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Effect of Chemical Additives on Availability of Heavy Metals (Pb, Cd and Zn) of Soil

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Availability of the heavy metals (Pb, Cd, and Zn) has been studied by the use of different additives on the soil of industrial areas of Amol. Collected soil samples, by complete mixed, were dried in oven, and after grinding they were passed through a polyethylene sieve with 2 mm diameter holes. Extraction process of heavy metals from soil has done by distilled water, calcium chloride, potassium nitrate, ammonium citrate and EDTA at different concentrations. The heavy metals have been measured by Atomic Absorption Spectrometer. Concentrations of Pb, Cd and Zn in the soils were determined as 50±12.5, 127±16.13510 and 3000±180 mic/gr respectively. Best concentration and extraction conditions for the heavy metals determined. Application of chemical additives such as EDTA and ammonium citrate plays an important role in dissolution of heavy metals and thus in increasing their availability in soil.

Key Words: Availability, Heavy metals, Soil, Additives.

INTRODUCTION

One of the major difficulties on remediation of soils from heavy metals by the use of bacteria and plants is the reduction of the availability and exposure of these toxic metals in soils[1-3]. In general, the concentration of heavy metals of soils is found in 3 forms. The available fraction is a part of heavy metals of soil which are naturally available to plants and other soil organisms. The potential available fraction is part of heavy metals which is transferred in the absence of available sections. Unavailable fraction is remaining heavy metals of the soil which is stabilized on the surface of soil particles due to binding with organic or silicate compounds of soil and will not been absorbed by soil microorganisms and plants[4-6]. Various factors including physical and chemical features of soil (soil texture, moisture, pH and organic carbon), production and secretion of organic compounds from plants roots influence on availability and uptake of heavy metals in soil by organisms and plants[7-9]. These compounds under the generic name of phytosyderofores, divided into two groups, plant chelating agent and metallothioneines[10]. The most appropriate method for determining and estimating the availability of heavy metals in soil is the extraction of its soluble part by chemical compounds. In this regards, it's better to use natural, low-cost and low hazardous chemical compounds[11-15]. Scientists use a variety of chemical compounds such as potassium nitrate, calcium chloride, potassium chloride, ammonium acetate, ammonium nitrate, citric and acetic acids, EDTA and DTPA for the dissolution and extraction of heavy metals in soil[16-24]. In present research, the effects of the type of chemical compounds and concentration of each on availability of Pb, Cd and Zn in soil have been studied.

EXPERIMENTAL

Soil sampling: In this research, 40 points were randomly selected as sampling point from different regions of industrial zone of Amol City which is contaminated by heavy metals. Approximately three lots of 500 g of soil were taken from each point of the polluted site. These samples were completely mixed by manual concrete mixer machine. The mixed sample dried in an oven at 70 ºC. Dried samples were grounded and were sieved using a 2 mm polyethylene sieve.

Soil extraction: The extraction process of studied heavy metals was done by distilled water and various chemical additives such as potassium nitrate, calcium chloride, ammonium citrate and EDTA with concentrations of 0.25, 0.5, 1, 2, 4 mol/L. In order to prepare each sample 0.5 g of collected soil was weighted with a 0.0001 g sensitive scale and transferred to plastic containers (150 mL). Then the extraction process continued for 10 h using a rotary Shaker. The extracts were filtered using Whatman No. 1 filter papers.

Detection method: Heavy metal concentrations were measured using a Perkin- Elmer flame atomic absorption spectrometer. The heavy metals (Pb, Cd and Zn) were measured at the wavelengths 283.5, 228 and 213.9 nm, respectively. Calibration curves constructed using standard solutions for each individual metal. In this study, standards were analyzed each time a set of samples are run. A calibration curve prepared for each metal by plotting absorbance versus the metal concentration in µg metal/mL. The best fit straight line was drawn for the data points. This calibration line or its equation used to obtain the metal concentration in the samples to be analyzed. To remove the possible effect of samples pH, ammonium acetate buffer solution has been used in this study. Statistical analysis of data was done by SPSS software, version[16].

