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Removal of Copper Ions from Contaminated Soil by Enhanced Soil Washing

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ABSTRACT: This study investigated the feasibility of using different extracting solutions at various concentrations to remove copper from low permeability silty loam soils, which have a high buffering soil, pH of 7.6, where it spiked with copper at concentration of about 1500 mg/kg to represent soil conditions. The most efficient extracting solutions could be used as purging/extracting solutions in other technologies such as soil washing. Several batch tests were conducted to be optimizing the various parameters like stirring speed, mixing time, surfactant-chelating agent concentration, and the liquid/solid ratio (L/S). The following extracting solutions were investigated for the removal of copper from the soils: distilled water, chelating agents (EDTA ethylenediaminetetraacetic acid), and surfactant (SDS, sodium dodecyl sulphate). The metal removal efficiency was found to be dependent on EDTA concentration at case used alone, with the increasing of EDTA concentration, the removal of Cu^{+2} increased and peaking at approximately 42.4% with increasing of EDTA concentration to 0.1M. The addition of 0.6% SDS retarded copper removal by EDTA, therefor, the removal become approximately 32 %, as compared when EDTA was applied alone.

Key words: Remediation of contaminated soils, Washing Soil, Copper Ions

INTRODUCTION

Recently, it has been reported that soil, contamination by heavy metals is increasing in various sites including residential areas near industrial complexes and reservoirs of drinking water. That has an enormous impact on the quality of ground water, soil and associated ecosystems. However, the solubility and extent of these contaminants in the subsurface system is influenced by the chemistry of the soil and groundwater. Factors such as pH, redox potential (Eh), cation exchange capacity (CEC), and complexation/ chelation with organic matter directly effect on the metal solubility (Evanko, and Dzombak, 1997; Kim et al., 2003; Saeedi *et al.*, 2009).

Remediation techniques include: (i) ex-situ (excavation) or in-situ (on-site) soil washing/leaching/ flushing with chemical agents, (ii) chemical immobilization/stabilization method to reduce the solubility of heavy metals by adding some non-toxic materials into the soils, (iii) electro kinetics (electro migration), (iv) covering the original polluted soil surface with clean soils, (v) dilution method (mixing polluted soils with surface and subsurface clean soils to reduce the concentration of heavy metals), (vi) phytoremediation by plants such as woody trees (Wuana *et al.*, 2010).

There are two fundamental technologies to remediate heavy metal contaminated soils. The first technology immobilizes heavy metals tightly bound solid matrix to minimize migration, another technology is to promote heavy metals. Mobility and migration to the liquid phase by desorption and solubilization in a washing solution (Zhan *et al.*, 2012). The use of diluted acids can dissolve soil matrix and damage soil physiochemical and biological properties. Chelating agents such as ethylenediaminetetraaceticacid (EDTA) and diethylenetrinitrilo pentaacetic acid (DTPA) have proven effective in removing metals from soils. Their biotoxicity, biorecalcitrance, and problems with recovery of heavy metals and extracting agents from supernatant severely limit their applications (Chang *et al.*, 2005).

A surfactant (SDS, sodium dodecyl sulphate) works as a remediation tool by lowering the contaminant water interfacial tension and thereby causing a degree of contaminant mobility, and enhanced contaminant solubility in water. The

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surfactant molecule is typically composed of a strongly hydrophilic (polar, water-loving) group, or moiety and a strongly hydrophobic (a polar, water fearing) moiety. The entire surfactant monomer is often referred to as amphiphilic (both loving) because the polar group has a large affinity for polar solvents, such as water, whereas nonpolar group has a great affinity for non-polar or hydrophobic solvents, which include most organic contaminants. The hydrophilic ‘head’ group often includes anions or cations such as sodium, chloride, or bromide. Hydrophobic portions or ‘tails’ are usually hydrocarbon chains typically containing 12 or more carbon atoms (Gupta et al., 2010). Surfactants at low concentrations exist as monomers and adsorb onto surfaces and interfaces. When surfactant concentrations increase above a certain level (i.e. critical micelle concentration, CMC), the monomers aggregate to form micelles, which have a hydrophobic interior and a hydrophilic exterior. Although anionic surfactants could increase heavy metal removal from soil, they are much less effective compared to chelating agents. The information on interactions of chelating agents and surfactants on soil metal removal is scarce (Chang et al., 2005). Therefore, soil washing is useful for treatment of soils contaminated with heavy metals, hydrocarbons but it is less effective for volatile organic compounds (VOCs), and pesticides. Accordingly, the significant aspects of the present study are: (1) investigation of the potential application of DW (Distilled water), SDS and/or $Na_2EDTA.2H_2O$ as washing solutions for the extracting of copper from contaminated clayey soil; and (2) determining the effect of carbonate on the extraction process.

