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# Mobility of adsorbed Lead in sandy loam and clay loam soils as influenced by *Alkylbenzenesulphonate surfactant*

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**ABSTRACT**
*Realease of lead onto the soils as a result of agricultural and industrial activities may pose a serious threat to the environment. A laboratory soil column experiments were conducted to determine the extent of Pb leaching from soil percolated with influent that contained the surfactant alkylbenzenesulphonate. The results of Pb breakthrough curves (BTCs) showed that more pore volumes of influents were required to reach the relative concentration ratio of 1 ($C/C_0$=1) for the two soils namely sandy loam soil and clay loam soil treated with the influent alkylbenzenesulphonate. The concentration of Pb in the column effluents of soils percolated with 0.01M KCl in 0.01% alkylbenzenesulphonate and with 0.01M KCl in 0.05% alkylbenzenesulphonate were significantly less than those percolated with 0.01M KCl with the same volumes of effluents collected. This clearly indicates that the anionic surfactant alkylbenzenesulphonate which are negatively charged have strong affinity for $Pb^{+2}$ in soils and stabililzed in soils and thus reduced lead mass leached from the soil columns. Further it is observed that the characteristics of soil components related to Pb adsorption affected the adsorption as well as desorption process and subsequent mobility of Pb in soil environment.*

**Keywords:** Lead, Mobility, Breakthrough Curves (BTCs), Leaching, Alkylbenzenesulphonate.

## INTRODUCTION

Lead, Zinc, Copper, Cadmium are commonly encountered hazardous heavy metals and are in the EPA's list of priority pollutants [1]. Main sources of lead into environment and soils are the manufacture of storage batteries, pigments lead glass, mining ,metal electroplating, painting , coating, smelting, petrochemical, plumbing fuels, photographic materials, matches and explosives. Apart from this , lead is also used in insecticides, plastic water pipes, beverages, ointments and medicinal concoctions for flavouring and sweetening . These industries discharge lead into the environment without adequate treatment [2]. The current Environmental Protection Agency (EPA) standard for lead in waste water and drinking water is 0.5 and 0.05 $mgL^{-1}$ respectively[3]. Lead has both acute and chronic effects in humans. It may cause anemia , head ache, chills, diarrhea and reduction in haemoglobin formation. Lead poisoning causes, severe damage to kidneys , nervous system, reproductive system, liver and brain[4 ].

Heavy metals in soils present in five forms, Exchangeable, carbonate, Fe – Mn oxide,organic and residual fractions[5]. The adsorption of heavy metal ions by soil particles involves cation exchange, specific adsorption, organic complexation and co-precipitation mechanisms [6]. Heavy metals are highly persistent in soil with residence time in the order of thousands of years. Excessive accumulation of heavy metals can have deleterious effects in soils fertility, affect ecosystem functions and constitute a health resik to animals and human beings[7]

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 [8,9,10,11,12,13,14]. The leaching agents with $p^H$ adjustor and surfactants may be added to the wash water for the enhanced metal removal from soil[15]. 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 Pb(II) from soils that were amended with influent containing the anionic surfactant, alkylbenzenesulphonate under saturated moisture conditions using column experiments and to study the Pb(II) adsorption capacity of both soils and the associated breakthrough points of the amount of Pb(II) as influenced by alkylbenzenesulphonate in soil columns.

## EXPERIMENTAL SECTION

***Materials and Methods***:

The two types of soils namely sandy loam soil and clay loam soil were collected to 40cm depth of soil profiles. The sandy loam soil (fine, loamy, siliceous, Isothyperthermic, Typic Ustorthents), was collected from Merlapaka village located in Yerpedu mandal of Chittoor District of Andhra Pradesh India (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), and the clay loam soil (Fine, Smetitic, Iso-hyperthermic, Vertic, Hapylustepts) was collected from RamachandrapuramVillage located in Ramachandrapuram mandal of Chittoor District of Andhra Pradesh, India ( 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).

