

# Complexation of a Ligand with a Surfactant Micelle for Soil Heavy Metal Desorption

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*The ligands iodide ( $I^-$ ) and thiocyanate ( $SCN^-$ ), alone or in admixture, in combination with a non-ionic surfactant, Triton X-100, were evaluated as washing agents for heavy metal desorption from a contaminated soil. After seven successive washings, selective sequential extraction (SSE) was performed to determine the heavy metal content that remained associated with each geo-chemical fraction of the soil. The surfactant with  $0.336 \text{ mol L}^{-1}$  of ligand  $I^-$  removed 75% Cd and 23% Cu, whereas the mobilization of Zn and Pb were not significant after 7 washings. At a concentration of  $0.286 \text{ mol L}^{-1}$ , the ligand  $SCN^-$  in the presence of surfactant removed 36% Cd, 44% Cu and 77% Zn. Among the washing agents, the combination of  $I^-$  and  $SCN^-$  produced the highest desorption efficiencies 95% Cd, 48% Cu, and 3.1% Pb, but not for Zn. The  $SCN^-$  ligand extracted the most Zn (77%). The SSE procedure indicated that the  $I^-$  removed metals from the exchangeable, carbonate and oxide fractions whereas  $SCN^-$  removed metals only from the exchangeable fraction. Both ligands, in the presence of surfactant, removed Cu from all fractions except the exchangeable sites, whereas only  $SCN^-$  plus surfactant removed Zn from all fractions. The ligand mixture plus surfactant mobilized only limited quantities of Pb from the oxide and residual fractions.*

**Keywords** Nonionic surfactant, ligand, heavy metal, sequential extraction, soil.

## Introduction

Soil contamination by heavy metals is of major concern because these metals can be taken up by plants and can exert an appreciable deleterious impact on the health of animals and humans as a result of food chain transfer. Common contaminating heavy metals include lead, mercury, arsenic, chromium, cadmium and copper (Yarlagadda *et al.*, 1995). According to estimations by the U.S. Environmental Protection Agency (U.S. EPA), over 20 million cubic

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yards of soil are currently listed among the National Priority Lists (NPL) as contaminated with heavy metals (Griffiths, 1995).

Various chemical reagents including chelating and extracting agents have been evaluated for their effectiveness in extracting heavy metals from soils (Abumaizar and Khan, 1996; Abumaizar and Smith, 1999; Allen and Chen, 1993; Chen *et al.*, 1992). 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, but can potentially affect the permeability of the treated soil (Abumaizar and Khan, 1996). Acid washing is also effective in removing heavy metals from soil, but it is less selective, alters soil properties by dissolving minerals non-selectively and by adversely acidifying the soil acid (Reed *et al.*, 1996).

Application of surfactants for heavy metal remediation has gained popularity in recent years. Surfactants (surface active agents) possess a hydrophilic functionality, increasing solubility in aqueous media, and a hydrophobic moiety, enabling them to adsorb to hydrophobic organic compounds. At concentrations in excess of the critical micelle formation (CMC) in aqueous solution, the surfactant molecules aggregate to form clusters called micelles that enhance the remediation capability of surfactant suspensions. 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 (Huang *et al.*, 1997; Noordman *et al.*, 1998; Zhang *et al.*, 1997) 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 (Herman *et al.*, 1995; Mulligan *et al.*, 1999a). Without changing the soil pH, surfactants can extract heavy metals when coupled with a ligand that forms a micelle-solubilized complex. The ligand interacts with the adsorbed metal that increases hydrophobic character of the product and results in preferential accumulation of the complex within the surfactant micelle. Such metal complexes are formed extensively within the micellar phase rather than in the aqueous phase. For example, metal complexation studies with the ligand  $\text{SCN}^-$ , in the presence of Cu, have evaluated the values of the formation constants for both the aqueous and micellar phase: the logarithmic formation constants ( $\log K_F$ ) in the aqueous phase vs. the micellar phase were estimated to be 1.0 and 2.4 ( $\text{mol}^{-1} \text{L}$ ) respectively, where  $K_F$  expresses the extent of the complexation process (Shin *et al.*, 1997). For Zn, the  $\log K_F$  values for  $[\text{Zn}(\text{NCS})_3]^-$  were 1.3 and 4.3, respectively. Cd also complexed with  $\text{I}^-$  favorably in micellar phase as  $[\text{CdI}_4]^{2-}$  with the larger negative enthalpy value of  $-15 \text{ kJ mol}^{-1}$  than the value of  $-5 \text{ kJ mol}^{-1}$  in aqueous phase (Shin *et al.*, 2000). The study also suggested that the anionic complexes of metal-ligand may form ion pairs in micelles such as  $\text{Na}_2[\text{CdI}_4]$  to keep electric neutrality and be stabilized in the hydrophobic environment of micelle. The behavior of metal complex formations in surfactant micellar solution has been demonstrated for aqueous solutions (Shin *et al.*, 1997; Shin *et al.*, 2000; Umabayashi *et al.*, 2001). So far, micelle-solubilized ligand systems have not been tested on soils.

The objective of this study was to evaluate the efficacy of two complexing reagents in combination with a surfactant to desorb heavy metals from soil. Cadmium, copper, zinc and lead were targeted as heavy metals. In the previous studies, heavy metals, Cd, Cu, and Zn could complex with the specific ligands, iodide ( $\text{I}^-$ ) or thiocyanate ( $\text{SCN}^-$ ) in the nonionic surfactant micelles; these ligands in combination with a nonionic surfactant, Triton X-100,

were selected as washing agents. For ligands such as  $I^-$  and  $SCN^-$ , they are not expected to be strongly adsorbed to the soil reaction site because of their negative charge. Unlike cyanide ( $CN^-$ ), thiocyanate has a relatively low toxicity and kinetic studies showed that free  $SCN^-$  can be degraded at a relatively high rate of  $292 \text{ mg L}^{-1} \text{ day}^{-1}$  (Boucabeille and Bories, 1994). Ligands are effective heavy metal complexing agents under neutral pH and therefore do not require soil acidification, resulting in less environmental impact. Selective sequential extraction (SSE) was performed to determine which soil-binding site(s) were affected by the surfactant-ligand extraction process.