MATERIALS & METHODS

Soil samples: Natural soil samples were obtained from local site in Hilla, a city located in the middle part of Iraq. The soil samples were taken from a depth ranged from 30 cm to 50 cm below the ground surface. It was cleaned, dried and well sorted with an additional sieving into 10 mm mesh to achieve satisfactory uniformity. The physicochemical properties of soil samples are illustrated in Table 1. The proper characterization and preparation of the soil samples was important in order to ensure high accuracy and precision in the experimental procedure adopted in this study.

Soil Contamination Procedure: To simulate the soil copper contamination, a solution of $CuSO_4$ (manufactured by SEELZE-HANNOVER, Germany) was prepared and added to the specimen to obtain representative concentration. $CuSO_4.5H_2O$ has a molecular weight of 249.68 g/mol and atomic weight of copper ions is 63.54 g/mol. To prepare a soil sample with copper concentration of 1500 mg/kg and initial moisture content equal to 40% by weight, 4.421 g of $CuSO_4.5H_2O$ dissolves in 300 ml of deionized water and this solution was added to 1 kg of dry soil. To determine total copper content different particle size soil samples were extracted by acid digestion ($HCl + HNO_3 + H_2O_2$) (Haswell, 1991).

Soil Washing Procedure: Surfactants and chelating agents such as SDS (>90% purity, Sigma, USA), and $Na_2EDTA.2H_2O$ (100% purity, Tedia, USA) (Table 2). Four sets of experiments were conducted to examine the effect of four influencing factors on copper removal with Na_2EDTA or SDS. The four factors were tested in the order of: (1) stirring speed (30, 110, and 160) were chosen, (2) mixing time experiment (90, 180, and 270 min) were chosen, (3) surfactant-chelating agent concentration, different concentrations 0.1, 0.01, and 0.001 M of Na_2EDTA, and 3, 0.6, 0.06, and 0.006% of surfactants (SDS) were chosen, (4) The liquid/solid

Table 1. Physicochemical characteristics of the soil samples used in the study.

Property	Value
Mineralogy	
Calcite ($CaCO_3$) : high value; Quartz (SiO_2): high value;	
Anorthite ($CaAl_2Si_2O_8$): high value; Kaolinite ($Al_2Si_2O_5(OH)_4$):	
low value; Nussovite ($KAl_2Si_3O_{10}(OH)_2$): low value	
Particle size distribution (ASTM D422)	
Sand (%): 4.7; Silt (%): 68 ; Clay(%): 27.3	
Atterberg limits (ASTMD 2487)	
Liquid limit (%): 38.9; Plastic limit (%): 25.05; Plastic index (%): 13.85	
Coefficient of permeability (cm/s)	$1.2 * 10^{-6}$
Cation exchange capacity (meq/100 g)	17.16
Surface area (m^2/g)	36.008
pH	7.6
Organic content (%) (ASTMD 2974)	0.24
Electrical conductivity EC (µS/cm)	2868
Porosity (*n*)	0.496
$CaCO_3$ (%)	26.41
Bulk density (g/cm^3)	1.37
Specific weight	2.75
Soil classification	Silty Loam

Table 2. Properties of surfactants and chelating agent used in this study (Chang *et al.*, 2005).

Type		Chemical formula	MW	CMC mM (mg L^{-1})
SDS	**Anionic surfactant**	$C_{12}H_{25}OSO_2ONa$	288	8.4 (2420)[2]
EDTA-Na_2	**Chelating agent**	$C_{10}H_{12}N_2Na_2O_8 . 2H_2O$	372.2	NA [3]

[2]Deshpande *et al*., 1999; [3]Chelating agent, NA = not applicable.

