



## EVALUATION OF CHELATING AGENTS FOR THE REMOVAL OF HEAVY METALS FROM CONTAMINATED SOIL

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### ABSTRACT

This work examines heavy metal mobilization from soil collected from a foundry site. Single and combined solutions of chelating agents were investigated at selected liquid /solid ratio. Soil samples were shaken with the different chelating agents and the metal desorbed was quantified using FAAS (Perkin Elmer Analyst 200). Chromium desorbed more easily when the concentration of ammonium citrate was 1.0 M. cadmium removal was enhanced when 1 % SDS was added to the extracting solution. At strong acidic conditions, ammonium citrate desorbed Mn, Ni and Cr more readily while sodium EDTA and ammonium oxalate were observed to desorb all the metals under mild acidic conditions. The recoveries of Ni, Cr, Cd, Mn and Pb were 88.2 %, 96.1%, 85.0 %, 82.0 % and 73.5 % respectively.

**KEYWORDS:** Chelating agents, contaminated soil, heavy metals, desorption.

### INTRODUCTION

Soil pollution can be described as the contamination of soil of a particular region. It is as a result of penetration of harmful pesticides and insecticides, or other chemicals from industries, spillage from oil pipes which brings about deterioration in soil quality, thus making it unfit for use. The emissions of heavy metals from floating, smelting, sterile stockpiles and a host of others determine the topsoil loading with chemicals which considerably exceeded the maximum limit, as in 100 mg/kg for Pb and Cu, 3 mg/kg for Cd, <sup>[1]</sup>. Background soil trace element levels are typically below the threshold for adverse health and environmental effects. However, elevated concentrations arise from burning of fossil fuels, mining, smelting, agricultural operations, industrial activities, and waste disposal practices. Biogeochemical mobilization of these elements can contaminate drinking water supplies or result in uptake by vegetation, leaching processes and potential food chain impacts. For many years, chelating agents and organic acids have been employed for analytical purposes to displace metals from soils and sediments <sup>[2]</sup>. Organic ligands with amino and carboxylic functional groups are most often reported as potential metal extracting reagents. Strength of metal complexation, reuse potential, toxicity, biodegradability, and cost are some of the factors dictating reagent selection. A number of process schemes exist for extracting metals from contaminated soils <sup>[3]</sup>, but operating details are guarded for proprietary reasons. Conditions for optimal soil washing are also surprisingly scarce in the literature.

Leaching heavy metals from the polluted soil using an acid or a chelating agent is the most appealing because it generally creates less surface damage, requires a minimal amount of facilities and reduces the potential for human exposure. Soil contaminants can have significant deleterious consequences for the ecosystem. There are radical soil chemistry changes which can arise from the Presence of many hazardous chemicals even at low

concentration of the contaminant species. These changes can manifest in the alteration of metabolism of endemic microorganisms and arthropods resident in a given soil environment. The result can be virtual eradication of some of the primary food chain, which in turn have major consequences for predator or consumer species. Even if the chemical effect on lower life forms is small, the lower pyramid levels of the food chain may ingest alien chemicals, which normally become more concentrated for each consuming rung of the food chain. Many of these effects are now well known, such as the concentration of persistent DDT materials for avian consumers, leading to weakening of egg shells, increased chick mortality and potential extinction of species. <sup>[4]</sup>

Contaminants typically alter plant metabolism, most commonly to reduce crop yields. This has a secondary effect upon soil conservation, since the languishing crops cannot shield the Earth's soil mantle from erosion phenomena. Some of these chemical contaminants have long half-lives and in other cases derivative chemicals are formed from decay of primary soil contaminants. Metal removal efficiency by the chemical extraction process depends on the soil geochemistry (e.g., soil texture, cation exchange capacity, buffering capacity, and organic matter content); metal contamination characteristics (type, concentration, fractionation, and speciation of metals); dosage and chemistry of extracting agent; and processing conditions (solution pH, residence time, number of successive extraction steps, mode of reagent addition, liquid/solid ratio, among others). The partitioning of metals according to their association with the soil substrates is usually determined by the sequential extraction procedure <sup>[5]</sup>.