## Materials and Methods

### Materials

The nonionic surfactant, Triton X-100, was tested in this study along with sodium iodide (NaI) and sodium thiocyanate (NaSCN) as ligands. Different combinations of washing agents including the surfactant and the ligands were prepared using distilled water. The natural soil used in the study was obtained from a landfill site and heavily contaminated with heavy metals such as Cd, Cu, Zn, and Pb.

Soil characterization was performed to establish the particle size distribution by mechanical sieving followed by the hydrometer method (Blake and Hartage, 1986). Soil pH was determined using a pH meter in a solution with a soil to water ratio of 1:5. After soaking in  $0.1 \text{ mol L}^{-1}$   $BaCl_2$  solution for 2 h (Hendershot *et al.*, 1993), the cation exchange capacity (CEC in  $\text{mol}(+) \text{ kg}^{-1}$ ) of the soil was obtained by measuring Ca, Mg, K, Na, Mn, Zn, Fe and Al desorbed by atomic absorption spectrophotometry (AAS). Organic matter content was determined by charring dried samples at  $350^\circ\text{C}$  for 4 h (Ball, 1964). The soil heavy metal content was measured after digesting using aqua regia (36% HCl:70%  $HNO_3$  at the ratio of 4:1) overnight at room temperature followed by drying the sample at  $140^\circ\text{C}$ . After cooling, 20% HCl was added and the sample mixture re-warmed at  $80^\circ\text{C}$  for 20 min, mixed and filtered using Whatman no. 40 filter paper (McGrath and Cunliffe, 1985). Digested samples were analyzed using a single beam atomic absorption spectrophotometer (GBC Model 903) at the specific wavelength of 228.8, 324.7, 213.9 and 217 nm for Cd, Cu, Zn and Pb, respectively. Standard solutions for each heavy metal were used to calibrate the equipment beforehand (APHA/AWWA/WEF, 1998).

### Batch Soil Washing Studies

Batch experiments were performed by soaking three replicate 1.0 g samples of contaminated soil in 15 mL of washing agents. To see the effect of ligand concentration, the following commonly used concentrations were used: 0, 0.168 and  $0.336 \text{ mol L}^{-1}$  for the ligand  $I^-$ , and 0, 0.143 and  $0.286 \text{ mol L}^{-1}$  for the ligand,  $SCN^-$ . For all tests, the ligand solution was used along with the surfactant since, without the surfactant, the metal-ligand complexes cannot be formed extensively in the aqueous solution (Shin *et al.*, 2000). A surfactant concentration of  $0.1 \text{ mol L}^{-1}$  of Triton X-100 was used throughout as it is sufficient in ensuring micelle formation. All soil-washing solutions had a pH of 7.5 ( $\pm 0.3$ ). The contaminated soil was also washed with distilled water as control treatment and with Triton X-100 alone in the absence of ligand.

All soil samples and washing agent solution (ligand and surfactant) were equilibrated by shaking at 150 rpm during 24 h. The resulting soil slurries were centrifuged at 4000 rpm. To

determine the quantity of heavy metals mobilized from the soil, the supernatant was analyzed for Cd, Cu, Zn and Pb levels by AAS. The percentage metal removal was determined as follows:

$$\% \text{ metal removal} = (\text{mg metal}_{\text{supernatant}}) / (\text{mg metal}_{\text{initial}}) \times 100\% \quad (1)$$

where

$$\begin{aligned} \text{mg metal}_{\text{supernatant}} &= (\text{mg/L metal}_{\text{supernatant}}) \times (1 \text{ L}/1000 \text{ ml}) \\ &\times \text{volume of extractants (mL)} \end{aligned} \quad (2)$$

$$\text{mg metal}_{\text{initial}} = (\text{mg metal}_{\text{initial}}/\text{kg soil}) \times (1 \text{ kg}/1000 \text{ g}) \times \text{weight of soil (g)} \quad (3)$$

A series of seven consecutive batch washings was performed on each soil sample by adding fresh washing solution to the treated soil sample, shaking again for 24 h on a rotary shaker, and then removing the solution by centrifugation (4000 rpm, 20 min). Between each washing, the supernatant was collected and analyzed for heavy metals.

### ***Selective Sequential Extraction Experiment***

After seven successive washes with each washing solution, selective sequential extraction (SSE) was used to determine the quantity of heavy metals that remained associated with each soil geo-chemical fraction. All soil samples were washed with the first SSE reagent, then dried before washing with each subsequent SSE treatment agent. The method partitions the heavy metals into six operationally defined chemical fractions: soluble (Sol), exchangeable (Ex), carbonate bound (Car), oxides and hydroxide bound (Ox), organic matter bound (Org), and residual (Res) (Yong *et al.*, 1993; Mulligan *et al.*, 1999b). Between SSE treatments, each washing supernatant fraction was collected and assayed for heavy metals by AAS.

### ***Statistical Analysis***

All treatments were conducted in triplicate to determine their significance using SAS software to compare means. Where significant F values were obtained, the Least Significant Difference (LSD) was used to identify the differences between individual means.

## **Results and Discussion**

### ***Soil Characterization***

Table 1 characterizes the experimental soil contaminated with high levels of heavy metals: 36.3 mg kg<sup>-1</sup> Cd, 3045.2 mg kg<sup>-1</sup> Cu, 1302.4 mg kg<sup>-1</sup> Zn and 7265.4 mg kg<sup>-1</sup> Pb. The soil had a pH of 7.5 and remained between 7 and 8 after exposure to the consecutive washings.