ratio (L/S) investigations were conducted by 20, 40, and 100 ml of surfactant-chelating agent, giving liquid/solid ratios of 4, 8, and 20 respectively. When each of the factors was tested at different values or modes, the other three kept constant. The value generating the best removal was liquid/solid ratio (L/S), stirring speed, mixing time, and surfactant-chelating agent concentration as follows: 8:1, 110 (rpm), 3 hrs., 3% SDS, and 0.1 M of Na_2EDTA respectively, which adapted in the following test. To prepare the different extractants, first, two-fold desired concentrations of surfactant (or chelating agent) were prepared with distilled water. To prepare the desired surfactant-alone (or chelating alone) solution, the 20 ml of surfactant solution was mixed with 20 ml of distilled water. To obtain desired surfactant-chelating agent solution, 20 ml of 3, 0.6, 0.06, and 0.006 % of surfactants (SDS, sodium dodecyl sulphate) and 20 ml of 0.1, 0.01, and 0.001 M $Na_2EDTA.2H_2O$ were mixed solution, the tests of extraction were conducted according to procedure reported by Chang et al. (2005). Then after that, the suspensions were centrifuged at 3000 rpm for 10-15 min and the liquid was separated from the solid particles through filtration with paper No. 42. The copper concentration was determined by atomic absorption spectrophotometer (AAS). Finally, the removal of each contaminant was calculated using the following equation (Reddy, and Chinthamreddy, 2000):

Contaminant Removal (%)=

$$\frac{\text{Contaminant Mass in Superntant } (C_L V_L)}{\text{Initial Contaminant Mass in Soil } (C_s M_s)} * 100 \quad (1)$$

Where C_L and C_L are the concentrations of contaminant in supernatant (in mg/L) and soil (in mg/kg), respectively, V_L is the volume of supernatant (in L), and M_L is the dry mass of the soil (in kg).

RESULTS & DISCUSSION

Kinetics of copper Extraction: In order to comprehend the washing process and determine the optimum condition that gives best removal was adapted in the following test as stirring speed, mixing time, surfactant-chelating agent concentration, and liquid to solid ratio (L/S).

Different stirring speed (rpm) 30, 110, and 160 were used, under conditions of concentration surfactant and chelating agent as 3% and 0.1 M respectively, S/L was equal to 1:8, mixing time was 3 hrs., extraction results shown in Fig. 1. As the stirring speed increases the extraction of heavy metal from soil also increases. Therefore, removal efficiency varies from 0.02-0.12% for SDS, while from 30-42.4% for Na_2EDTA.

liquids to solids ratio (L/S) is an important parameter in soil washing, higher L/S indicates greater capacity of solubilization (Peng and Chen, 2011), a tests of extraction were conducted maintaining conditions as follows: concentrations of Na_2 EDTA and SDS at 0.1 M, and 3%, respectively, mixing time was 3hrs., speed of stirring (rpm) was 110. The results shown in fig. 2. Increasing the liquid/solid ratio had a positive effect on the extraction of heavy metals. Mohanty and Mahindrakar (2011) showed that with the same concentration i.e. 0.01 M increasing the liquid/solid ratio means Na_2EDTA dose

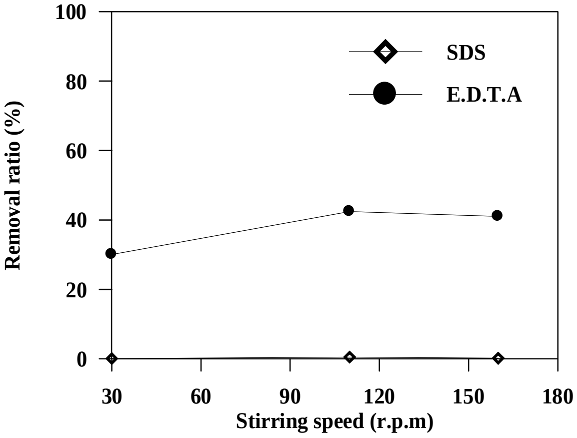

Fig. 1. Effect of stirring speed (rpm) on removal of Copper.

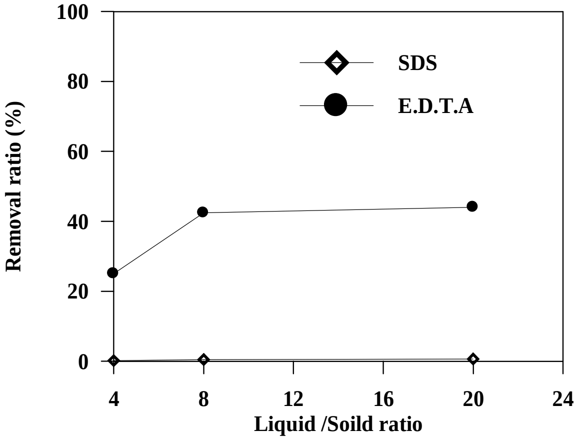

Fig. 2. Effect of liquid/solid ratio (L/S) on removal of Copper.