The fractions most amenable to metal removal by chemical leaching are: (1) exchangeable; (2) associated with carbonates; and (3) associated with reducible Fe–Mn oxides of soils <sup>[6]</sup>. However, extraction of metal bound to exchangeable and carbonate fractions was faster compared

to extraction of metal bound to Fe–Mn oxides [7]. Organically bound metals can be extracted along with the target organic contaminants by the solvent extraction method. The removal efficiency of metals from the distinct fractions depends on the extracting reagents used. For instance, due to dissolution effects, certain acid leaching processes may partially remove metals from the crystalline lattice [8].

Removal efficiency often depends on the metal type to be extracted and the valence of the element. Generally, the extractability of most cationic heavy metals (e.g., Cd, Cu, Pb, and Zn) increases when the solution pH decreases. At low pH, adsorption on to soil of the cationic heavy metals decreases and the dissolution of metal compounds increases. On the other hand, the solubility of oxy-anions of the metalloid As increases when the solution pH increases while the adsorption of chromium Cr(VI) species is enhanced at low pH [9]. Hence, the simultaneous treatment of both anionic and cationic metal species that has dissimilar chemical behavior in aqueous solution can be ineffective.

If metal is not under an adsorbed form, the removal efficiency depends on solubility of metal compounds in the washing fluid, which are governed by the solubility product (K<sub>sp.</sub>) values. The treatment of particulate forms of metals is more difficult to achieve compared to the adsorbed ionic forms. Factors that may limit the applicability and effectiveness of the chemical process include: (1) high clay/silt content; (2) high humic content; (3) high content of Fe and Ca element; (4) high calcite content or high buffering capacity; (5) simultaneous contamination of both cationic or anionic heavy metals; (6) high heterogeneity of soil; and (7) metals associated with residual soil fraction, imbedded in the mineral lattices, or discrete particle forms. The fine-grained soils may require longer contact times and may reduce chemical extraction efficiency [10,11]. The corresponding cations of major element Fe and Ca may interfere with chelating process. High calcite content or high buffering capacity may decrease the acid leaching efficiency [12, 13]. High heterogeneity of soils can affect formulations of extracting fluid and may require multiple process steps.

Conditions for optimal soil washing are surprisingly scarce in the literature. Therefore, this study investigates combination of the selected chelating agents and organic acids as reagents for metal removal from contaminated soils. It ascertains the extraction efficiency of three chelating agents: Na<sub>2</sub>-EDTA, ammonium oxalate and ammonium citrate as washing solutions for the removal of heavy metals from contaminated soil.

## MATERIALS AND METHODS

### Reagents

Reagents used were obtained from the Chemical Store, Chemistry Department of the University of Lagos. Some were also obtained from Finlab, Anthony Village, Lagos, and Mato Chemical Stores, Jibowu. All reagents used are of analytical grade. Atomic Absorption Spectrophotometer Perkin Model A Analyst 200 was used. All glasswares used in this study were pre-washed with 14% HNO<sub>3</sub> and rinsed with distilled water, drained and oven dried at a regulated temperature for 30 minutes.

**Sampling** Soil samples were collected at a foundry site at Ikeja, located close to Lagos State Teaching Hospital, Ikeja, Lagos. The soil was sampled within a depth of 20 cm using a stainless steel scoop. Sampled soil was allowed to air-dry for two weeks, ground and sieved through a 2-mm stainless steel mesh to remove large stones and debris to obtain soil sample with particles less than 2mm. The soil was thoroughly mixed in order to obtain a representative sample and was stored at room temperature (25°C) in the laboratory for further analysis.