### ***Metal Removal in the Absence of Ligand***

The heavy metal desorbing capabilities of seven successive washes for the control and the nonionic surfactant Triton X-100 in the absence of ligand is illustrated in Figures 1A and 1B, respectively. After 7 washings, the control consisting of distilled water, desorbed less

**Table 1**

Physical-chemical characteristics of the experimental soil	
Parameters	Soil
Sand (%) (0.02–2 mm)	79.6
Silt (%) (0.002–0.02 mm)	6.8
Clay (%) (<0.002 mm)	13.6
Organic matter (%)	11.4
CEC (cmol(+) kg <sup>-1</sup> )	7.8
Soil pH	7.6
Cd (mg kg <sup>-1</sup> )	36.3
Zn (mg kg <sup>-1</sup> )	1302.4
Cu (mg kg <sup>-1</sup> )	3045.2
Pb (mg kg <sup>-1</sup> )	7265.4

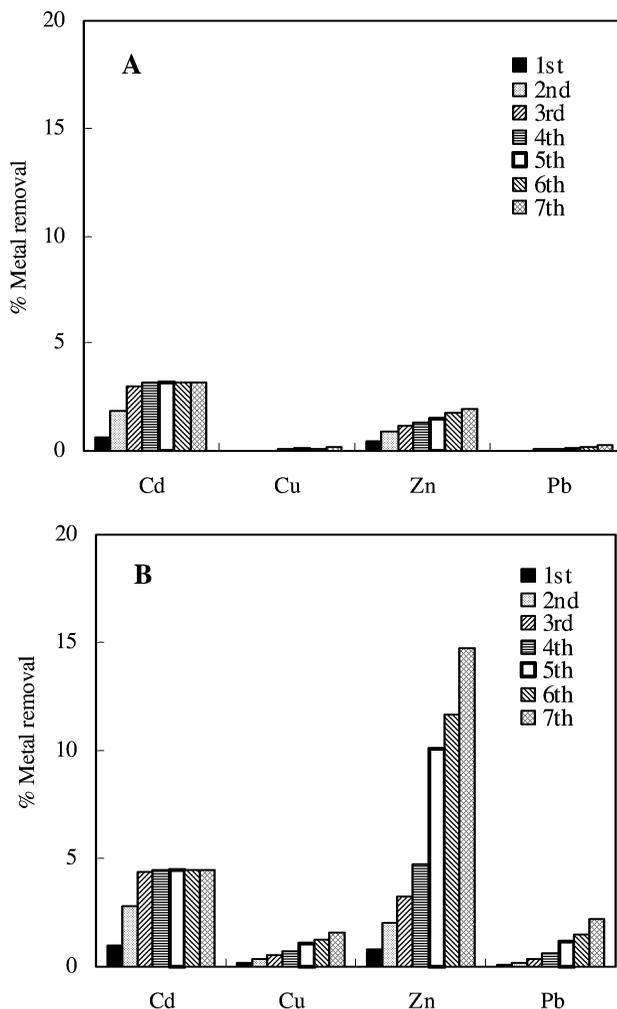
than 1% Cu and Pb, 1.9% Zn and 3.1% Cd. Cadmium desorption peaked after 3 successive washings.

Compared to the control washes with distilled water, Triton X-100 generally desorbed a progressively higher levels of heavy metals with each successive washing. Among the heavy metals, Cd desorption did not change after 3 washings. Although a gradual desorption of Cu and Pb was observed with successive washings, the level of desorption was so limited that it would not be considered significant between washings. The desorption of Zn did increase significantly with successive washings and reached a level of 14.7% after 7 washes. Triton X-100 alone extracted 14.7% of the Zn and 3.6% of the Cu. Although Triton X-100 proved to be a more efficient washing agent than distilled water, its ability to desorb metals remained limited since the surfactant has limited capability in solubilizing heavy metals. To increase soil metal desorption capacity, the ligands must be used along with the surfactant.

### ***Metal Removal with Surfactant Micelle-Solubilized Ligand***

In the presence of Triton X-100, the heavy metal desorption efficiencies of the ligands I<sup>-</sup>, SCN<sup>-</sup>, and the combination of I<sup>-</sup> and SCN<sup>-</sup> are presented in Figures 2, 3, and 4. The ligand, I<sup>-</sup> desorbed 75.5% Cd, followed by 23.1% Cu, 2.9% Pb and 2.7% Zn at the maximum tested ligand concentration of 0.336 mol L<sup>-1</sup> after 7 washings. Cadmium and Cu desorption increased with the number of successive washings, whereas Zn and Pb desorption did not increase significantly (Figures 2A and B). The desorption efficiency for heavy metals increased with increasing ligand concentration except for Zn (Figures 2A and 2B). More Zn was desorbed at the lower ligand concentration, implying that I<sup>-</sup> has a reverse effect on extracting Zn. Therefore, the micelle complex composed of the ligand I<sup>-</sup> and the surfactant Triton X-100 had the greatest affinity for Cd resulting in the highest extraction capability from the soil.

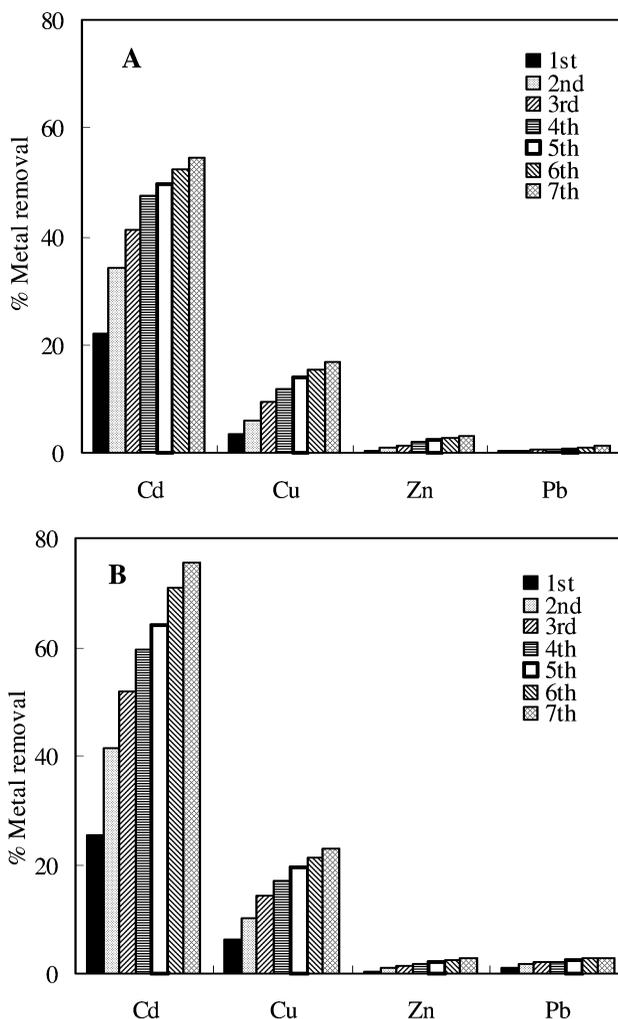
Seven successive washes with 0.286 mol L<sup>-1</sup> SCN<sup>-</sup>, in combination with Triton X-100, desorbed 77.5% Zn, followed by 44.4% Cu, 36.4% Cd and 1.6% Pb (Figure 3B). Increased ligand concentrations and numbers of washes resulted in increased heavy metal mobilization except for Pb, where only insignificant quantities were desorbed by consecutive washings (Figures 3A and 3B).



