

Understanding Complexation and Desorption of Copper Ion in Three contaminated Soil Types in Palestine Using Series of Different Surfactants and Ligands

Shehdeh Jodeh*, Ahmad A.Abu-Obaid, Radi Salim

Department of Chemistry, Najah University, P.O. Box 7, Nablus, Palestine.

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Abstract

In this study we have investigated the efficiency of surfactants and ligands on cleaning artificially contaminated red, sandy and white chalk soil samples from copper ion. Various concentrations of four different surfactants: Triton, X-100, SDS, Tergitol and Tween 80 were used as washing solution for remediation of contaminated soils. Different concentrations of three different ligands (I^- , SCN^- and EDTA) along with nonionic surfactant, Triton X-100, were applied as soil washing agents to desorb copper from artificially contaminated soils.

Keywords: Adsorption; Ligands; Copper; Leachate; Isotherm.

Introduction

Heavy metals often affect human health, because humans are constantly exposed to heavy metals in soil through the food chain and by direct ingestion of soil particles^[1]. Chelating agents, such as ethylenediaminetetraacetic acid (EDTA), are also widely used for metal leaching from soils, due to their capacity to complex with metals. However, strong acids and chelating agents also leach out important quantities of soil nutrients and alter soil's properties. Several mechanisms have been suggested as to how surfactants along with alkali or acid solutions enhance metal leaching: ion exchange, electrostatic interaction, and solubilization^[2-5]. Because surfactants are more specific and less aggressive, they are less damaging to soil environment.

Solubilization results from the partitioning of contaminants into the hydrophobic core of surfactant micelles. Therefore, contaminant solubilization increases with the number of micelles in solution.

Molecular adsorption mainly occurs through Van der Waals attraction and hydrogen bonding, and hydrophobic bonding to soil humic and fulvic acids^[6-7].

Since they have relatively little impact on the soil environment compared to strong acid and chelating agents, surfactants are promising agents for the remediation of soils contaminated by either heavy metals or organics. However, one type of

* Corresponding author: e-mail: sjodeh@najah.edu; Tel:970-9-2995744; Fax: 970-9-234-5982.

surfactant alone can only effectively desorb a single type of contaminant, being either hydrophilic heavy metals or hydrophobic organics.

Recently, it has been demonstrated that ligand ions can form hydrophobic complexes with heavy metals^[8-9]. Specific ligand ions can form complexes with specific heavy metals in the surfactant solution, and, as a result, the metal-ligand complex becomes hydrophobic and can be desorbed by the surfactant micelle. This leads to the simultaneous desorption of both heavy metals and hydrophobic organics by a single surfactant-ligand solution.

Numerous studies on the complexation behavior of heavy metals with ligand ions in the presence of surfactant solution have been reported^[8-10]. The complexation of heavy metals can be enhanced by ligands in the presence of surfactant solution.

The more specific research objectives pertaining to the remediation of soils contaminated with copper ion are to understand the complexation and desorption of heavy metals from contaminated soil, using a surfactant along with a ligand, and to measure the copper ion desorption efficiency using four different surfactants (Triton X-100, Tween 80, SDS and Tergitol) from three types of contaminated soil in the absence of ligands and using Triton X-100, with different ligand ions (I⁻, SCN⁻ and EDTA) using the three types of contaminated soil.

Materials and Methods

Soil Sampling and Characterization

Soil samples of the most common types of Palestine were selected for this study. The soils were identified and classified based on sieve analysis and hydrometer test (ASTM H-152). The organic matter of the soil was determined by chromic acid method (WREP-125 2nd Edition, 1998), and the electrical conductivity was measured by using conductivity meter (IS 2720-part 21, 1977). Total soluble solid was estimated from electrical conductivity, the soil pH was measured by using a direct reading type pH meter (JENWAY 3540 PH & Conductivity Meter) with glass electrode and calomel reference electrode. The specific gravity was determined by pycnometer method (IS 2720-part 3/sec 1, 1987). The moisture percentage of each soil was determined, and taken into account when an exact weight was required for analysis. The properties of the collected soils are given in table 1. The soils were sieved through IS (International Standard) sieve No. 40 (0.42 mm aperture as per IS 2720-part 4, 1987). The fraction passing through the sieve was collected and preserved in air tight plastic containers for further studies.