### Acid Digestion

The potentially bioavailable lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr) and manganese (Mn) in the soils were extracted by acid digestion using aqua regia (hydrochloric acid (HCl):nitric acid (HNO<sub>3</sub>); 3:1) according to method 3050B (USEPA, 1994) [14]. A 200 ml portion of aqua regia was added to 10 g of sample in Kjeldahl flask and the contents digested on a hotplate for 2 hours.

Following cooling, 5 ml of 65% HNO<sub>3</sub> (dilute) and 2.5 ml of 30% H<sub>2</sub>O<sub>2</sub> were slowly added to prevent foaming and were subsequently kept for 48 hours at room temperature. Thereafter, the solution mixture was made up to 500 ml with distilled water after filtration. After filtration, five heavy metals; Cd, Pb, Cr, Mn and Ni were determined using Flame Atomic Absorption Spectrophotometer (FAAS).

### The Extraction Procedure

Single and mixed solution/ soil washing experiments were performed on 1.0 g portions of the soil placed in conical flasks. Different volumes of (i) 0.1 M and 0.2 M Na<sub>2</sub>EDTA, (2) 0.5 M and 1.0 M ammonium citrate and (3) 0.1 M and 0.5 M ammonium oxalate maintained at different pH values in the single reagent washing were employed according to the procedure reported by Khodadoust et al [15]. Slight modification using a soil to solvent ratio of 1:40 (1g of the soil to 40 ml of the extracting solution) was employed in a 250 ml conical flask. The contents of the flask were covered with a Teflon cork for 48 hours. Each flask was, thereafter, shaken on a mechanical shaker for two hours. The resulting soil – solution mixture was filtered (made up to 50ml) and analyzed for the concentration of Cr, Mn, Ni, Pb and Cd using FAAS. In the mixed reagent washing approach, 1g portion of the soil sample was treated with the most effective reagent identified in the single extraction approach. For instance, 1.0 M citrate, 0.5 M oxalate and 0.2 M Na<sub>2</sub>-EDTA were mixed in the ratios of 1:1:2, 1:2:1 and 2:1:1. Subsequent treatment was as described for the single extraction. A solution of 1% SDS was added at different times to some of the mixed washing solutions to enhance desorption.