RESULTS AND DISCUSSION

Concentration of Zn, Cd and Pb in soils of the different regions was determined 13510 ± 1241, 127 ± 16.50 and 3000 ± 1780 mg/kg soil, respectively. The extraction of Zn by control (distilled water) was minimum (210 ± 74 mg/kg) and by EDTA was maximum (7892 ± 711 mg/kg). The extraction of Cd in soil by distilled water was low (1.50 ± 0.50 mg/kg). ANOVA analysis showed that there was a significant difference in heavy metal contents in blank and chemical additives samples (calcium chloride, potassium nitrate, ammonium citrate and EDTA) ($p < 0.05$).

Availability of Cd by EDTA was more than the other chemical compounds, but this difference was not statistically significant ($p > 0.05$). The mean extraction of Pb by distilled water was minimum (4 ± 1.50 mg/kg) and was maximum by EDTA (2110 ± 618 mg/kg). This amount was also significant with ammonium citrate and potassium nitrate compared to the control sample ($p < 0.05$).

Fig. 1 showed that the extraction of zinc by chemical additives in soil is linearly related to zinc molar concentration. As Fig. 1 showed the correlation coefficient between the zinc extraction from the soil and the molar concentration of additive metal recover chemicals is above 80 %. Also Fig. 1 showed the EDTA additive chemical has the highest zinc extraction efficiency than to the other two materials. The potassium nitrate is the least we can retrieve it.

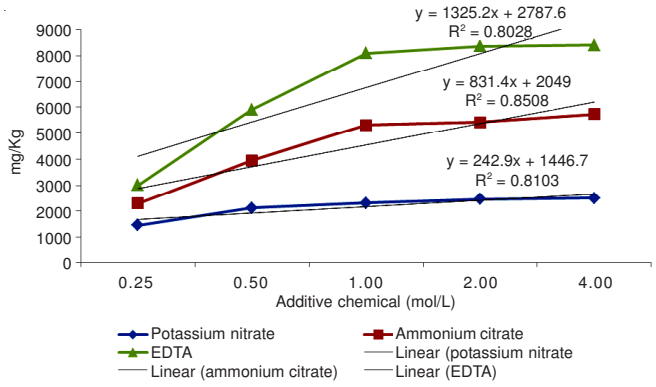

Fig. 1. Extracted concentration of Zn in soil by several additives

According to Fig. 2, the extraction of cadmium by three chemical additives in soil is linearly related to additives molar concentration. As Fig. 1 shows the correlation coefficient between the metal extraction from the soil and the molar concentration of additive metal recover chemicals is above 90 %. Fig. 2 also shows the EDTA additive chemical has the highest cadmium extraction efficiency than to the other two materials. The potassium nitrate is the least we can retrieve it.

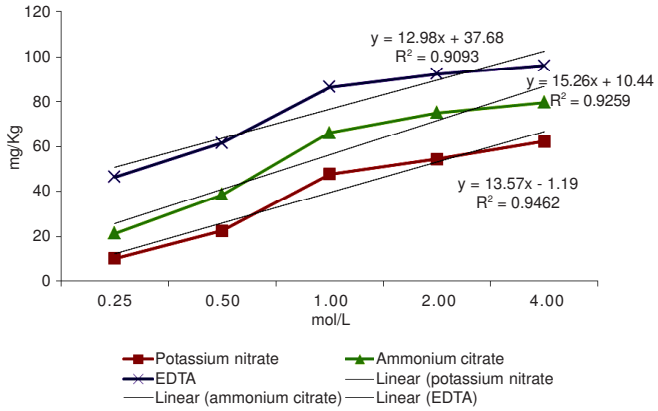

Fig. 2. Extracted concentration of Cd in soil by several additives

According to Fig. 3, the extraction of Pb by three chemical additives in soil is linearly related to additives molar concentration. Fig. 3 shows the correlation coefficient between the Pb extraction from the soil and the molar concentration of additive metal recover chemicals is 79, 92 and 88 %. Fig. 3 also shows the EDTA additive chemical has the highest cadmium extraction efficiency than to the other two materials. The potassium nitrate is the least we can retrieve it.