Table 1: Properties of Different Soils Used for the Present Study

Soil properties	Red Soil	Chalk Soil	Sandy Soil
specific gravity (g/cm^3)	2.5	2.2	2.7
pH value *	8.5	7.1	8.5
Electrical conductivity, (Ec), s	230.0	184.1	84.5
Clay (%)	39.0	46.0	2.0
Silt (%)	61.0	54.0	3.0
Organic matter (%)	9.6	8.4	0.3
Moister content (%)	8.0	2.0	0.2

* The soil pH was determined by shaking 5 g of air-dry soil with 10 mL of deionized water for 60 min, letting the solution rest overnight, and then measuring the solution with a pH meter.

Cleaning Soil

A special column was prepared for this purpose (50 cm long with a radius of 2.5 cm with a stopcock to control the rate flow of washing solution). In each column 200 g of soil was washed by 500 ml of distilled water followed by 500 ml of 0.1 M perchloric (which is suitable for Beckman flame Atomic Absorption (R. Salim 1980)) acid then 500 ml of distilled water. The soil was dried at 95 °C for 24 hours using universal ovens (Mettler UNB 100-500, U B 400-500).

1.0 g of soil was digested with concentrated nitric acid (Method 3050A, Acid Digestion of Sediment, Sludges, and Soil by Neil Wilson 9/5/95) and tested for elemental analysis. No metal (Cu^{2+}) was present in the cleaned soil.

Desorption of copper from soils using surfactants

To study the effect of desorption of copper from soil, a 1.0 kg sample of each soil (red, sandy and chalk) were taken and added to 4.0 liters of a 5.0 M concentration of copper solution. The soil was soaked in the solution for two days. After that, the solution was put in a cloth bag to filtrate the solution out. The contaminated soil left in the cloth bag was dried in the oven at 95°C for 24 hours.

A sample of 1.0 g of the dried contaminated soil of each kind was placed in a glass bottle.

Five different concentrations (0.005, 0.05, 0.5, 0.1, and 0.2 M) of four surfactants: anionic surfactant SDS (Sodium dodecyl sulfate, $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}^+$), the nonionic surfactant Triton X-100 (octylphenyleneoxide, $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OC}_2\text{H}_4)_{10}\text{OH}$), the nonionic surfactant Tween-80 (Polyoxyethylene (20) Sorbian monooleate and nonionic surfactant Tergitol (Branched Secondary Alcohol Ethoxylate) were tested in the study.

These prepared different surfactants were added to each 1.0 g of the soil in the bottle. A total of sixty solutions were prepared; twenty solutions of each soil. The prepared solutions were shaken for 24 hours using the shaker (Wrist Action, SHAKER,

BURRELL, and MODEL 75) and 10 ml of each one were centrifuged at 2500 rpm. The supernatant was analyzed using atomic absorption. The results are shown in figure. 1 result for the three types of soil.