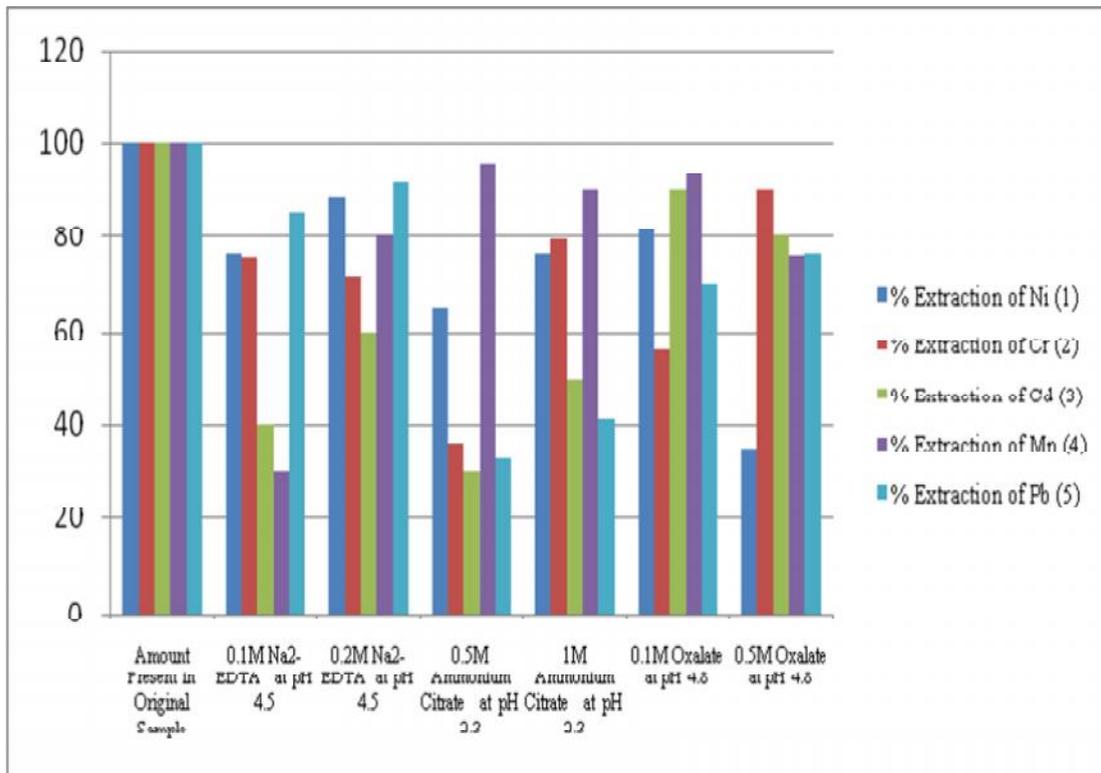
## RESULTS AND DISCUSSION

The results of the analysis / investigations are presented in Tables 1 and graphically illustrated in figures a – b. The amount of heavy metals removed from the soil was measured directly from the concentration determined by the Flame Atomic Absorption Spectrophotometer. This concentration was calculated as a relative value compared to the original concentration of each of the heavy metals in the soil sample and the percentage extracted calculated as

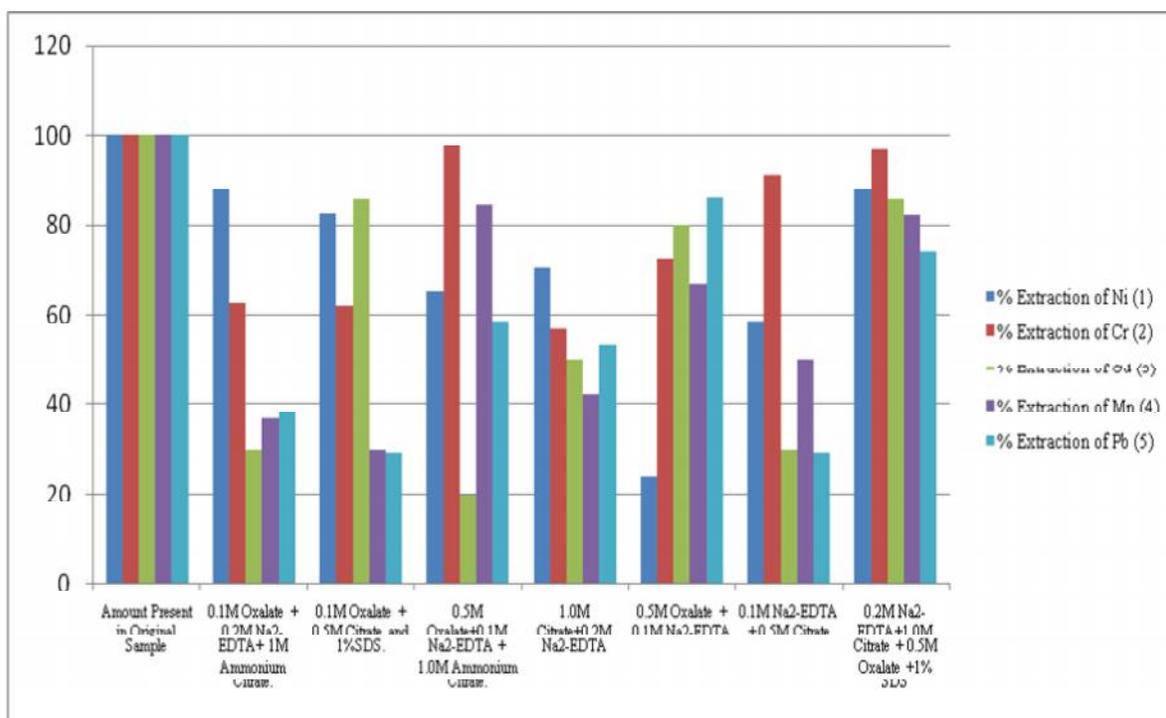
follows: **Percentage Recovery = Amount extracted by solution X 100 / Initial amount in soil sample.**

