with different remediation methods. Plant Soil Environmental. 52 (1): 25–34.

4. Mohammadirouzbahani M., Abedikoupaei J., 2009. Study of hyperacumulator plants application in remediation of soil contaminated with Ni. International Journal of Environmental Science and Technology. 11(4): 449-457.

5. Ghorbani S., Tabandeh F., Yakhchali B., Mehnia M.R., 2008. Heavy metals, environment effects and

its removing environmental procedures. Iranian Journal of Chemistry & Chemical Engineering 50.

6. Pouzeshshirazi M., Samavat S., Zolfibavaryani M., Fakhri F., Moradi G.H., 2011. Study of organic matter effect of different resources on physical and chemical properties of soil and plant function in Bushehr province.Soil studies two trimonthly 4(25): 285-293.

7. Khaleghi M., Golchin A., 2011. Immobilizing heavy metals in contaminated soil by different additives.Environmental Engineering Speciality Congress.

8. Pedersen M.B., Kjar C., Elmegaard N., 2000. Toxicity and Bioaccumulation of Copper to black bindweed (Fallopia convolvulus) in relation to bioavailability and the age of soil contamination. Archives of Environmental Contamination and Toxicology. 39, 431- 439.

9. Lim T.T., Tay J.H., The C.I., 2002. Contaminant time effect on Lead and Cadmium fraction in tropical coastal clay. Journal of Environmental Quality. 31, 806–812.

10. Bataillard P., Cambier P., Picot C., 2003. Short-term transformation of Lead and Cadmium compounds in soil after contamination. European Journal of Soil Science. 54, 365– 376.

11. Davies N.A., Hodson M.E., Black S., 2003. The influence of time on Lead toxicity and bioaccumulation determined by the OECD earthworm toxicity test. Environmental Pollution.121, 55–61.

12. McGrath S.P., Cegarra J., 1992. Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil. European Journal of Soil Science. 43, 313-321.

13. Weng L., Temminghoff E.J., Lofts S., Tipping E., Van Riemsdijk W.H., 2001. Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil. International Journal of Environmental Science and Technology. 36, 4804-4810.

14. Almas A., Singh B.R., Salbu B., 1999. Ature and organic matter.Journal of Environmental Quality. 28, 1742-1750.

15. Strobel B.W., Borggard O.K., Hansen H.C.B., Andersen M.K., Raulund Rasmussen K., 2005. Dissolved organic carbon and decreasing pH mobilize Cadmium and Copper in soil. European Journal of Soil Science. 56, 189-196.

16. Montazeri N., Baher E., Barami Z., Ghourchbeigi M., 2010. Kiwi role in removing environmental contaminations and study of its effect factors (Regional study of kiwi in Tonekabon). Iranian Journal of Natural Resources and Science. 1(5).

17. McBride M., Martinez C.E., Sauve S., 1998. Copper (II) in aged suspensions of goethite and organic matter. SoilScience Society of America Journal. 62, 1542-1548.

18. Naidu R.P., Harter R.D., 1998. Efeect of different organic ligands on Cadmium sorption by and extractability from soil. Soil Science Society of America Journal. 62, 644-655.

19. Narwal R.P., Singh B.R., 1998. Effect of organic materials on partitioning extractability and plant uptake of metals in an alum shale soil. Water Air Soil Pollution. 103, 405-421.

20. Tessier A., Campbell P.G.C., Bisson M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. International journal of Environmental Science and Technology. 51, 231-235.

21. Galali M., khanlariVaraste Z., 2008. Effect of aging peocess on the fractionation of heavy metals in some calcareous soils of Iran. Geoderma. 143, 26-40.

22. Rowell D.I., 1994. Soil science method and application, longmangrop, Pp. 345 Limitation Score. Computers & Geosciences. 33, 1316-1326.

23. Salbu B., Krekling T., Oughton D.H., 1998. Characterization of radioactive particle in the environment. Analist. 123, 843-849.

24. Terzano M., 2007. Microscopic single particle characterization of zeolithes synthesized in a soil polluted by Copper or Cadmium and treated with coal fly ash. Journal Applied Clay Sience. 35, 128-138.