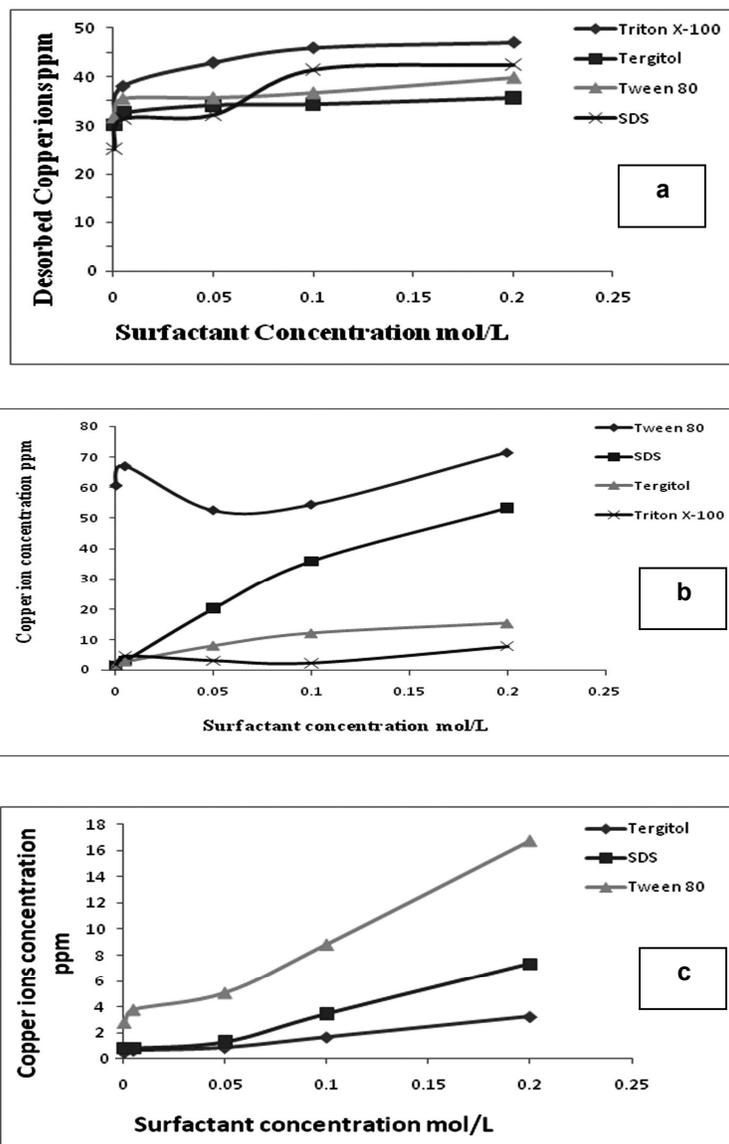


Figure 1: Desorption of copper ions from artificially contaminated a) red b) sandy and c) white chalk soil using surfactants in the absence of ligands.

Desorption of copper from soils using surfactants with ligands

From the study of surfactants in the previous section, it was shown that Triton X-100 was the best amongst other surfactants for red soil. So 0.01 % of Triton X-100 was prepared in a 2.0 litter flask.

Different weights of KI (0.83, 1.66, 3.33, 4.98 and 6.64g) which were equivalent to 0.05 , 0.1, 0.2, 0.3 and 0.4M KI respectively; were added to a 100 ml volumetric flask. The flask was filled with the 0.01 % of Triton X-100. The whole solution of KI and Triton X-100 (100 ml) was transferred to the bottle which has 4.0 grams contaminated soil.

The same solutions were prepared in the same way using SCN^- and EDTA. This preparation of solutions was repeated for the three types of soil. The results are shown in figures 2 and 3.

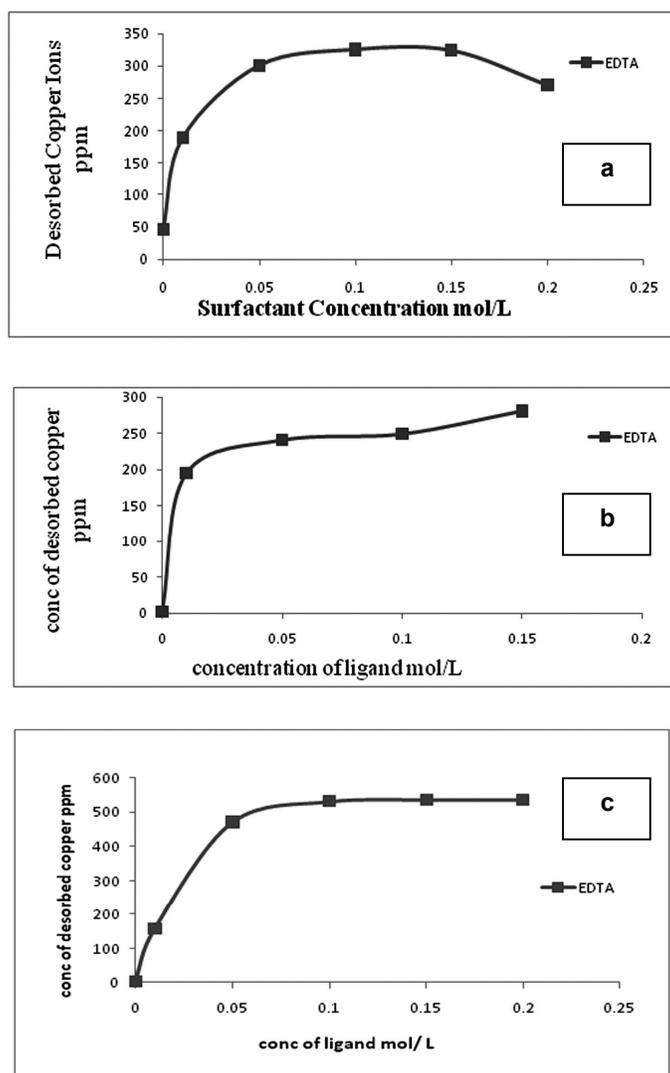


Figure 2: Desorption of copper ions from artificially contaminated a) red b) sandy and c) white chalk soil using Triton X-100 with EDTA.