Each soil was 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 $p^H$ was measured in 1:2.5 (w/v) soil / water 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 [16]. 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 [17]. 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) [18,19], 0.2M Oxalate – Oxalic acid (pH 3) [19] and 0.1M Sodium pyrophosphate (pH 10) [20,21] respectively and determined by atomic absorption spectrophotometer. Total nitrogen content was estimated by modified Kjeldhal method using sulphuric salicylic acid mixture [22]. The sand, silt , and clay contents, cation exchangeable bases were determined by using standard methods. Total lead content in soil was extracted with con.$HNO_3$ and HCl digestion method and quantified by using Shimadzu atomic absorption spectroscopy AA-6300.

**Table 1: Some selected characteristics of the Soils[a]**

| **Soil Characteristics** | Clay loam soil of Ramachandhrapuram Village | Sandy loam Soil of Merlapaka village |
|---|---|---|
| Texture | Clay loam | Sandy loam |
| Sand % | 43.7 | 66.30 |
| Slit % | 28.2 | 5.27 |
| Clay % | 28.1 | 8.43 |
| Bulk Density $g/m^3$ | 1.47 | 1.249 |
| 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 % | 0.071 | 0.049 |
| C/N ratio | 10 | 8.98 |
| $CaCO_3$ % | 1.30 | 3 |
| PH | 7.7 | 7.86 |
| EC $dsm^{-1}$ | 0.020 | 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 Lead content ($mg\ Kg^{-1}$) | 40.61 | 36.33 |
| 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 ( $g\ Kg^{-1}$ | 54.6 | 44.7 |
| 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 |

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

### *Alkylbenzenesulphonate surfactant:*

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

### *Lead nitrate Solution:*

Stock solution (1000 mg/L) of Pb (II) was prepared by dissolving $Pb(NO_3)_2$ in deionized double distilled water. Working standards were prepared by progressive dilution of stock metal solution using deionized doubled distilled water.

***Soil Column leaching studies:***

Borosilicate glass columns (18 mm inner diameter, 500 mm in length) were used in the experiments . A 1cm layer of glass wool was applied in the bottom of the columns. Each glass column was packed with 50g of sandy loam soil of Merlapaka village or 50g 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 0.01M 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) 0.01M KCl in 0.01% Alkylbenzenesulphonate with Pb concentration of 50 $mgL^{-1}$ (2) 0.01M KCl in 0.05% Alkylbenzenesulphonate with Pb concentration of 50 $mgL^{-1}$ (3) 0.01 M KCl with Pb concentration of 50 mg $L^{-1}$ (4) 0.01M KCl in 0.01% Alkylbenzenesulphonate (5) 0.01M KCl in 0.05% Alkylbenzenesulphonate or (6) 0.01M KCl only. 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 Pb concentration in the effluents were determined with the atomic absorption spectrophotometer Shimadzu AA-6300. Relative concentration ($C/C_o$) was calculated as the ratio of the Pb concentration in effluent to the Pb concentration in influent. The pore volumes ($V_o$) of sandy loam soil, 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 $gcm^{-3}$ for sandy loam soil and 1.47 $gcm^{-3}$ for clay loam soil. In order to study the Pb adsorption capacity of both soils and the associated break through points of the amounts of Pb as influenced by alkylbenzenesulphonate in soil columns, Pb concentration of 50 mg $L^{-1}$ in (1) 0.01 M KCl, (2) in 0.01 M KCl in 0.01% Alkylbenzenesulphonate and (3) in 0.01 M KCl in 0.05% alkylbenzenesulphonate was prepared in the influent of soil column leaching experiments. The breaks through curves (BTCs) were plotted using relative concentration ($C/C_o$) versus fractional volume ($V/V_o$), where V is the cumulative drainage volume and $V_0$ is pore volume.