**Figure 1.** Cumulative percent metal removed from soil with water control (A) or Triton X-100 (B) solution. Triton X-100 was applied at  $0.1 \text{ mol L}^{-1}$ . The different bar shapes refer to the different washings.

Each ligand-surfactant micelle combination demonstrated a different affinity for specific heavy metals. The  $\text{SCN}^-$  surfactant combination demonstrated a greater affinity for Zn, as compared to that using  $\text{I}^-$ , which demonstrated virtually no affinity for Zn but a great affinity for Cd. Apparently, cadmium iodide was more stable than cadmium thiocyanate, in micellar solution. Copper preferred the  $\text{SCN}^-$  complex whereas Pb preferred the  $\text{I}^-$  complex, although both  $\text{SCN}^-$  and  $\text{I}^-$  complexes desorbed only limited quantities of Pb. Lead proved to be relatively immobile as compared to other heavy metals, possibly 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 (Shin *et al.*, 1997; Shin *et al.*, 2000).

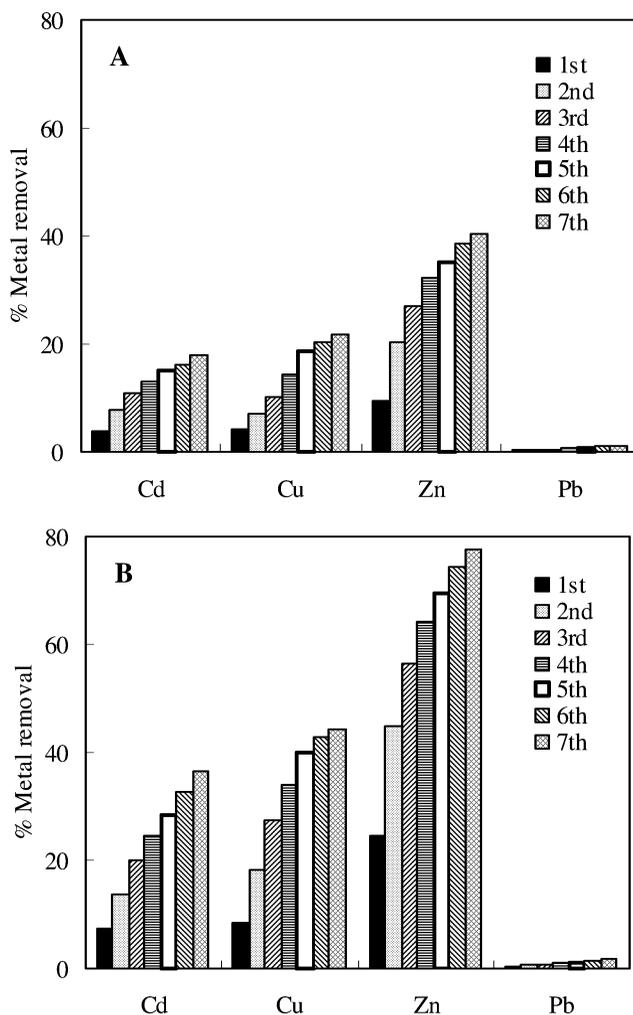
Figure 4 presents the levels of heavy metals desorbed with the ligand mixture ( $\text{I}^-$  plus  $\text{SCN}^-$ ), in combination with Triton X-100. Compared to quantities desorbed by individual



**Figure 2.** Cumulative percent metal removed from soil using Triton X-100 ( $0.1 \text{ mol L}^{-1}$ ) with ligand,  $\text{I}^-$ , at concentrations for A and B of  $0.168$  and  $0.336 \text{ mol L}^{-1}$ , respectively. The different bar shapes refer to the different washings.

ligands, the mixture of both ligands increased the desorption levels of heavy metals, especially for Cd and Cu but not for Zn (Figures 4A and 4B). Nevertheless, Zn desorption was increased significantly with the successive number of washings only at the higher ligand concentration of  $0.336$  and  $0.286 \text{ mol L}^{-1}$ . None of the various ligand concentrations efficiently increased Pb desorption with successive washings. At  $0.336$  and  $0.286 \text{ mol L}^{-1}$  for  $\text{I}^-$  and  $\text{SCN}^-$ , after 7 consecutive washings, the ligand mixture had desorbed 95.5% Cd, followed by 48.6% Cu, 42.8% Zn and 3.2% Pb (Figure 4B).