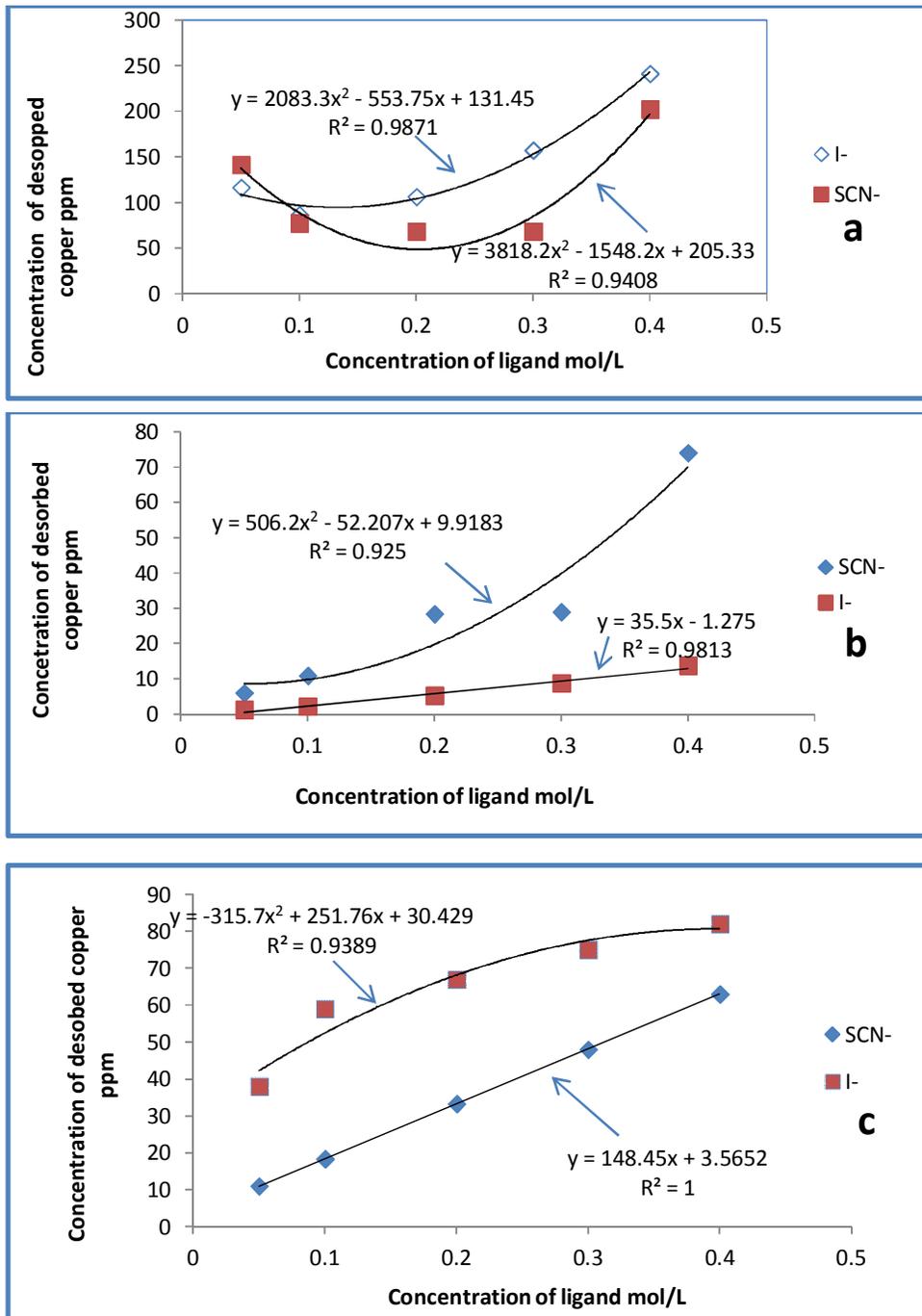


Figure 3: Desorption of copper ions from a) red b) sandy and c) white chalk soil using Triton X-100 with I⁻ and SCN⁻ ligands

Results and Discussion

Desorption of copper from soils using surfactants

The objective of this study was to measure the desorption rates of selected heavy metals from artificially contaminated three types of soil in the presence of various surfactants. Four surfactants were evaluated in this study; the anionic surfactant SDS, the nonionic surfactant Triton X-100, the nonionic surfactant Tween 80 and nonionic surfactant Tergitol. The surfactant concentrations used in the study were 0.2, 0.1, 0.05, 0.005 and 0.0005 M.