## RESULTS AND DISCUSSION

***Soils:***

Both soils, one collected from Merlapaka village and another from Ramachandrapurm village were slightly alkaline and their texture was sandy loam and clay loam respectively. The organic ‘C’ content of the two soils were not high (Table 1). The total Pb contents in sandy loam soil of Merlapaka village and clay loam soil of Ramchandrapuram village were 36.33mg $kg^{-1}$ and 40.61 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 Alkylbenzenesulphonate surfactant on Pb mobility in soils.***

Both sandy loam soil columns of Merlapaka village and clay loam soil columns of Ramachandrapuram village were leached with 0.01M KCl or 0.01 M KCl in 0.01% alkylbenzenesulphonate or 0.01M KCl in 0.05% alkylbenzenesulphonate. The effect of alkylbenzenesulphonate on the leaching of Pb from clay loam soil of Ramachandrapuram village is shown in Figure 1. Concentration of Pb in the effluents of soil columns treated with 0.01M KCl, and 0.01M KCl in 0.01% alkylbezenesulphonate, and 0.01 M KCl in 0.05% alkybenzenesulphanate was almost the same up to near 12 pore volumes ($V/V_o \simeq 12$) (Figure 1). However, after 12 pore volumes, Pb concentration in the effluent in 0.01M KCl treatment ( control) was higher than that of 01M KCl in 0.01 % alkylbenzenesulphonate treatment which was a little higher than that of 0.01 M KCl in 0.05 % alkylbenzenesulphonate treatment . After 26 pore volumes, significant difference in concentration of Pb in effluents between 0.01M KCl treatment, 01M KCl in 0.01% alkylbenzenesulphonate treatment, 0.01M KCl in 0.05% alkylbenzenesulphonate treatment was observed with higher concentration of Lead in the effluent of 01M KCl treatment than with the other two treatments (figure 1).

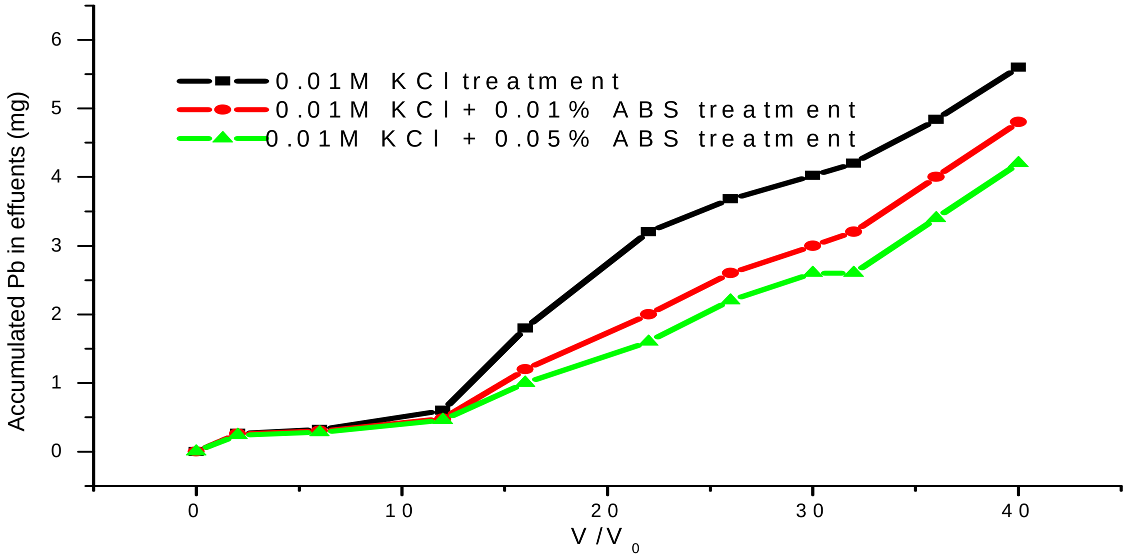


**Figure1: The accumulated Pb in the effluents of clay loam soil column leached with 0.01M KCl in absence and in the presence of alkylbenzenesulphonate (ABS).**