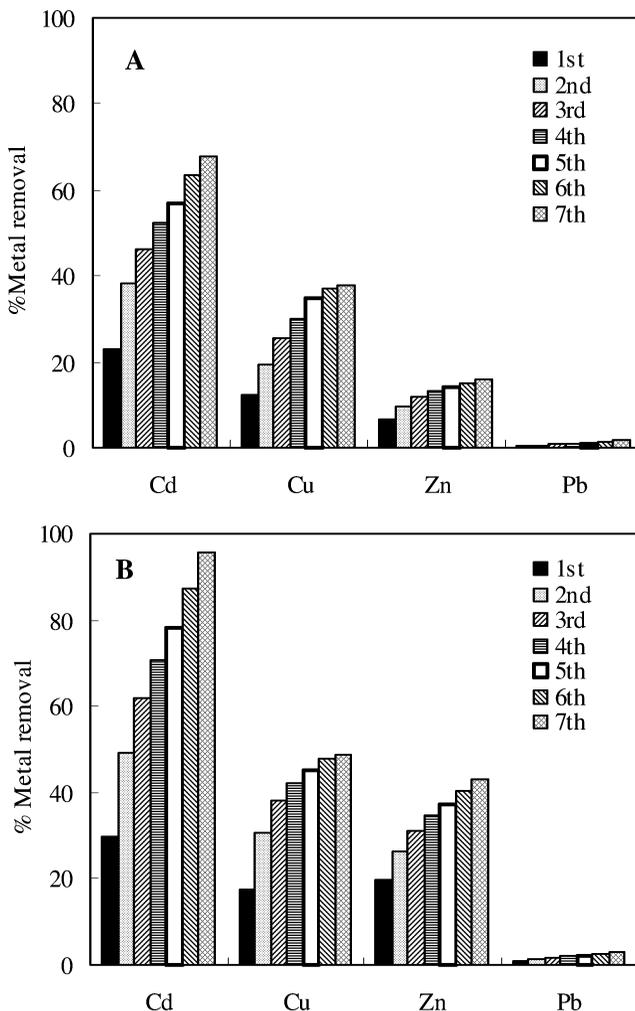
The use of higher levels of  $\text{I}^-$  as a ligand had a reverse effect on Zn desorption. Thus, if  $\text{SCN}^-$  was mixed with  $\text{I}^-$ , Zn desorption decreased as compared to  $\text{SCN}^-$  alone. Thus, the ligand  $\text{I}^-$  was used for three successive washings followed by the use of ligand  $\text{SCN}^-$  for a further four successive washings (Figure 5). Having mobilized 68.4% Cd, 28.6%



**Figure 3.** Cumulative percent metal removed from soil using Triton X-100 ( $0.1 \text{ mol L}^{-1}$ ) with ligand,  $\text{SCN}^-$ , at concentrations for A and B of  $0.143$  and  $0.286 \text{ mol L}^{-1}$ , respectively. The different bar shapes refer to the different washings.

Cu, 22.2% Zn and 2.5% Pb, this process produced significantly decreased heavy metal desorption efficiencies, when compared to the mixture of both or either ligand.

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. The ligand  $\text{I}^-$  used with a surfactant can desorb significant amounts of Cd, but not Zn and Cu. The ligand  $\text{SCN}^-$  was used with a surfactants, more specifically desorbed Zn and Cu. A given ligand can complex with a specific metal, probably because of the specific coordination mode between the two. For example, the N portion of the ligand  $\text{SCN}^-$  binds specifically with Zn to form  $[\text{Zn}(\text{NCS})_4]^{2-}$  and this complex is relatively insoluble in water because of its weak hydrogen-bonding S portion (Shin *et al.*, 2000; Umabayashi *et al.*, 2001). As a result, this complex is more soluble once adsorbed within the hydrophobic



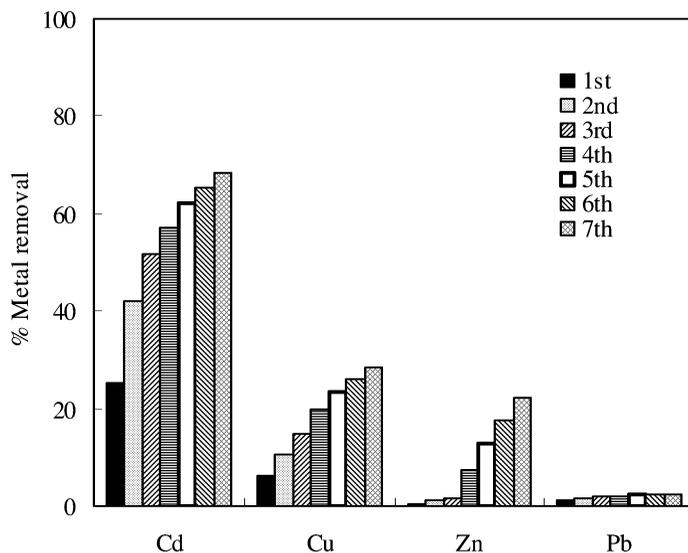
**Figure 4.** Cumulative percent metal removed from soil using Triton X-100 ( $0.1 \text{ mol L}^{-1}$ ) with ligand,  $\text{I}^-$  and  $\text{SCN}^-$ , at concentration for A and B of  $0.168 (\text{I}^-)$  and  $0.143 (\text{SCN}^-) \text{ mol L}^{-1}$ , and  $0.336 (\text{I}^-)$  and  $0.286 (\text{SCN}^-) \text{ mol L}^{-1}$ , respectively. The different bar shapes refer to the different washings.

micelles. However, with Cd ions, the ligand  $\text{SCN}^-$  does not form strong complex in the micelles, as compared to  $\text{I}^-$ . This leads to less Cd ions being desorbed from the soil.

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 (Reed *et al.*, 1996).

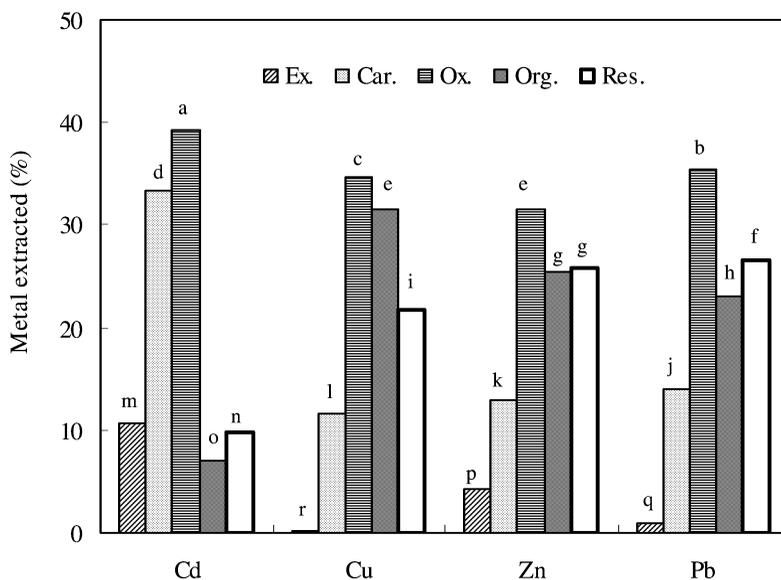
### Selective Sequential Extraction

Selective sequential extraction (SSE) was performed on all soil samples prior to treatment and after 7 successive washings (Figure 6). Before the washings, Cd was adsorbed mostly to the oxide fraction (40%), followed by the carbonate and hydroxide fraction (33%) and