The results of desorption of the four surfactants (Triton X-100, Tergitol, SDS and Tween 80) on artificially contaminated red soil in the absence of ligand is illustrated in figure. 1a. The maximum amount of adsorbed copper on red soil was found to be 330, 250 for sand soil and 290 mg/g for the white chalk soil. The control washed with pure distilled water adsorbed 42.8 mg/g which is 13% of the original amount of adsorbed copper on red soil and 0.1 M of Triton X-100 without ligands adsorbed 45.5 mg/g which is 14% of the original amount of adsorbed copper on red soil.

Triton X-100 generally desorbed higher level of copper metals than the control which was only washed with distilled water. A gradual increase on desorption of copper was observed by Triton X -100, it was able to desorb 14% of copper ions from the original contaminated red soil. Triton X -100 (0.1 M) proved to be a more potent washing agent for red soil than distilled water and other surfactants; however its ability to desorb heavy metals remains limited. The other surfactants like Tergitol and Tween 80 did not show remarkable changes.

The results of desorption of the four surfactants mentioned previously on artificially contaminated sandy soil in the absence of ligand are shown in figure. 1b. As shown Tween 80 generally desorbed a higher level of copper metals than the control washes with distilled water and surfactants. Results for all surfactants show that desorbed copper concentration increases with increasing surfactant concentration until the concentration of surfactant reaches a value equal to two times the critical micelle concentration (CMC) value, above 0.1M surfactant concentration. The removal of copper ions does not alter very much (Figure 1b).

The results suggest that the micelles indirectly cause the mobilization and removal of copper ions, as mentioned by others^[11-13]. Anionic surfactants are expected to exhibit better metal removal efficiency than nonionic surfactants, because amphoteric and cationic surfactants tend to form strong complexes with soil minerals. However, present results; indicate that significant differences in copper extraction using neutral and anionic surfactants were not present.

Similar results were obtained for white chalk. Results are shown in figure 1c.

Desorption of copper from soils using surfactants with ligands.

The purpose of this study was to evaluate the effect of Triton X-100 and different ligands like EDTA, I^- and SCN^- on desorption of copper ions from three artificially contaminated types of soil. The maximum amount of adsorbed copper on red soil found to be 330 mg/g.

The surfactant concentration used in the test was 0.1 mol/L which is higher than the CMC level of Triton X-100 surfactant. Therefore, surfactant monomers are expected to form micelles in the experimental solution used, the same results was obtained by Chu and Chan^[14].

In the presence of Triton X-100, the heavy metal desorption efficiencies of the ligands I^- , SCN^- , and EDTA are presented in figures (2 and 3). The ligand I^- desorbed 18% Cu at the maximum tested ligand concentration of 0.4 mol/L. From the results shown in the figures, the desorption efficiency for heavy metals increased with increasing ligand concentration, except for the lower ligand concentration of 0.05 M I^- and SCN^- , the desorption of copper was 35% higher than 0.1 M I^- . The same thing happened in the case of 0.05 M SCN^- ; the desorption was 84% higher than that of 0.1 M SCN^- .

When 0.4 M solution of ligands I^- and SCN^- in the presence of Triton X-100, it desorbed 18% and 15% Cu. It is also shown that increasing ligand concentration will increase heavy metal mobilization.

Copper preferred the SCN^- complex at very low concentrations but it preferred the I^- complex at high concentrations of ligand in the presence of Triton X-100, (Figure. 3a). Although both SCN^- and I^- complexes desorbed only limited quantities of copper, they proved to be relatively immobile as compared to other ligands like EDTA, because of its smaller hydrated ionic radius, and therefore its greater attraction for soil adsorption sites.

The results of these experiments were consistent with heavy metal complexation behavior in surfactant micellar suspension in aqueous media^[9, 15]. The same observation noticed when those ligands were applied to both the sandy and white soil, but with less desorption than in red soil (Figure 3b, 3c). The desorption in sandy and white soil using I^- showed a linear desorption.

