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# Mobility of Adsorbed Zinc in Sandy Loam and Clay Loam Soils as Influenced by *Alkylbenzene Sulphonate Surfactant*

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## ABSTRACT

Release of zinc into the soils as a result of agricultural and industrial activities may pose a serious threat to soil and water pollution. Laboratory soil column experiments were conducted during 2011 to determine the extent of Zn leaching from soil percolated with influent that contained the surfactant alkylbenzene sulphonate. The results of the experiment showed that the mobility of zinc in the two soils namely sandy loam soil and clay loam soil treated with the influent alkylbenzene sulphonate decreases and is also inversely proportional to the concentration of alkylbenzene sulphonate. The concentration of Zn in the column effluents soils percolated with 0.01*M* KCl in 0.01% alkylbenzene sulphonate and with 0.01M KCl in 0.05% alkylbenzene sulphonate were significantly less than those percolated with 0.01*M* KCl with the same volumes of effluents collected. This clearly indicates that the anionic surfactant alkylbenzene sulphonate which is negatively charged have strong affinity for $Zn^{+2}$ in soils and stabilized in soils and thus reduced the mass of zinc leached from the soil columns. Further, it is observed that the characteristics of soil components related to Zn adsorption, affected the adsorption as well as desorption process and subsequent mobility of Zn in soil environment..

**Key words :** Alkylbenzene sulphonate, Leaching, Mobility, Zinc.

Zinc, lead copper, cadmium etc, are commonly encountered hazardous heavy metals and are in the EPA's list of priority pollutants cameron (1992) . Main sources of Zinc into water bodies and soils are electroplating and several alloy industry. It is an integral part of certain enzymes, carbonic anhydrase and alkaline phosphotase. It is micronutrient for plants and an essential element for the growth of humans and animals. General symptoms of zinc toxicity are retardation of plant growth and chlorosis. Excess zinc in soil reduce the urease and acid phosphotase activity and depressed respiration rate.

The leachabillity or mobility of heavy metals in a soil mainly depend on biogeochemical processes such as adsorption and dissolution which are in turn affected by soil p$^{H}$, ionic strength and composition of the soil solution, the clay and organic matter content of the soil and the amount of kind of heavy metals in the soil (Gray *et al.,* 1999). The leaching agents with pH Fadjustor and surfactants may be added to the wash water for the enhanced metal removal from soil (Deuron *et al.*, 2002). Among these, surfactant enhanced removal of heavy metals appears to be an attractive method since surfactants are low cost and bio-degradable and hence they would not accumulate in soils.

The aim of the present study was to determine the extent of leaching Zn(II) from soils that were amended with influent containing the anionic surfactant, alkylbenzene sulphonate under saturated moisture conditions using column experiments

## MATERIAL AND METHODS

The two types of soils namely sandy loam soil and clay loam soil were collected from 40 cm depth of soil profiles. The sandy loam soil (fine, loamy, siliceous, isohyperthermic, Typic Ustorthents) was collected from Merlapaka village(lies between $13^{0}36^{1}$ and $13^{0}40^{1}$ North latitude and $79^{0}18^{1}$ and $79^{0}28^{1}$ East longitude) located in Yerpedu mandal of Chittoor District of Andhra Pradesh, India and the clay loam soil (fine, smetitic, isohyperthermic, Vertic Haplustepts) was collected from Ramachandra puram Village ( lies in between $13^{0}27^{1}$ and $13^{0}31^{1}$ North latitude and $79^{0}33^{1}$ and $79^{0}37^{1}$ East longitude) located in Ramachandrapuram mandal of Chittoor District of Andhra Pradesh, India

The soils were air dried and ground to pass through a 2 mm sieve and stored in plastic bags before use. The selected physical and chemical properties of the two soils are listed in Table 1. Soil pH was measured in 1:2.5 (w/v) soil / water

Table 1. Some selected characteristics of the soils.