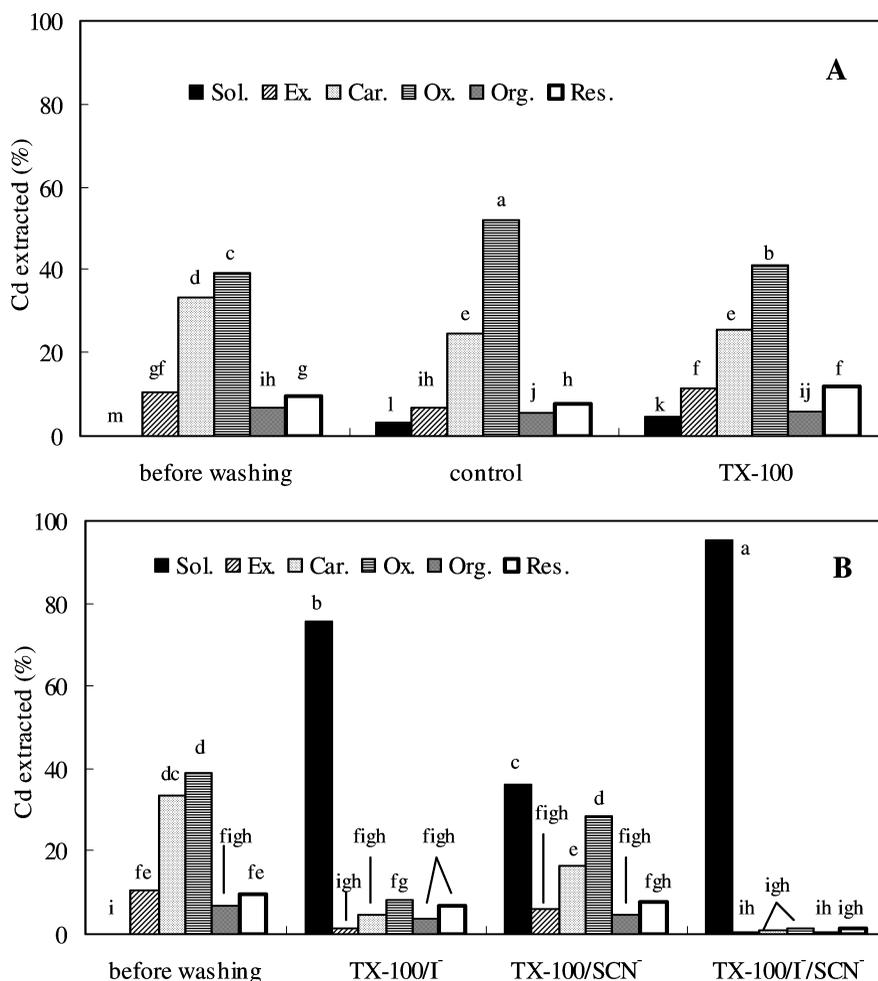


**Figure 5.** Cumulative percent metal removed from soil using Triton X-100 ( $0.1 \text{ mol L}^{-1}$ ) with ligand,  $\text{I}^-$  ( $0.336 \text{ mol L}^{-1}$ -1st to 3rd washing) and  $\text{SCN}^-$  ( $0.286 \text{ mol L}^{-1}$ -4th to 7th washing). The different bar shapes refer to the different washings.

the exchangeable sites and the organic and residual fractions at 11.7 and 10%. Cu was adsorbed primarily by the oxide fraction (34%), followed by the organic fraction (33%), the residual fraction (22%), and the carbonate and hydroxide fractions (12%), with almost no Cu adsorbed by the exchangeable sites. Zinc and Pb were adsorbed at similar levels mostly by the oxide fraction (32 and 34%), followed by the organic and residual fractions (27 and 26%, on the average) and then the carbonate and hydroxide fractions (14%), with



**Figure 6.** Fractionation of metals in soil before treatment. Means of triplicate samples with the same letters are not significantly different (95% confidence level).

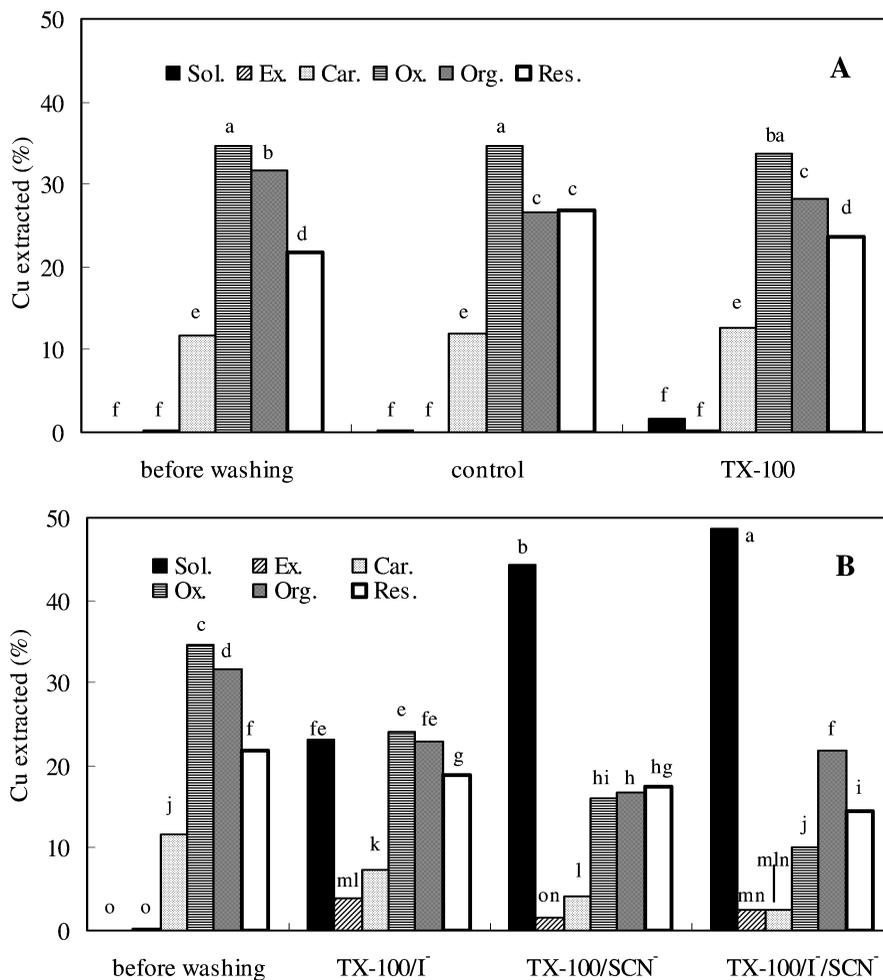


**Figure 7.** Selective sequential fractionation of Cd in soil after treatment in the absence (A) or presence (B) of ligands. For both A and B, means of triplicates with the same letter do not differ significantly (95% confidence level).

