

Leaching of Heavy Metals from Contaminated Soils using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and Atomic Absorption Spectrometer (AAS)

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Abstract: The clean-up of soils contaminated with heavy metals is one of the most difficult tasks for environmental engineering. Heavy metals are highly persistent in soil and a number of techniques have been developed that aim to remove heavy metals from contaminated soil. A method has been adopted to evaluate dynamic leaching of metal contaminants from industrial soil samples obtained from textile industrial sites in Lahore, Pakistan. In the extraction procedures employed five different leaching liquors were used: 0.01M CaCl₂, 1 M HNO₃, a 1:1 mixture of 0.1M HCl and 0.1M NaCl, 0.01M EDTA and pH controlled 0.5M acetic acid. The qualitative and quantitative analyses were carried out by Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). The results indicate that Cu, Zn, Cd, Ni, Pb, Fe and As were extracted in the soil samples in varying concentration when using the different leach liquors. The predominant metals which were leached were As 78.7ng/ml in 0.01M EDTA; Zn 1.81 µg/ml and Fe 898.96 µg/ml in HNO₃.

Keywords: Heavy metals, soil, leaching, textile, extraction

Introduction

Heavy metals continue to receive increasing attention due to the better understanding of their toxicological importance in ecosystems, agriculture and human health. Multiple studies have been conducted to characterize the metal content in different substrates such as soil^[1], air^[2], food^[3], water^[4], paints^[5,6], dust^[7] and teeth^[8].

Soils may also be contaminated by heavy metals such as zinc (Zn), cadmium (Cd), lead (Pb) and copper (Cu), due to different environmental impacts such as sludge or urban composts^[9], pesticides and fertilizers^[10], emissions from municipal waste incinerators^[11], car exhausts^[12], residues from metalliferous mining and the metal smelting industry^[13]. These, and other heavy metals, are also considered to be essential

micronutrients and are required in trace amounts for plants to complete their life cycles^[14]. However, the widespread accumulation of metals and other forms of soil pollutants is becoming one of the most critical challenges facing the environment.

Heavy metal content in soil has greater importance due to the fact that soils effectively act as a reservoir which, after temporary storage of metals, can act as a source under certain conditions. Therefore, soil is both a source and a sink for metal pollutants. The factors controlling the total and bioavailable concentrations of heavy metals in soil are of great importance for human toxicology and agricultural productivity^[15].

For understanding the chemistry of

heavy metals in their interaction with other soil components such as clay minerals, organic matter and soil solution, or to assess their mobility and retention as well as their availability to plants, the usual approach is to use selective chemical extraction^[16]. It has been shown that several soil variables other than pH, such as texture, organic matter and clay contents, cation exchange capacity and redox potential may influence the behaviour and availability of heavy metals^[17].

Many approaches based on desorption or adsorption phenomena have been designed to carry out metal determinations^[18], but extraction procedures are the most widely accepted and utilised method in soil science. These procedures, using a single extractant, provide a relative empirical method for evaluating the potential availability of soil pollutants for plant uptake. Moreover, they are also well-established procedures for the evaluation of soil chemical fertility and nutrient deficiency^[19].

The increasing improvement for element determination in an extract, together with the evidence that exchangeable metals correlate better with plant uptake, has led to the development of single extraction methods which use less aggressive solutions^[20].

Limited work has been done to determine the rates of extraction, and the factors which influence the rate^[21]. This is important since extraction efficiency depends on many factors such as the lability of heavy metals in soil, the strength of leachates, electrolytes, pH and soil matrix^[22].

One test which has been developed to characterize the suitability of solid wastes for disposal in land fills and to

characterize the hazardous nature of wastes is the Toxicity Characteristic Leaching Procedure (TCLP)^[23]. However, the use of chelating agents to wash metal contaminated soil is increasing. An ideal complexing agent to mobilize metals is one that is soluble in water, chemically stable under environmental conditions, not strongly bound to soil particles, and has a high affinity for complexing metals with the additive property of removing Pb, Zn, Cu and Cd from polluted soils. One such complexing agent is EDTA^[24].

Mild extractants such as CaCl_2 show low leaching capacities whereas acetic acid (CH_3COOH) and complexing agents such as EDTA are more effective than these mild extractants in remobilising trace metals from soils. In soils, mild extractants are frequently used as indicative of soil-to-plant transfer in a given soil and for certain plant conditions^[25].

The main problem in the use of single extraction methods lies in the lack of uniformity in the different procedures used. In consequence, the results obtained are operationally defined depending on the experimental conditions used, such as the chemical nature and concentration of extractants, soil mass, volume ratio, contact time and speed of agitation. These parameters cause adversities in data comparison and prevent the standardization of these methods^[26].