| Soil Characteristics | Clay loam soil of Ramachandhrapuram Village | Sandy loam Soil of Merlapaka village |
|---|---|---|
| Texture | Clay loam | Sandy loam |
| Sand % | 43.70 | 66.30 |
| Slit % | 28.20 | 5.27 |
| Clay % | 28.10 | 8.43 |
| Bulk Density $g/m^3$ | 1.47 | 1.24 |
| Particle Density $Mg\ m^{-3}$ | 2.46 | 2.47 |
| Water holding Capacity % | 38.51 | 41.11 |
| Volume Expansion % | 17.35 | 6.73 |
| L.O.I % | 5.85 | 6.35 |
| Organic Carbon ( $g\ kg^{-1}$) | 13.84 | 10.76 |
| Total Nitrogen % | 0.07 | 0.04 |
| C/N ratio | 10.00 | 8.98 |
| $CaCO_3$ % | 1.30 | 3.00 |
| PH | 7.70 | 7.86 |
| EC $dsm^{-1}$ | 0.02 | 0.23 |
| CEC $Cmol(p^+)Kg^{-1}$ | 24.47 | 16.87 |
| $SiO_2$ % | 80.40 | 78.38 |
| $Fe_2O_3$ % | 2.18 | 5.72 |
| $Al_2O_3$ % | 9.57 | 10.96 |
| Total Zinc content ($mg\ Kg^{-1}$) | 28.60 | 21.40 |
| CBD extractable Fe ( $g\ Kg^{-1}$) | 4.98 | 3.96 |
| CBD extractable Al ( $g\ Kg^{-1}$) | 0.98 | 0.69 |
| CBD extractable Mn ( $g\ Kg^{-1}$) | 0.18 | 0.14 |
| Oxalate extractable Fe ( $g\ Kg^{-1}$ | 54.60 | 44.70 |
| Oxalate extractable Al ( $g\ Kg^{-1}$) | 9.34 | 6.02 |
| Oxalate extractable Mn ( $g\ Kg^{-1}$) | 5.08 | 3.20 |
| Na- Pyrophosphate extractable Fe ( $gKg^{-1}$) | 5.96 | 8.46 |
| Na- Pyrophosphate extractable Al( $g\ Kg^{-1)}$ | 2.01 | 1.86 |
| Na- Pyrophosphate extractable Mn ( $g\ Kg^{-1}$) | 0.36 | 0.24 |

** Note: Each measurement or determination is the mean of three replicates and the standard deviation for each data is within 5% of each mean.

suspension. Electrolytic conductivity (EC) of the soils samples was determined in saturation extract by using Systronics conducting bridge 305. Organic carbon content was determined by the Walkley-Black's wet combustion method (Nelson and Sommer 1982).The free $CaCO_3$ content of soil samples was determined by treating the soil with known volume of standard HCl and back titrating the unused acid with standard alkali using bromothymol blue as an indicator (Piper 1966). The crystalline and non-crystalline forms and the form bound to organics of Fe, Al, and Mn in soils were extracted with Citrate – Bicarbonate – Dithionite (CBD) (Mehra and Jackson 1960 ), 0.2M Oxalate – Oxalic acid (pH 3) (Mckeague and Day 1966),and 0.1M Sodium pyrophosphate ($P^H$ 10) (Loveland and Digby 1984 )respectively and determined by atomic absorption spectrophotometer. Total nitrogen content was estimated by modified Kjeldhal method using sulphuric salicylic acid mixture. The sand, silt , and clay contents, cation exchangeable bases were determined by using standard methods. Total zinc content in soil was extracted with con.$HNO_3$ and HCl digestion method and quantified by using Shimadzu atomic absorption spectroscopy AA-6300.

**Alkylbenzene sulphonate surfactant**

Alkylbenzene sulphonate was collected from Exodetergents industry, Kodur, Kadapa district, Andhra Pradesh, India. 0.01% Alkylbenzene sulphonate and 0.05% alkylbenzene sulphonate solutions were prepared from the stock reagent.

**Zinc sulphate solution**

Stock solution (1000 mg/L) of Zn (II) was prepared by dissolving zinc sulphate in deionised double distilled water. Working standards were prepared by progressive dilution of stock metal solution using deionised doubled distilled water.