limited amounts being adsorbed by the exchangeable sites (4 and 1%). Therefore, the heavy metals contaminating the soil were mostly adsorbed by the oxide fraction, followed by either the organic or the carbonate and hydroxide fractions, the residual fraction and finally the exchangeable sites.

The result of SSE performed on Cd after 7 washings using various washing agents is presented in Figure 7. The control washings desorbed Cd from all fractions with the exception of the oxide fraction (Figure 7A). In the absence of ligand, Triton X-100 desorbed Cd only from the carbonate and hydroxide fractions (Figure 7A) and only at levels that were similar to that obtained with distilled water.

If I<sup>-</sup> was used in combination with surfactant, substantial quantities of Cd were removed from the exchangeable, carbonate and oxide fractions, while with the ligand SCN<sup>-</sup> appreciable amounts of Cd were desorbed from only the carbonate and hydroxide fractions (Figure 7B). Except for the organic fraction, all other fractions desorbed substantial amounts

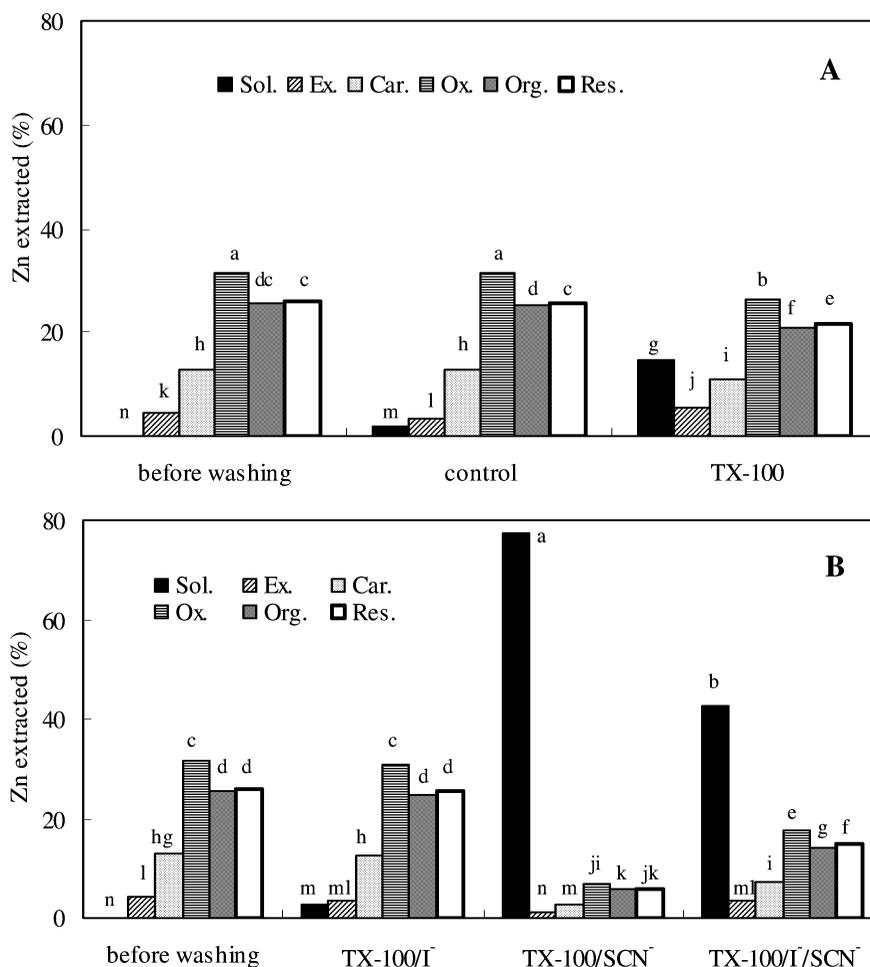


**Figure 8.** Selective sequential fractionation of Cu in soil after treatment in the absence (A) or presence (B) of ligands. For both A and B, means of triplicates with the same letter do not differ significantly (95% confidence level).

of Cd when the ligand mixture was used with Triton X-100 and only the ligand mixture desorbed Cd from the residual fraction (Figure 7B).

The SSE results for Cu are presented in Figure 8, after 7 successive washings. In the absence of ligand (Figure 8A), distilled water and Triton X-100 desorbed similar limited quantities of Cu only from the organic fraction. With I<sup>-</sup> and/or SCN<sup>-</sup>, the desorption of Cu was significant for all fractions except for that of the exchangeable fraction (Figure 8B). Furthermore, the ligand SCN<sup>-</sup> alone or in combination with I<sup>-</sup> desorbed considerable quantities of Cu from the oxide and organic fractions. None of the washing agents desorbed significant amounts of Cu from the exchangeable fraction since this fraction had been burdened with only limited quantities of Cu.