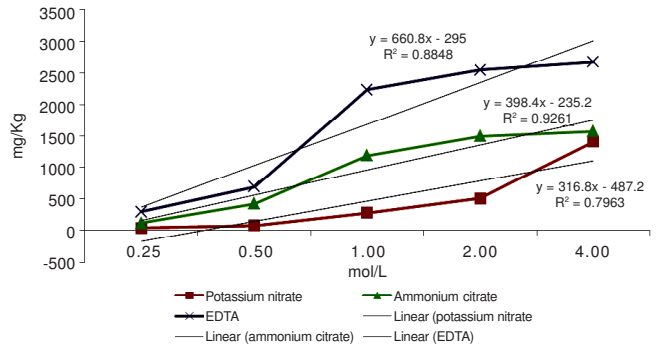

Fig. 3. Extracted concentration of Pb in soil by several additives

In Fig. 3, the extraction of Pb in soil has increased by the increment of molarity in different additives. As can see from the Fig. 3 extraction amount of the Pb at concentration of 1 mol/L was maximum (1125 and 2110 mg/kg) for ammonium citrate and EDTA, but extraction increasing in the potassium nitrate was done until molarity 4 mol/L.

In this study, Zn has the highest extraction ability by different additives. The results show that Zn has a high availability and exposure to microorganisms of soil and plants and this is one of the important reasons of its high concentration compared to other heavy metals in plants and underground waters. The results of other researches have also shown that Zn and Cd have a high natural dissolution and the presence of chelating agents such as EDTA and organic acids would not influence much on the increase of their dissolution in soil[13-15]. But it should be mentioned that various studies have been

presented regarding the effects of chelating compounds on Zn availability. For instance in some studies the effect of EDTA on dissolution increase of Zn has been reported significant[18,22,24]. In present study, EDTA and ammonium citrate have also contributed to maximum dissolution of Zn and Cd. According to the results of this study, Pb has a low solubility and extraction in distilled water and calcium chloride, while its ability was significant in EDTA and ammonium citrate. According to other researches, Pb extraction is low due to the formation of insoluble compound such as pyromorphyte and chloropyromorphyte substances of Pb and insoluble lead carbonate. So, regardless of its high concentration in soil, it is low in plants and underground waters[6,7,18]. Application of compounds such as EDTA and organic acids is one of the methods to increase Pb exposure and availability for remediation of soil by microorganisms and plants[1-4].

In this research, the best concentration of EDTA and ammonium citrate for extraction of Pb has been on 2 mol/L. While the effect of these compounds on solubility of Zn and Cd was significant by concentration of 1 mol/L and was not so significant for higher concentrations. Thus, 1-2 mol/L of EDTA and ammonium citrate will be the most appropriate concentrations in economic and environmental issues for Zn, Cd and Pb extraction. Studies by some researchers on the application of EDTA for the increase of Zn and Cd uptake in plants have suggested the ineffectiveness of this additive[7,22]. However several researchers have shown the increasing effect of EDTA on the absorption of these two elements in soil and plants[18,24]. It should be mentioned that other factors such as physical and chemical features of soil or plant type are also effective. Many discussions have been done regarding the influence of ammonium citrate and EDTA on solubility of Pb and its uptake increase by plants. Blaylock and Huang demonstrated the simultaneous influence of ammonium citrate and EDTA on Pb absorption by corn[11,14]. But Baker *et al.* showed the ineffectiveness of ammonium citrate in this area and related its main reason to pH decline of soil[25]. In another study, by EDTA increase of contaminated soil with Pb, this metal uptake in corn increased from 550 mg/kg soil (without EDTA) to 3350 mg/kg soil, in sample contained EDTA[11]. Yet, there are many different ideas about the influence of chelating compounds such as EDTA and DTPA on Pb mobility and uptake in plants, but some scientists emphasized on positive role of this materials in availability increase of Pb[4,5,14].

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