***Soil column leaching studies***

Borosilicate glass columns (18 mm inner diameter, 500 mm in length) were used in the experiments . One cm layer of glass wool was applied in the bottom of the columns. Each glass column was packed with 50 g of sandy loam soil of Merlapaka village or 50 g of clay loam soil of Ramachandrapuram village and on the top another acid-washed glass wool layer was applied.. The soil columns were saturated from the bottom with 0.01 *M* KCl. After saturation the soils were leached with 0.01*M* KCl until the input and output solutions had the equal concentration of electrolytes, which was 16 pore volumes for sandy loam soil and 11 pore volumes for clay loam soil. The influent solution was then changed to (1) 0.01*M* KCl in 0.01% Alkylbenzene sulphonate (2) 0.01*M* KCl in 0.05% Alkylbenzene sulphonate. During the leaching period of the soil columns, the water head of 2cm height was maintained manually for every 2-3 days.

All treatments were conducted in duplicate. The column effluents were collected for 3-4 days. The volumes of effluents (V) were recorded and the Zn concentration in the effluents were determined with the atomic absorption spectrophotometer of Shimadzu AA-6300. Relative concentration ($C/C_o$) was calculated as the ratio of the Zn concentration in effluent to the Zn concentration in influent. The pore volumes ($V_o$) of sandy loam soil and clay loam soil were 28 $cm^3$ and 30 $cm^3$, respectively. This was calculated from the difference of weights between water saturated and oven-dried soil columns. The water contents at saturation of sandy loam soil column and clay loam soil column were 0.68 $cm^3$ and 0.84 $cm^3$, respectively. Based on the volumes of soil columns, the bulk densities calculated were found to be 1.249 g / $cm^3$ for sandy loam soil and 1.470 g / $cm^3$ for clay loam soil.

## RESULTS AND DISCUSSION

**Properties of soils**

Both soils collected from Merlapaka village and Ramachandrapurm village were slightly alkaline in reaction and their texture was sandy loam and clay loam, respectively. The total Zn content in sandy loam soil of Merlapaka village and clay loam soil of Ramchandrapuram village were 21.40 mg $kg^{-1}$ and 28.60 mg $kg^{-1}$, respectively. Without concerning, whether the crystalline and non-crystalline forms or the form bound to organics of Fe, Al and Mn, the sequence of the amount extracted was Fe > Al > Mn. Moreover, the non-crystalline from of Fe, Al and Mn was the highest amount extracted among the three forms for both soils. However, except for the amount of Na-pyrophosphate extractable Fe, the extracted amounts of the three forms of Fe, Al, and Mn of clay loam soil of Ramachandrapuram village were higher than those of sandy loam soil of Merlapaka village. CEC, organic carbon (%), total nitrogen (%), exchangeable bases, $CaCO_3$ (%), slit( %), clay (% ), except sand (%) of clay loam soil of Ramachandrapuram village were higher than those of sandy loam soil of Merlapaka village.

**The effect of Alkylbenzene sulphonate surfactant on Zn mobility in soils**

Both sandy loam soil columns of Merlapaka village and clay loam soil columns of Ramachandrapuram village were leached with 0.01*M* KCl or 0.01 *M* KCl in 0.01 % alkylbenzene sulphonate or 0.01*M* KCl in 0.05% alkylbenzene sulphonate. The effect of alkylbenzene sulphonate on the leaching of Zn from clay loam soil of Ramachandrapuram village is shown in Figure 1. Concentration of Zn in the effluents of soil columns treated with 0.01*M* KCl, and 0.01*M* KCl in 0.01% alkylbenzene sulphonate, and 0.01 *M* KCl in 0.05% alkylbenzene sulphonate was almost the same up to near 8 pore volumes ($V/V_o$ H" 8) (Figure 1). However, after 8 pore volumes, Zn concentration in the effluent in 0.01*M* KCl treatment ( control) was higher than that of 01*M* KCl in 0.01 % alkylbenzene sulphonate treatment which was a little higher than that of 0.01 *M* KCl in 0.05 % alkylbenzene sulphonate treatment . After 18 pore