For Zn, desorption occurred from the exchangeable sites with distilled water and, with Triton X-100 alone, from all fractions except the exchangeable sites (Figure 9A). With I<sup>-</sup>, no appreciable desorption was observed from any fraction, whereas with SCN<sup>-</sup>, desorption

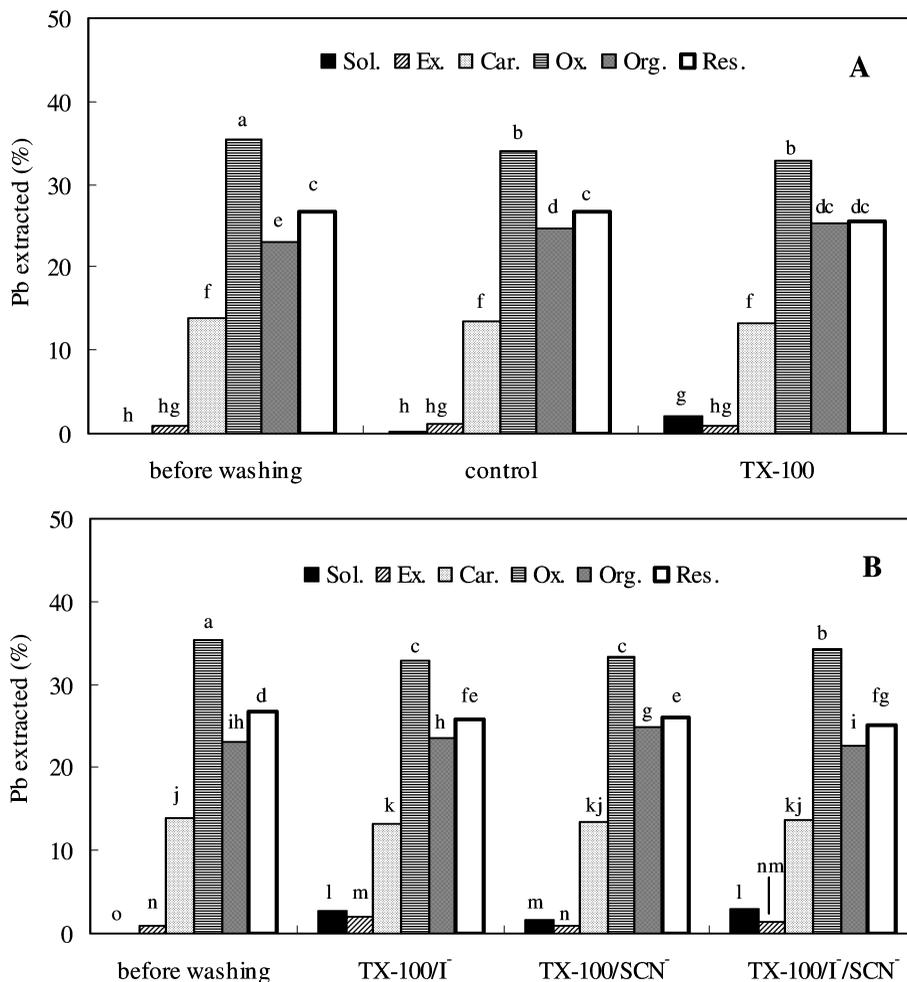


**Figure 9.** Selective sequential fractionation of Zn in soil after treatment in the absence (A) or presence (B) of ligands. For both A and B, means of triplicates with the same letter do not differ significantly (95% confidence level).

occurred from all fractions (Figure 9B). The ligand mixture desorbed Zn from all fractions except from the exchangeable sites. Among agents, only the ligand  $\text{SCN}^-$  with Triton X-100 desorbed Zn from the exchangeable fraction.

As for Pb, both distilled water and Triton X-100 desorbed similar limited quantities from the oxide fraction (Figure 10A). With  $\text{I}^-$ , only limited desorption occurred from the carbonate, hydroxide, oxide and residual fractions, whereas with  $\text{SCN}^-$  or the ligand mixture, a similar lack of desorption was observed for only the oxide and residual fractions (Figure 10B).

In summary, the SSE procedure indicated that each heavy metal metal exhibited a unique behavior. With Cd,  $\text{I}^-$  was more effective than  $\text{SCN}^-$ , since only  $\text{I}^-$  could remove Cd from the exchangeable fraction. For Cu,  $\text{SCN}^-$  was more effective than  $\text{I}^-$ , desorbing Cu from the oxide fraction as well as the others. The limited quantity of Cu initially bound to the exchangeable fraction made it impossible to demonstrate the effectiveness of  $\text{SCN}^-$  in desorbing Cu from these sites. Only  $\text{SCN}^-$  was capable of desorbing Zn from the



**Figure 10.** Selective sequential fractionation of Pb in soil after treatment in the absence (A) or presence (B) of ligands. For both A and B, means of triplicates with the same letter do not differ significantly (95% confidence level).

exchangeable sites because of its selectivity for this metal. Since no reagent combination was effective in desorbing Pb, no appreciable changes were observed with the SSE procedure.

The SSE procedure also indicated that metal desorption from the soil's exchangeable fraction can only be achieved with a ligand having a high affinity for the target metal(s), such as I<sup>-</sup> for Cd. This suggests that the extraction mechanism of the solubilized micelle complex results from an initial complexation between the ligand and the metal adsorbed onto the soil particles, followed by the solubilization of the metal-ligand complex into the surfactant micelle.

## Conclusions

From this study of heavy metal desorption from a contaminated soil using different ligands with the nonionic surfactant, Triton X-100, it can be concluded that:

1. Seven successive washes with only Triton X-100 mobilized only limited quantities of heavy metal (5% of Cd, Cu and Pb and 15% Zn) from the contaminated soil;
2. Seven successive washes with ligand plus surfactant desorbed up to 95% of Cd from the soil;
3. Triton X-100 with  $I^-$  preferentially desorbed Cd whereas Triton X-100 with  $SCN^-$  preferentially desorbed Cu and Zn, indicating that a given metal has specific affinity for a ligand and that the maximum desorption level can only be reached with the appropriate ligand. None of the ligands removed Pb efficiently;
4. The mixture of  $I^-$  and  $SCN^-$ , in combination with Triton X-100, desorbed the highest amounts of all heavy metals except for Zn, which was adversely affected by the presence of  $I^-$ . The most efficient desorption of Zn was obtained using  $SCN^-$  alone with the surfactant.
5. Cd or Zn, respectively, could only be desorbed efficiently from the exchangeable fraction by either  $I^-$  or  $SCN^-$ . This suggests that the extracting mechanism of the solubilized micelle complex results from an initial complexation between the ligand and the metal, followed by the solubilization of the metal-ligand complex within the surfactant micelle.

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