In the present work soil samples were studied for heavy metal content by extraction using 5 different leachates. In the present investigation we report the degree of similarity, exchangeability and retention of heavy metals in the soil samples by the following leach liquors: 0.5N CH_3COOH , concentrated HNO_3 , 0.01M EDTA, 0.01M CaCl_2 and 0.1M

HCl/0.1M NaCl. The results indicate an overview and comparison of the information derived from the application of the extraction tests used.

EXPERIMENTAL

Sampling

Five soil samples of 500g weight were collected from the same site of a predominantly occupied textile industrial area in Lahore, Pakistan. Contamination of the soil was evident due to contributing factors such as geology, mining activities and pollution by wastewater resulting in different toxicological effects of the environment. The samples were air-dried, hand ground with a pestal and mortar and passed through a 2mm sieve of aluminium foil. Gravel, stones and plant fragments were discarded to obtain a homogenous sample. The samples were then air-dried, crushed and sieved to ensure a homogenous sample. All reagents used for this study were of analytical reagent grade.

Material and Method

The pH-meter used in the study consisted of combined electrodes: a glass indicator electrode and a calomel reference electrode.

The shaker used to carry out the experiments was Model: GFL 3033.

For analysis Atomic Absorption Spectrometer (AAS) model: AAS-GBC 932 PLUS provided with a hydride generator GBC HG 3000 was used.

In addition to this an Inductively Coupled Plasma-Optical Emission Spectrometer was used, Model: ARL-3580.

The extraction of heavy metals from the sample was carried out by the following leach liquors: EDTA ($\text{Na}_2\text{H}_2\text{Y}$), CaCl_2 , HNO_3 , CH_3COOH and HCl/NaCl over a range of pH values. All samples were

oven dried at 35.5°C except for the sample used in the acetic acid extraction. After extraction the solutions were filtered using Whatman filter paper of 0.45 mm pore size, to obtain a clear liquid for analysis of the extracted heavy metals. Table 1 shows the different leaching conditions.

Sample preparation in 0.01M EDTA

100ml of distilled water was added to 20g of the soil sample in a 250 ml conical flask. The mixture was then covered with aluminium foil and agitated at a speed of 105 rpm for 1 hour at 20°C . The soil suspension was centrifuged for 15 minutes and the supernatant was decanted. After filtration the sample was extracted with 100 ml of 0.01 M EDTA using a shaker for 16 hours. The sample was then centrifuged for 15 minutes and filtered after which the filtrate was ready for analysis.

Sample preparation in 0.01M CaCl_2

250ml of 0.01M CaCl_2 was added to 25 grams of the soil sample. The mixture was agitated at 105 rpm for 2 hours at 20°C and the pH was measured. After shaking the mixture and the soil suspension was centrifuged. The volume of the filtrate was raised to 250 ml by adding distilled water and then analyzed.

Sample preparation in conc. HNO_3

15 ml of 1M HNO_3 was added to 15 g of oven dried soil sample after which 30ml of distilled water was added to the mixture. The solution was left covered for 24 hours after which distilled water was added to the sample to increase the volume by weight to 150g. The sample was centrifuged and then filtered.

Sample preparation in 0.1M HCl/NaCl

250ml of 0.1M HCl/NaCl was added to 1.5 grams of the soil sample. The mixture was covered and agitated at 105 rpm for 1

hour at 20°C. The soil suspension was centrifuged and filtered. The volume of the filtrate was raised to 250 ml by adding distilled water ready for analysis.

Sample preparation in 0.5M CH₃COOH

400 ml of distilled water was added to 25 grams of equivalent weight of un-dried soil sample in a cylindrical bottle. The mixture was agitated at 105 rpm for 15 minutes at 20°C and the pH was noted. A sufficient volume of 0.5M acetic acid was then added to the solution to raise the pH between 5.0 ± 0.2. Continuous stirring of the sample was necessary during addition of acetic acid and pH measurement. The solution was then agitated for a further 24 hours with pH adjustments at 2hr, 6hr and 24hr. Once the extraction period was complete, the volume of the solution was raised to 500ml by adding distilled water and the final pH of the solution was noted. The sample was centrifuged and filtered and the filtrate retained for analysis.

Results and Discussion

Analysis of the extracted filtrates by Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) showed the presence of the following heavy metals: zinc, cadmium, copper, iron, nickel and lead. In addition to this Atomic Absorption Spectrometer (AAS) was used to analyze the concentration of arsenic in the samples. The concentrations (µg/ml) of heavy metals leached using ICP-OES are presented in Table 2 and the concentration (ng/ml) of arsenic leached using AAS is presented in Table 3.