The changes in the trends of accumulated Pb in the effluents of sandy loam soil columns of Merlapaka village leached with 0.01 M KCl or 0.01M KCl in 0.01% alkylbenzenesulphonate or 0.01 M KCl in 0.05% alkylbenzenesulphonate were different from those of clay loam soil columns of Ramachandrapuram village (Figures 2 and 1). From the beginning of 18 pore volumes, Pb concentration in the effluent of 0.01 M KCl treatment (control) is higher than that of in .01M KCl in 0.01 % alkylbenzenesulphonate which was little higher than that of 0.01M KCl in 0.05 % alkylbenzenesulphonate treatment (Figure 2).

For the leached pore volumes around 21 to 24 significant difference in the amount of Pb accumulated between the two soil columns leached with 0.01 M KCl, 0.01M KCl in 0.01 % aklylbenzenesulphonate and 0.01M KCl in 0.05 % alkylbenzenesulphonate were observed. From near 32 pore volumes, the Pb concentration in the effluent of 0.01 M KCl treatment was significantly higher than in the effluent of 0.01M KCl in 0.01% alkylbenzenesulphonate which was a little higher than 0.01M KCl in 0.05% alkylbenzenesulphonate. These results clearly indicated that the input of the anionic surfactant alkylbenzenesulphonate retarded the mobility of

Pb in soil. Further as the concentration of alkylbenzenesulphonate increased, the mobility of Pb in soil also decreased. The reasons for the above trend is due to that lead strongly bound to organic and mineral components of the soil. Hence its leachability is very low. In the presence of anionic alkylbenzenesulphonate leachability of lead further decreases as Pb is bound to anionic alkylbenzenesulphonate which was strongly adsorbed in the soil components.