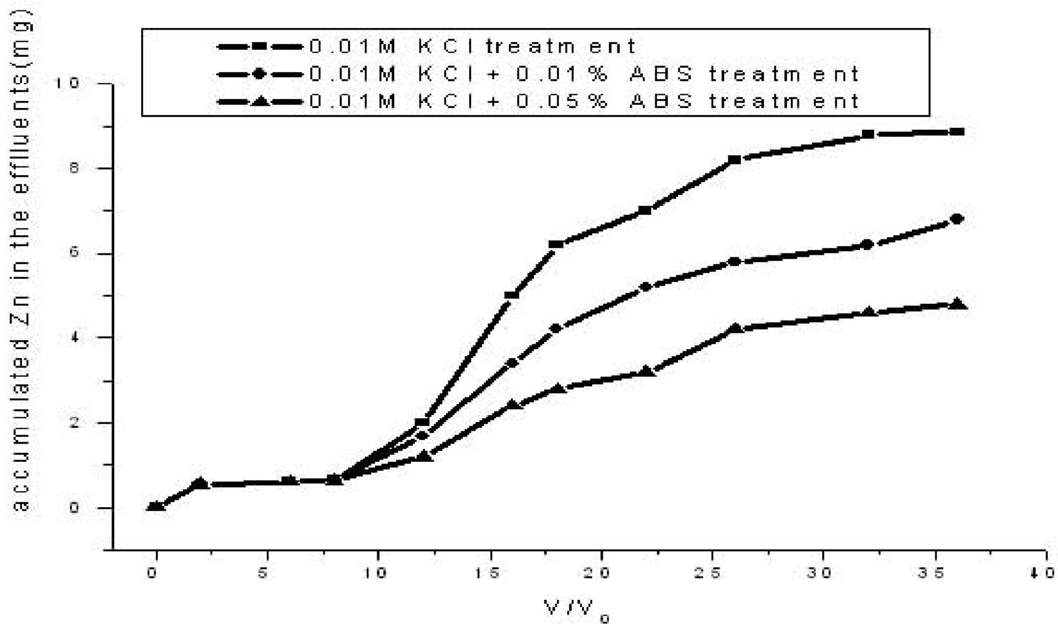


Fig. 1. The accumulated Zn in the effluents of clay loam soil column leached with 0.01M KCl in absence and in the presence of alkylbenzene sulphonate (ABS).

Note: Each data point in the figure is the mean of duplicated determination and the standard deviation for each data point is within 5% of each mean.