The different extractions were performed via chelation with 0.01M EDTA; 0.01M CaCl₂; 0.1M HCl/NaCl; concentrated HNO₃ and 0.5M TCLP (CH₃COOH) to predict the mobility of the metal content in the soils of the sample zone as well as

to determine the potency for the decampment of heavy metals.

Zinc, also known as spelter, was detected in the range of (0.02 – 0.69) µg/ml using saline mixture, acetic acid and EDTA extraction methods. It was found to be in undetectable limits in the CaCl₂ extraction with a maximum amount of Zn (1.81 µg/ml) being leached in nitric acid. Although Zn is an essential requirement for good health, excessive amounts can result in suppression of iron and copper absorption. The free zinc ion in solution can also be harmful and highly toxic to plants and invertebrates.

Cadmium, which is considered to be a potential environmental hazard, was detected at 0.43 µg/ml in HNO₃ and 0.05 µg/ml in EDTA whereas it was not in detectable limits in CaCl₂, HCl / NaCl and CH₃COOH. The higher concentration of cadmium leached in the HNO₃ extractant can be attributed to the formation of the Cd(NO₃)₂ formed by the dissolution of cadmium in this acidic medium.

Iron has been extracted in appreciable amounts (µg/ml) of 898.86, 6.80, 1.16 in HNO₃, EDTA and HCl/NaCl respectively. In CaCl₂ and CH₃COOH the level of iron extracted was 0.07 and 0.54 µg/ml. Iron is essential to almost every living thing for various reasons. Its ferrous iron form is essential to plant growth because it is essential in the production of chlorophyll, which in turn is significant because it is necessary for photosynthesis. However, the most plentiful form of iron in the soil is ferric iron, and ferric iron compounds cannot be absorbed by the roots. The pH of soil determines which form of iron is present, with ferrous iron available in acidic soil and ferric iron available in basic soils. The data obtained by ICP-OES shows a relatively high concentration of iron

content with the use of nitric acid. Nickel was detected only in HNO₃ and EDTA extractants. Most of the nickel released into the environment ends up in soil or sediment where it strongly attaches to particles containing iron or manganese. Under acidic conditions, nickel is more mobile in soils and is likely to seep into groundwater. Lead was also extracted in only the HNO₃ and EDTA extractants at concentrations of 1.66 and 0.59 (µg/ml).

As the concentration of arsenic was lowered, analysis was carried out by

AAS with the addition of a hydride generator to convert arsenic metal in the solution to the gaseous arsenic hydride. With this technique arsenic analysis was improved by 100%. Arsenic was extracted at 78.7 ng/ml (Fig.1) with the EDTA extraction procedure indicating that lack of charge on the As(III) species implies less potential for charge dependent associations with solid phases, such as clay minerals and oxyhydroxides in soils. A generalization made from this indicates that As (V) species are less mobile than As (III) species in many environmental systems.

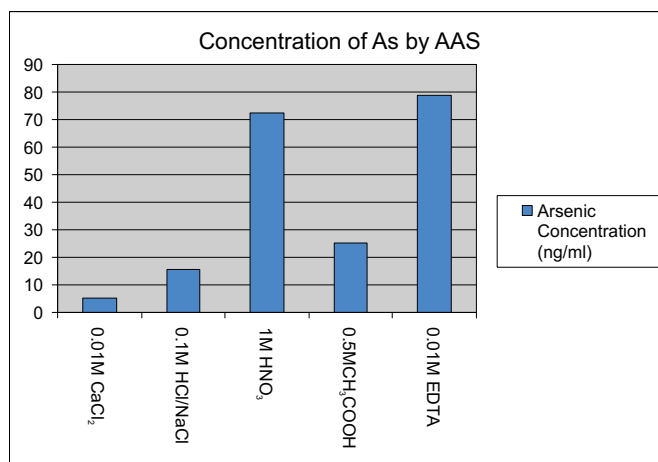


Fig. 1 Concentration of As by AAS.

Conclusion

Chemical analysis of the soils collected from the sample industrial area shows that the soil is polluted with the heavy metals Zn, Cd, Cu, Ni, Fe, Pb and As in varying concentrations. These heavy metals have accumulated in varying concentrations in some soils due to the prolonged hazardous impact of the environment. It is feasible to extract heavy metals using different leach liquors from soils and to determine their bioavailability by an extraction procedure which allows for prediction of toxic levels of heavy metals in soils.

Among the five leach liquors used nitric acid was found to be the most aggressive

extractant in the leaching of heavy metal content. EDTA also showed good extractive efficiency, with classic complexation reaction of the different heavy metal cations.

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