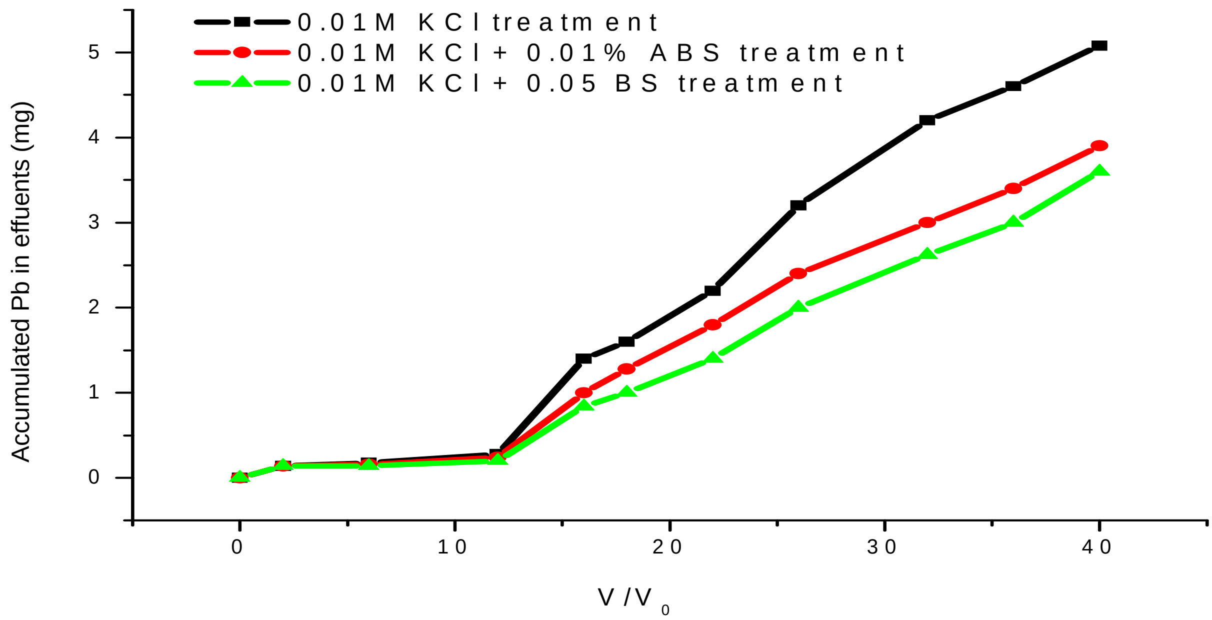


**Figure2: The accumulated Pb in the effluents of sandy loam soil column leached with 0.01M KCl in absence and in the presence of alkylbenzenesulphonate (ABS).**

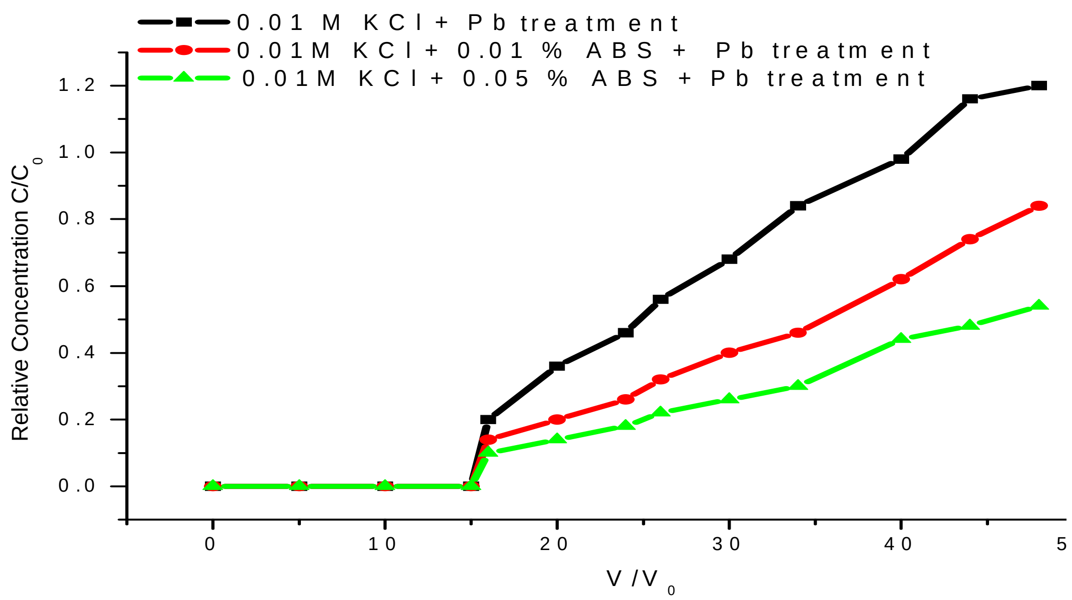


**Figure3: The Pb breakthrough curves of clay loam soil column treated with 0.01% and 0.05% concentration of alkylbenezenesulphonate influent.**

The adsorption of Pb by the two soils and the mobility of Pb in the soil columns were analysed by the breakthrough curves (BTCs) of Pb in soil columns. The Pb BTCs of the two soils showed that the added Pb in influent can be retained by soil components to some extent. For both soils, the added Pb was leached out in effluents, when the influent used.