**TABLE 1:** Mean Concentration of Heavy Metals Determined In Soil Samples

	Single Extractant	Ni (ppm)	Cr (ppm)	Cd (ppm)	Mn (ppm)	Pb (ppm)
*	Amount Present in Soil Sample	0.017	0.485	0.01	0.05	0.034
	<b>Single Extractant</b>					
1	0.1M Na <sub>2</sub> -EDTA at pH 4.5	0.013	0.367	0.004	0.015	0.029
2	0.2M Na <sub>2</sub> -EDTA at pH 4.5	0.015	0.350	0.006	0.040	0.031
3	0.5M Ammonium Citrate at pH 2.3	0.011	0.177	0.003	0.048	0.011
4	1M Ammonium Citrate at pH 2.3	0.013	0.385	0.005	0.045	0.014
5	0.1M Oxalate at pH 4.8	0.014	0.270	0.009	0.047	0.024
6	0.5M Oxalate at pH 4.8	0.006	0.436	0.008	0.038	0.026
	<b>Mixed Extractants</b>					
1	0.1M Oxalate + 0.2M Na <sub>2</sub> -EDTA+ 1M Ammonium Citrate.	0.015	0.303	0.003	0.018	0.013
2	0.1M Oxalate + 0.5M Citrate and 1%SDS.	0.014	0.300	0.0085	0.015	0.010
3	0.5M Oxalate+0.1M Na <sub>2</sub> -EDTA + 1.0M Ammonium Citrate.	0.011	0.472	0.002	0.042	0.020
4	1.0M Citrate+0.2M Na <sub>2</sub> -EDTA	0.012	0.271	0.005	0.021	0.018
5	0.5M Oxalate + 0.1M Na <sub>2</sub> -EDTA	0.004	0.350	0.008	0.033	0.029
6	0.1M Na <sub>2</sub> -EDTA + 0.5M Citrate	0.010	0.441	0.003	0.025	0.010
7	0.2M Na <sub>2</sub> -EDTA+1.0M Citrate + 0.5M Oxalate +1% SDS	0.015	0.466	0.0085	0.041	0.025



**FIGURE A:** Percentage Recovery of the five heavy metals in soil using single washing solution.



**FIGURE B:** Percentage Recovery of the five heavy metals in soil using mixed reagent (washing solution)

When 0.1 M Na<sub>2</sub>EDTA solution at pH 4.5 was employed as the extractant, 85.29% of lead was removed from the contaminated soil. However, this solution could only remove 30% of manganese as shown in Table A1. This extractant would be effective in the removal of lead from a contaminated soil. However, when 0.2 M Na<sub>2</sub>EDTA at pH 4.5 was employed, there was considerable increase in the amount of heavy metals removed. This solution would be effective in the removal of lead, nickel and manganese from a contaminated soil. When a higher concentration of ammonium citrate was employed, there was an increase in the amount of heavy metals extracted, except for manganese where there was a decrease in extraction. This solution at a concentration of 0.5 M under a strong acidic condition is highly recommended for the removal of manganese from contaminated soil. In the use of 0.1 M ammonium oxalate as the extractant, 94% and 90% removal were observed for manganese and cadmium respectively as shown in Table 1. This solvent would not be useful for the extraction of nickel (35.29%) especially in a single treatment of contaminated soil.