Table 3. Removal of Copper from clay soil using chelating agents and surfactants concentration.

Parameter	chelating agents concentration (Na_2 EDTA)			surfactants concentration (SDS)			
	0.1 M	0.01 M	0.001 M	3%	0.6%	0.06%	0.006%
Cu^{+2} removal (%)	42.4	34	11	1.5	0.75	0.71	0.21

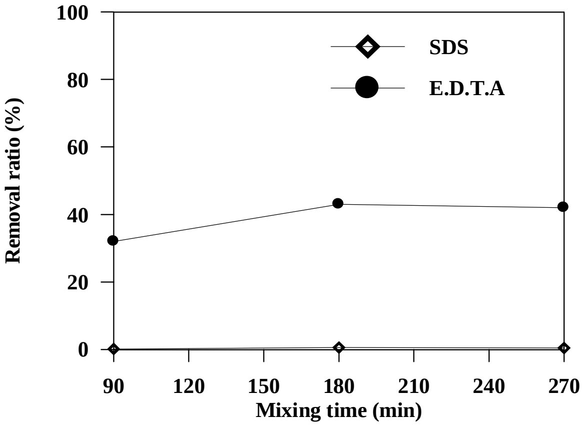

Fig. 3. Effect of mixing time (min.) on removal of Copper.

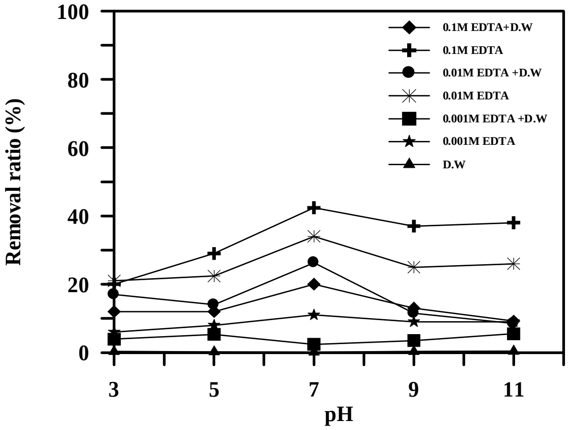

Fig. 4. The effect of different pH on removal efficiencies of copper with distilled water (DW), and Na_2EDTA mixture washing solutions.

is increased. It seems that when increasing the Na_2EDTA dose, only a small portion was effectively transformed into metal-chelant complexes, while the excess remained in free from or might form complexes with other cations like Ca, Mg, Fe, and Al etc. In this study the maximum removal efficiency shown at liquid/solid ratio of 8 for both Na_2EDTA and SDS. The removal efficiency was 42.4% for Na_2EDTA and 0.45% for SDS. Therefore, L/S ratio of 8:1 can be taken as the optimal in this case. Extraction time plays a very important role in soil washing. In order to comprehend the washing process and determine the optimum contact time for contaminants removal (Mohanty, and Mahindrakar, 2011). In this test was carried on with stirring speed and L/S of 110 rpm 8:1 as the optimal value determined in above steps (Stirring speed and Effect of Liquid/Solid Ratio (L/S)**)**, with concentration of Na_2 EDTA and SDS at 0.1 M, and 3% , respectively. It can be seen from Fig. 3, which close to 39% removal ratio was achieved at mixing time of 90 min., while close to 43% removal ratio was achieved at mixing time of 180 min. Further above mixing time of 180 min., leads to decrease of removal ratio.

Table 3 shows the copper removal from silty loam soil using Na_2 EDTA and SDS at different concentrations. Chelating agents modify metal concentrations in soil solution by forming various soluble complexes, thus enhancing metal removal (Reddy, and Chinthamreddy, 2000). While, Anionic surfactant SDS was chosen for soil washing since it is biodegradable and the degree of its adsorption on the soil surface is very low. The removal of copper (Cu^{+2}) increased from 11 to 42.4%, with increased Na_2EDTA concentration. Similar results were observed by Peters et al. (1996) on a field-contaminated soil, as cited by Reddy, and Chinthamreddy (2000). While, the removal of considered contaminants was not affected by the activity of the surfactant (SDS).