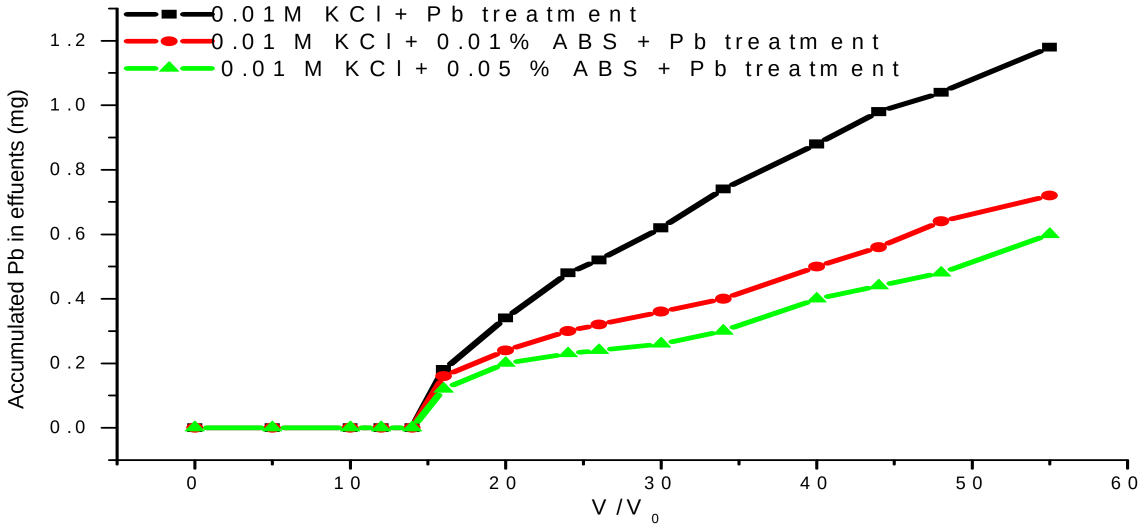


**Figure4: The Pb breakthrough curves of sandy loam soil column treated with 0.01% and 0.05% concentration of alkylbenezenesulphonate influent**

was above 16 porevolumes (Figures 3 and 4). The Pb breakthrough point ($C/C_o$=1) for clay loam soil of Ramachandrapuram village treated with the influent of 50mg $L^{-1}$ Pb and 0.01M KCl was 40 pore volumes, while the $C/C_0$ was only 0.5 at near 36 pore volumes for soil column treated with the influent of 50 mg $L^{-1}$ Pb in 0.01M KCl in 01 % alkylbenzenesulphonate and while the $C/C_0$ was only 0.5 at near 48 pore volumes for soil column treated with the influent of 50 mg $L^{-1}$ Pb in 0.01M KCl in 05% alkylbenzenesulphonate . This indicates that in the absence of anionic surfactant alkylbenzenesulphonate leachabillity of lead is more compared to its leachability in the presence of the added alkylbenzenesulphonate.

The Pb break through point ($C/C_o$=1) was near 46 pore volumes for sandy loam soil of Merlapaka village, when treated with the influent of 50 mg $L^{-1}$ Pb and 0.01 M KCl and while C/Co was only 0.5 at near 40 pore volumes for sandy loam soil of Merlapaka village when treated with influent 50 mg $L^{-1}$ Pb and 0.01 M KCl in 0.01% alkylbenzenesulphonate, $C/C_0$ was 0.5 at near 52 porevolume while treated with influent of 0.01M KCl in 0.05% alkylbenzenesulphonate, This clearly indicates that anionic alkylbenzenesulphonate shows negative effect on the leachabillity of Pb from the soil column . It can be attributed that lead can form complexes with alkylbenzenesulphonate, these complexes may be strongly adsorbed by soils matrix and has low mobility. As the concentration of alkylbenzenesulphonate increased in the soil the leachabillity of lead decreases.

## CONCLUSION

The soil column leaching experiments showed that the addition of alkylbenzenesulphonate in the influent decreased the Pb concentrations in the effluents of the two soil columns. Moreover Pb BTC s showed that more pore volumes were required for the soils treated with influent that contained alkylbenzenesulphonate than those for the corresponding soils treated with influent that contained no alkylbenzenesulphonate to reach the relative concentration ratio of (C/Co) . The result obtained thus implicate that alkylbenzenesulphonate immoblilzes the mobility of Pb in the soils and decrease the risk of ground water contaminated by Pb originated from Pb containing soils in the presence of alkylbenzenesulphonate surfactant released from urban waste water.

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