The removal of nickel from the contaminated soil was highest when 0.1 M ammonium oxalate, 0.2 M Na<sub>2</sub>-EDTA and 1 M ammonium citrate when combined together. This would suggest that the washing solution mixture would be effective in the removal of nickel from any contaminated soil. The same was true when 0.1 M oxalate, 0.5 M citrate and 1% SDS were combined as extractant mixture. The removal of cadmium was 85%. This mixture would be effective in the removal of cadmium. It is not advisable to use this solution for the removal of manganese and lead since only 29% and 30% removal were observed. The mixture of 0.5 M oxalate, 0.1 M Na<sub>2</sub>EDTA and 1.0 M citrate proved to be highly effective in the removal of chromium from the contaminated foundry soil (97.32%).

The combination of 1.0 M citrate and 0.2 M Na<sub>2</sub>EDTA could only extract about 50% of the heavy metals from the soil sample as shown in figure b. When 0.5 M oxalate and 0.1 M Na<sub>2</sub>EDTA mixture was employed, the extraction of cadmium and lead was higher than others. This solution would be effective in the removal of these metals from the contaminated soil. When 0.1 M Na<sub>2</sub>EDTA and 0.5 M ammonium citrate was employed, 90.93% of chromium in the contaminated soil was extracted. This solution, though not recommended for the extraction of cadmium and lead in a single treatment would be highly effective for the removal of chromium. The removal of chromium was 96% when the mixture of 0.2 M Na<sub>2</sub>EDTA, 1.0 M citrate, 0.5 M oxalate and 1% SDS was employed. Nickel, cadmium and manganese were also removed from the contaminated soil with removal efficiency of 88.24%, 85% and 82.0% respectively. This combination would be highly effective in the removal of all the metals at an appreciated amount as shown in Table 1. The solution of 0.2 M Na<sub>2</sub>EDTA maintained at pH 4.5 extracted substantial amount of nickel. Similar observation was obtained when 0.1 M ammonium oxalate was combined with 0.2 M Na<sub>2</sub>EDTA and 1 M ammonium citrate in the ratio of 1:2:1. It was observed that the addition of SDS to the solution played only a slight significant role in the extraction process. It is not advisable to use oxalate at a high concentration and in a mild acidic medium in a single extraction for nickel. The use of 0.5 M oxalate was able to extract a considerable amount of chromium as illustrated in Figure a. However, 0.5 M ammonium oxalate combined with 0.1 M Na<sub>2</sub>EDTA and 1 M ammonium citrate, in the ratio of 2:1:1 added to 1% SDS would effectively extract chromium up to 96% in the soil sample. The use of this mixed reagent is thereby recommended for the extraction of chromium.

A 0.1 M ammonium oxalate maintained at a pH 4.8 gave most extraction efficiency for most of the metals. It is suggested that 1% SDS be added when a combination of extractants is used. In the removal of manganese, 0.5 M ammonium citrate maintained at a pH 2.3 was able to remove as much as 96% followed by 0.1 M ammonium oxalate. Na<sub>2</sub>EDTA was able to extract only 80% at a mild acidic condition. In most of the cases, it was obvious that the single extraction favoured manganese extraction as far as the work is concerned. In the washing process of lead, 0.2 M Na<sub>2</sub>EDTA at a pH of 4.5 happened to be the most effective. Its combination with co-extractants might not be necessary.

### CONCLUSION

Various washing solutions were investigated for the removal of heavy metals in contaminated soil. A 0.2 M Na<sub>2</sub>-EDTA solution maintained at a pH of 4.5 would be employed for the removal of lead; 0.5 M ammonium citrate maintained at a pH of 2.3 for the removal of manganese; 0.1 M ammonium oxalate maintained at a pH of 4.8 for the removal of cadmium; a combination of 0.5 M ammonium oxalate, 0.1 M Na<sub>2</sub>-EDTA, and 1.0 M ammonium citrate for the removal of chromium while 0.2 M Na<sub>2</sub>-EDTA maintained at a pH of 4.5 was effective in the removal of nickel in the contaminated soil. The removal of chromium was 96% when the mixture of 0.2 M Na<sub>2</sub>-EDTA, 1.0 M citrate, 0.5 M oxalate and 1% SDS was employed. Nickel, cadmium and manganese were also removed from the contaminated soil at 88.24%, 85% and 82.0% respectively using a mixture of 0.2 M Na<sub>2</sub>-EDTA, 1.0 M citrate, 0.5 M oxalate and 1% SDS. This combination would be highly effective in the removal of all the metals at an appreciable amount. The combination of Na<sub>2</sub>-EDTA, ammonium oxalate and ammonium citrate would be a good soil washing solution where various heavy metals contaminants are to be removed at once and within the shortest possible time.