The micelle-solubilized ligand complex was therefore quite efficient at removing heavy metal from soil if the ligand selected had an appreciable affinity for the target heavy metal. Finally, the micelle-solubilized ligand complex did not require acidification of the soil to desorb the heavy metals, as is required for certain other soil washing agents. This is an appreciable major environmental advantage because of the adverse effects of acidic conditions on microbial populations and plant growth^[16]. Various chemical reagents including chelating and extracting agents have been evaluated for

their effectiveness in extracting heavy metals from soils^[17-20]. Most studies have focused on comparisons of various chelating and extracting agents in batch tests with the conclusion that metal desorption efficiency depends on the soil type and on the composition of the washing solution. One chelating agent, ethylenediaminetetraacetic acid (EDTA), is quite effective in removing heavy metals. 0.1 M EDTA with 0.1 M desorbing more than 98% of copper adsorbed in red soil as shown in Figure.2a, but can potentially affect the permeability of the treated soil^[17].

Since micelles are composed of an inner hydrophobic core and a hydrophilic exterior surface, the surfactant micelles can solubilize both ionic and non-ionic compounds, such as heavy metals and PCBs. Many studies directed to the extraction of hydrophobic contaminants from soils using surfactant micelles^[3, 21-22] have demonstrated that solubilization can be attributed to the incorporation of hydrophobic contaminants within the hydrophobic core of the surfactant micelles in solution.

Some surfactants have been found to remove heavy metals from soils, under both acidic and alkaline conditions, through direct complexation followed by solubilization. These results were reported by Herman and Mulligan^[23-24]. Without changing the soil's pH, surfactants can extract heavy metals when coupled with a ligand that forms a micelle-solubilized complex. The ligand interacts with the adsorbed metal which increases hydrophobic character of the product and results in preferential accumulation of the complex within the surfactant micelle. The results of these experiments were consistent with heavy metal complexation behavior in surfactant micellar suspension in aqueous media^[9, 15].

In figures (2b, 3b) we found that the concentration of Cu^{+2} desorbed by distilled water from sandy soil was about 1.1 ppm. This means that most copper ions were desorbed in sandy soil. After addition of 100 mL of 0.1 M Triton X-100 to the contaminated sandy soil and analyzing Cu^{+2} in the aqueous solution, the concentration of Cu^{+2} in the aqueous phase was found to be 1.4 ppm.

The experiment was done using Triton X-100 with different ligands like EDTA, I^- and SCN^- and the desorbed Cu^{+2} was as follow : 1.2 ppm for 0.05 M I^- , 1.95 ppm for 0.01 M EDTA, and 5.90 ppm for 0.05 M SCN^- . The other results were observed as if we increased the concentrations of ligands from 0.05 M I^- to 0.4 M I^- , the desorption of Cu^{+2} increases from 1.2 ppm to 13.7 ppm. The same observations occurred for both EDTA and SCN^- .

Increasing concentration of EDTA will increase the removal of Cu^{+2} ions. In the case of 0.15 M EDTA more than 98% Cu^{+2} was removed, while using 0.01 M EDTA only 68% Cu^{+2} removed. These results agree with previous research^[12, 18, 25]. Soil flushing tests performed on a sandy loam showed that complete lead and copper removal can be achieved by using a solution containing 0.01 M EDTA^[25].

The excess dosage would insure that there were always sufficient molecules of chelating agents available to these heavy metals, even though some molecules of the chelating agents might have been participated, adsorbed by the soil, or might have formed complexes with other cations (Ca, Mg, Fe, Al, and other trace heavy metals) that were originally present in the soil. When this study was done on white chalk soil, (Figures 2c, 3c), we found the same behavior of surfactant and ligands on desorbing copper from it as if it was done in sandy soil.

Conclusions

Surfactants showed efficient soil remediation agents for heavy metals. Triton X-100 was the best surfactant to desorb copper from red soil. Tween 80 was the best surfactant to desorb copper from sandy and white chalk soils.

In general, Cu removal was increased with higher ligand concentrations. Using SDS, Cu removal decreased with increasing ligand concentration indicating that the ligand I⁻ along with anionic surfactants, SDS, could not extract Cu.

(الرجاء كتابة المراجع حسب تعليمات المجلة مثل المرجع رقم 2، ولا داعي لكتابة عناوين الأبحاث المنشورة في المجلات مع مراعاة تنسيق اسم المجلة بشكل مائل).

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