Solution pH is another important factor determining the efficiency of soil washing. Because it can influence the soils retention of metals by adsorption. In this studying was investigated for using different concentrations of chelating agent (Na_2EDTA) on removal of copper within range of pH from 3 to 11. As shown in fig. 4, when the pH of 0.001 M Na_2EDTA solution is below 7, the removal efficiency was found to be for range 6-8%, and then slowly increased to 11% at pH was equal to 7. Thereafter, the removal efficiency decreased. For this, during the extraction Na_2EDTA can form stable and soluble complexes with heavy metals thus greatly improving the solubility and mobility of Na_2EDTA, making the precipitate become soluble and react with heavy metals (Mohanty and Mahindrakar, 2011). Therefore, the removal efficiency of 0.1 M Na_2EDTA was 42.4% shown in fig. 4, which depended on soil solution pH. For copper highest removal efficiency was at pH 7. Whereas the addition of distilled water to Na_2EDTA at different concentrations was decreased removal of copper. The removal of heavy metals increased with increased EDTA concentration. These results show that even though pH is relatively high, a significant increase in metal removal when compared with removal using water was achieved. This is mainly attributed to the formation of soluble complexes of heavy metals with EDTA. Where heavy metals form complexes with EDTA preferably over OH^- (Stumm and Morgan, 1996) as cited by (Reddy and Chinthamreddy,

Table 4. Experimental program that explained relation between reduction of pH and carbonate content

Parameter	Experiments	
	E-1	E-2
Initial soil pH	7.6	4.7
$CaCO_3$ (%)	26.41	11

2000). It seems in case mixing EDTA with distilled water as shown in fig. 4, desorption decreases dramatically as solution pH increased. It is possible for the presence of complexing ligands to interfere with this relationship (Jiang et al., 2011). The removal efficiency of 3% SDS was found to be only 1.5% that slowly decreased to 0.09% at a concentration of 0.006%, (i.e. there was no consistent change in the removal of Cu with increasing concentrations of SDS) as shown in fig. 5. Khodadoust et al. (2004); Chang et al. (2005) found that, in the case of heavy metals, surfactants do not have any chelating properties because of the inorganic nature of the heavy metals, i.e. surfactants do not have ability for transfer of the soil bound- heavy metals to the liquid phase through ion exchange processes, because of the sorption characteristics of surfactant (SDS) should be also considered because the amount of the adsorbed surfactant may reduce its solubilization ability and cause secondary contamination. While, the addition of distilled water to SDS at different concentrations was decreased removal of copper.

Soil washing experiments were performed with different concentration of SDS-EDTA mixture were used to investigate their effects on copper removal. The soil solution pH values were varied between 3 to 11 following mixing with various concentrations of EDTA, and surfactant (SDS). The metal removal efficiency was found to be dependent on EDTA concentration at case used alone, with the increasing of EDTA concentration, the removal of Cu^{+2} increased and peaking at approximately 42.4% with increasing of EDTA concentration to 0.1 M. The addition of 0.6% SDS retarded copper removal by EDTA, therefor, the removal become approximately 32%, as compared when EDTA was applied alone, as shown in fig. 6. It is hypothesized that most SDS is sorbed on soil at low SDS concentration. Similar results were observed by Chang et al. (2005), the sorbed SDS prevented the EDTA-copper complex being desorbed from soil and reduced the copper removal capacity of EDTA.

An experiment was conducted to test the effect of the initial pH of silty loam soil on the amount of carbonate are really for effective on the efficiency of heavy metal removal from soil by enhanced soil washing. As stated in Table 4, the test (E-1) was conducted as a baseline (i.e. carbonate content was equal to 26.6% at pH H”7.6). Whereas, the test (E-2) was conducted to investigate the effect of the initial soil pH on the carbonate content. As known, most of Iraqi soils are classified as alkaline soils, i.e. pH > 7, as for the soil used in test (E-1). The pH of this soil was lowered in this test (E-2) by addition aluminum sulfate. This compound will change the soil pH instantaneously because the aluminum will produce the acidity as soon as dissolved in the soil. Changing pH affects the concentration of ions such as H^+ and OH^-, this latter result lead to reduce content of carbonate which become to about 11% at pHH”4.7. According to report by Ouhadi et al. (2010) showed that an increase in the quantity of carbonate caused a noticeable increase on the contaminant retention of soil and on the resistance of soil to the contaminant removal by electro kinetic method. Because the presence of carbonates in the soil increases its buffering capacity, acidification is reduced, resulting in a decrease in the rate of heavy metal removed from the contaminant soil. As the result in Fig. 7 shows that the increasing of carbonate decreases the sensitivity of soil to the pH variation of pore fluid. The removal of copper from contaminated