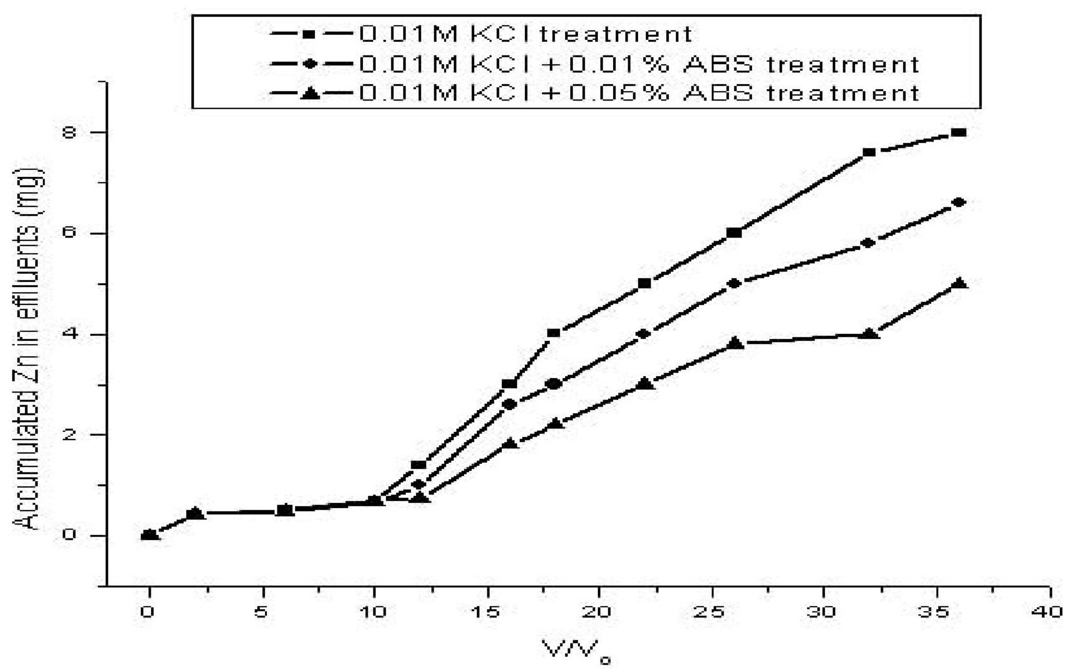


Figure 2. The accumulated Zn in the effluents of sandy loam soil column leached with 0.01M KCl in absence and in the presence of alkylbenzene sulphonate (ABS).

Note: Each data point in the figure is the mean of duplicated determination and the standard deviation for each data point is within 5% of each mean.

volumes, significant difference in concentration of Zn in effluents between 0.01*M* KCl treatment, 01*M* KCl in 0.01% alkylbenzene sulphonate treatment, 0.01*M* KCl in 0.05% alkylbenzene sulphonate treatment was observed with higher concentration of Zinc in the effluent of 01M KCl treatment than with the other two treatments (Figure 1).

The changes in the trends of accumulated Zn in the effluents of sandy loam soil columns of Merlapaka village leached with 0.01 M KCl or 0.01M KCl in 0.01% alkylbenzene sulphonate or 0.01 M KCl in 0.05% alkylbenzene sulphonate were different from those of clay loam soil columns of Ramachandrapuram village (Fig. 2 and 1). From the beginning of 10 pore volumes, Zn concentration in the effluent of 0.01 *M* KCl treatment (control) is higher than that of in .01*M* KCl in 0.01 % alkylbenzene sulphonate which was little higher than that of 0.01M KCl in 0.05 % alkylbenzene sulphonate treatment (Fig. 2). For the leached pore volumes around 16 to 22 significant difference in the amount of Zn accumulated between the two soil columns leached with 0.01 *M* KCl, 0.01*M* KCl in 0.01 % aklylbenzene sulphonate and 0.01*M* KCl in 0.05 % alkylbenzene sulphonate were observed. From near 26 pore volumes, the Zn concentration in the effluent of 0.01 *M* KCl treatment was significantly higher than in the effluent of 0.01*M* KCl in 0.01% alkylbenzene sulphonate which was a little higher than 0.01M KCl in 0.05% alkylbenzene sulphonate. These results clearly indicated that the input of the anionic surfactant alkylbenzene sulphonate retarded the mobility of Zn in soil. Further, as the concentration of alkylbenzene sulphonate increased, the mobility of Zn in soil also decreased. The reasons for the above trend is due to that zinc strongly bound to organic and mineral components of the soil. Hence, its leachability is very low. In the presence of anionic alkylbenzene sulphonate leachability of zinc further decreases as Zn is bound to anionic alkylbenzene sulphonate which was strongly adsorbed in the soil components.

The soil column leaching experiments showed that the addition of alkylbenzene sulphonate in the influent decreased the Zn concentrations in the effluents of the two soil columns. This indicates that mobility of zinc in the two soils namely sandy loam soil and clay loam soil treated with the influent alkylbenzene sulphonate decreases and is also inversely proportional to the concentration of alkylbenzene sulphonate. The result obtained thus implicate that alkylbenzene sulphonate immoblilzes the mobility of Zn in the soils and decrease the risk of ground water contaminated by Zn originated from Zn containing soils in the presence of alkylbenzene sulphonate surfactant released from urban waste water.

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