### REFERENCES

- [1]. Kloke, A. and Richwerte, M. (1980). Orientation for Tolerable Elements in Soil, *Env. Pollution*, 2, 9-11.
- [2]. Bradshaw, A.D. (1993). Natural rehabilitation strategies. In: *Integrated soil and sediment research: a basis for proper protection* (H.J.P. Eijsackers and T. Hamered), pp 533-544.
- [3]. Mercier, G., Duchesne, J. and Blackburn, D. (2002). Treatment of metals from contaminated soils by mineral processing techniques followed by chemical leaching. *135 (1)* 105–130.
- [4]. Key, S.H., Scholten, M.C. Th. and Bowner, C.T. (1988). Mobility of soil contaminants in an ecosystem of tree growing on dredged material – the Broekpolder (Rotterdam, The Netherlands) TNO Rep. R88/488, TNO, Delft, The Netherlands.
- [5]. Kuo, S., Lai, M.S. and Lin, C.W. (2006). Influence of solution acidity and CaCl<sub>2</sub> concentration on the removal of heavy metals from metal-contaminated rice soils. *Envir. Pollut.* 144., 918–925.
- [6]. Finzgar, N. and Lestan, D. (2006). Heap leaching of Pb and Zn contaminated soil using ozone/UV treatment of EDTA extractants. *Chemosphere* 63 (10), 1736–1743.
- [7]. Williford, C.W. and Bricka, R.M. (2001) Physical separation of metal-contaminated soils, in: I.K. Iskandar (Ed.), *Environmental Restoration of Metals*, 78. 17-21.
- [8]. Luttrell, G.H., Westerfield, T.C., Kohmuench, J.N., Mankosa, M.J., Mikkola, K.A. and Oswald, J. (2006). Development of high-efficiency hydraulic separators: *Min. Metallur. Process.* 23 (1), 33–39.
- [9]. Lim, T.T., Tay, J.H. and Wang, J.Y. (2004). Chelating agent-enhanced heavy metal extraction from a contaminated acidic soil, *J. Environ. Eng.* 130. Pp59–66.
- [10]. Zhang, W. and Lo, L.M.C. (2006). EDTA-enhanced washing for remediation of Pb and/ or Zn-contaminated soils, *J. Environ. Eng.* 132, 1282–1288.
- [11]. Mulligan, C.N., Yong, R.N. and Gibbs, B.F. (1999). The use of biosurfactants for the removal of heavy metals from oil-contaminated soil, *Environ. Prog.* 18.50–54.
- [12]. Mulligan, C.N., Yong, R.N. and Gibbs, B.F. (1999). Metal removal from contaminated soil and sediments by the biosurfactantsurfactin, *Environ. Sci. Technol.* 33, 3812–3820.
- [13]. Tejowulan, R.S. and Hendershot, W.H. (1998). Removal of trace metals from contaminated soils using EDTA incorporating resin trapping techniques, *Environ. Pollut.* 103 (1). 135–142.
- [14]. USEPA, A Literature Review Summary of Metals Extraction Processes Used to Remove Lead from Soils, Project Summary, EPA/600/SR-94/006, Office of Research and Development, Cincinnati, OH, 1994.
- [15]. Khodadoust, L., Amid P., George A., Wilson, G. J., Suidan, M. T., Griffiths, A., and Brenner, C. (1999) Integrated system for remediation of contaminated soils, *Jour of Envir.Eng.* 125, 11, 45.