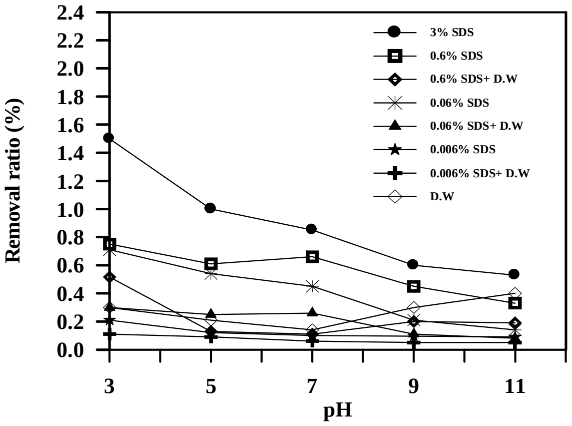

Fig. 5. The effect of different pH on removal efficiencies of copper with distilled water (DW), and SDS mixture washing solutions.

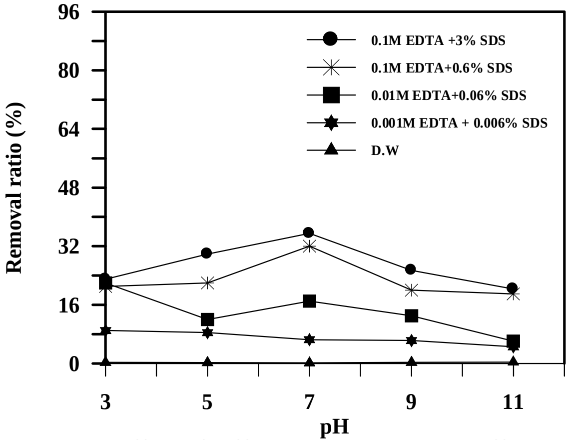

Fig.6. The effect of different pH on removal efficiencies of copper with washing solutions of SDS, and Na_2EDTA mixture.

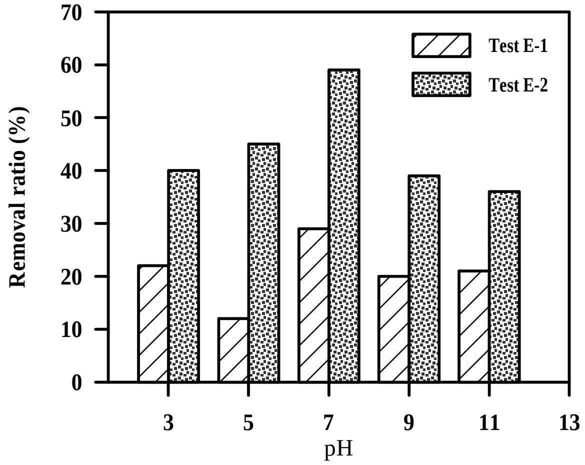

Fig. 7. Removal ratio of copper from contaminated soil after soil washing by 3% SDS, and 0.1 M Na_2EDTA mixture.

soil after soil washing by 3% SDS (sodium dodecyl sulphate), and 0.1M Na_2 EDTA mixture was increased in test (E-2) reached to 59%, when compared with removal in test (E-1) was equal to 29% for the same conditions, it seems that the soluble and exchangeable state is the most susceptible to transfer from soils to plants~ The carbonate combined form is relatively easy effected by pH and released back into the aqueous phase, and it is also absorbed by organism (Wang, 2004) as cited by Zhan et al. (2012). This may be due to the fact soil in test (E-1) had relatively high carbonate fractions, and the presence of carbonate controls the extent of their contaminant retention, because of the retention of heavy metals in HM-CO_3 forms.

CONCLUSIONS

Based on the results obtained from the present experimental measurements, the following conclusions can be drawn:

1- The removal efficiency of copper was 42.4% when, using EDTA. While, it reached 1.5% for test that used SDS. Therefore, EDTA can be more effective on copper removal than SDS.

2- The addition of 0.6% SDS retarded copper removal by EDTA, therefor, the removal become approximately 32%, as compared when EDTA was applied alone.

When pH for this soil was reduced from 7.6 at carbonate content was equal to 26.6% (test E-1) to 4.7 at carbonate content was equal to 11% (test E-2) by addition of aluminum sulfate. The removal of copper from contaminated soil after soil washing by 3% SDS (sodium dodecyl sulphate), and 0.1M Na_2 EDTA mixture was increased in test (E-2) reached to 59%, when compared with removal in test (E-1) was equal to 29% for the same conditions.

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