25. Lu A., Zhuzhen Z.H., Xiao- quan S.H., 2005. Time effect on the fractionation of heavy metals in soils. Geoderma. 125, 225-234.

26. Ahumada I., Escudero P., Carrasco A., Castillo G., Ascar L., Fuentes E., 2004. Use of sequential extraction to assess the influence of sewage sludge amendent on metal mobility in Chilean soils. Journal of Environmental Monitoring and Assessment. 6(4): 327-334.

27. Ghosh M., Singh S.P., 2005. A review on phytoremediation of heavy metals and utilization of its byproducts. Applied Ecology and Environmental Research. 3(1): 1-18.

28. Young kim R., Kyung sung R.J., Cheolkim S., Choonjang B., Sik O.K.Y., 2010. Effect of calcined eggshell on fractional distribution and plant uptake of Cd, Pb and Zn in contaminated soils near mine. 19th Word Congress of Soil Science, Soil Solutions for a Changing World, Brisbane, Australia, 80-81.

29. Oluwatosin G.A., Adeyolano O.D., Dauda T.O., Akinbola G.E., 2008. Levels and geochemical fractions of Cd, Pb, and Zn in valley bottom soils of some urbancitiesnin south western Nigeria. African journal of Biotechnology. 7(19): 3455-3465.

30. Rasmos L., Hernandez L.M., Gonzalez M., 1994. Sequential fractionation of Copper, Lead, Cadmium and Zink in soils form or near Donana National park. Journal of Environmental Quality. 23, 50-57.

31. Sposito G., Lund L.J., Chang A.C., 1982. Trace metal chemistry in avidzone field soils amended with sewage sludge in fractionation of Ni, Cu, Cd and Pb in solid phases. America Journal of Soil Science Society. 46, 260-264.

32. McBride M.B., 2001. Heavy Metals in the Environment. Journal of Environmental Quality. 30, 78-84.

33. Clemente R., Escolar A., Bernal M., 2006. Heavy metals fractionation and organic matter mineralisation in contaminated amended with calcareous soil organic materials. Bio resource Technology. 97 (15): 1894-1901.

34. Rajai M., Karimian N., 2008. Effect of cadmium added and incubation time on chemical form sof cadmium in two group sof soil texture. Journal of Science and Technology of Agriculture and Natural Resources. 11(1): 97-108.

35. Misra A.K., Sarkunan V., Das M., Nayar P.K., 1990. Transformation of added heavy metals in soils under flooded condition. Journal of the Indian Society of Soil Science. 38, 416-418.

36. Rieuwerts J.S., Thornton I., Farago M.E., Ashmore M.R., 1998. Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. Journal of Environmental Quality. 10, 61–75.

37. Sauve S., McBride M.B., Hedershot W.H., 1997. Speciation of lead in contaminated soils. Environmental Pollution. 98, 149–155.

38. Janssen R.P.T., Peijnenburg W.J.G.M., Posthuma L., Van Den Hoop M.A.G.T., 1997. Equilibrium partitioning of heavy metals in Dutch field soils.1. Relationship between metal partitioning coefficient and soil characteristics. Environmental Toxicology and Chemistry. 16(12): 2470 - 2478.

39. Neal R.H., Sposito G., 1986. Effects of soluble organic matter and sewage sludge amendments on Cd sorption by soils at low cadmium concentrations. Soil Science. 142, 164–172.

40. Sabir M., Ghafoor A., Saifullah U.R., Muhammad Z., Murteza G., 2008. Effect of organic amendents and incubation time on extractability of Ni and others metals from contaminated soils. Pakistan Journal of Agricultural Sciences. 45(1): 18-24.

41. Kasraei P., 2010. Cadmium. Electronic Journal of Ecology. 1-3.

42. Erfanmanesh M. Efuni M. Environment contamination (water, soil, air), Arkan: Esfahan, 2006. 15 - 40.

43. Cui Y.S., Du X., Weng L.P., Zhu Y.G., 2008. Effect of rice straw on the speciation of Cadmium (Cd) and Copper (Cu) in soils. Geoderma 146, 370-377.

44. Karaca A., 2004. Effect of organic wastes on the extractability of Cadmium, Copper, Nickel, and Zinc in soil. Geoderma. 122, 297-303.