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Mobility of adsorbed chromium in sandy loam and clay loam soils as influenced by Alkylbenzenesulphonate surfactant

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ABSTRACT

A laboratory soil column experiments were conducted to determine the extent of Cr leaching from soil percolated with influent that contained the surfactant alkylbenzenesulphonate. The results of Cr breakthrough curves (BTCs) showed that less 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 Cr in the column effluents of soils percolated with 0.01M KCl in 0.05% alkylbenzenesulphonate and with 0.01M KCl in 0.01% alkylbenzenesulphonate were significantly higher 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 higher potential for competing the adsorption sites with Cr on soils, leading to increasing mobility of Cr which also exists as anion ($Cr_2O_7^{2-}$) in soil. Further it is observed that the characteristics of soil components related to Cr adsorption affected the adsorption as well as desorption process and subsequent mobility of Cr in soil environment.

Key words: Chromium, Carcinogenic, Mobility, Breakthrough Curves (BTCs), Leaching, Alkylbenzenesulphonate.

INTRODUCTION

The mobility of the metals deposited in soil depends on interaction with solid phases during transport by water through open spaces. Both water circulation and the chemical processes that act on charged species of metals are dependent on the hydrological, mineralogical and chemical

properties of the soil [1]. The main sorption surfaces are clay particles and organic matter [2,3]. Organic matter content, cation exchange capacity, specific surface area, carbonate content and iron oxide content P^H are the principal soil characteristics that determine the capacity to retain metal pollutants [4]. Two mechanisms influence the adsorption of heavy metals by soils. One is non-selective adsorption in which the metallic cations act as counter ions in the diffuse layer. The other is selective adsorption in which surface complexes are formed [5]. The importance of each of these mechanisms depends on the metal and the type of soil in which the study is carried out [6]. Chromium exists in two stable oxidation states, Cr (III) and Cr (VI). The Cr (VI) state is of particular concern because this form is hazardous to health due to its carcinogenic properties [7]. Chromium is introduced into the natural bodies of water from industries like electroplating, leather tanning, cement industries, steel industries, photography and inorganic chemical productions [8]. Cr (VI) causes skin irritation resulting in ulcer formation. Exposure to Cr(VI) leads to liver damage, pulmonary congestion and oedema [9].

The objective of this study was to determine the extent of leaching of Cr (VI) that exists as $Cr_2O_7^{2-}$ from soils that were percolated with influent containing the anionic surfactant alkylbenzenesulphonate under saturated moisture conditions using soil column experiment and to study the Cr adsorption capacity of both soils and the associated break through points of the amounts of Cr 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, Isohyperthermic, Typic Ustorthents), was collected from Merlapaka village located in Yerpedu mandal of Chittoor District of Andhra Pradesh India (lies between $13^{\circ}36'$ and $13^{\circ}40'$ North latitude and $79^{\circ}18'$ and $79^{\circ}28'$ East longitude), and the clay loam soil (Fine, Smetitic, Iso-hyperthermic, Vertic, Haplustepts) was collected from Ramachandrapuram Village located in Ramachandrapuram mandal of Chittoor District of Andhra Pradesh, India (lies in between $13^{\circ}27'$ and $13^{\circ}31'$ North latitude and $79^{\circ}33'$ and $79^{\circ}37'$ East longitude).

Each soil was air dried and ground to pass through a 2 - mm sieve. Physical and chemical properties of the two soils are listed in table 1. Soil pH was measured in 1:1 (w/v) soil / water suspension. Organic carbon content was determined by the walkley-Black's wet combustion method [10]. Chromium in soil as water soluble Cr and the chromium bound to the components of Al (Al-Cr), Fe (Fe-Cr) and Ca (Ca-Cr) was sequentially extracted with 16 M HNO_3 , 8.8 M (30%) H_2O_2 , concentrated HF [11]. Then the total chromium content was determined in the extract by using atomic absorption spectrophotometer. 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) [12,13], 0.2M Oxalate – Oxalic acid (pH 3) [13] and 0.1M Sodium pyrophosphate (pH 10) [14,15] respectively and determined by atomic absorption spectrophotometer.

Table 1: Some selected characteristics of the soils^a

Soil	Texture	H	Organic 'C' (g kg ⁻¹)	Cr (mg kg ⁻¹)	Water soluble Cr (mg kg ⁻¹)	Al-Cr (mg kg ⁻¹)	Fe-Cr (mg kg ⁻¹)	Ca-Cr (mg kg ⁻¹)	CBD extractable			Oxalate extractable			Na-Pyrophosphate extractable		
									Fe (g kg ⁻¹)	Al (g kg ⁻¹)	Mn (g kg ⁻¹)	Fe (g kg ⁻¹)	Al (g kg ⁻¹)	Mn (g kg ⁻¹)	Fe (g kg ⁻¹)	Al (g kg ⁻¹)	Mn (g kg ⁻¹)
Clay loam soil of Ramachandrapuram	Clay loam	7.89	13.84	26.8	ND ^b	6.02	8.38	4.06	4.98	0.98	0.18	54.6	9.34	5.08	5.96	2.01	0.36
Sandy loam soil of Merlapaka	Sandy loam	7.6	10.76	14.8	ND ^b	2.03	3.42	1.86	3.96	0.69	0.14	44.7	6.02	3.20	8.46	1.86	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

^bNot detectable (<0.002 mg kg⁻¹)

Alkylbenzenesulphonate surfactant:

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

Potassium dichromate Solution:

Stock solution (1000 mg/L) of Cr (VI) was prepared by dissolving K₂Cr₂O₇ 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:

Each glass (borosilicate glass) column (18 mm inner diameter, 500 mm in length) was packed with 50g of sandy loam soil of Merlapaka village or 50g of clay loam soil of Ramachandrapuram village (particle size distribution was <0.25 mm 25%, 0.25-0.05mm 25%, and 0.5-2mm 50%). 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 Cr concentration of 50 mgL⁻¹ (2) 0.01M KCl in 0.05% Alkylbenzenesulphonate with Cr concentration of 50 mgL⁻¹ (3) 0.01 M KCl with Cr 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 Cr concentration in the effluents were determined with atomic absorption spectrophotometer. Relative concentration (C/C_0) was calculated as the ratio of the Cr concentration in effluent to the Cr concentration in influent. The pore volumes (V_0) of sandy loam soil, clay loam soil were 30 cm^3 and 28 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 Cr adsorption capacity of both soils and the associated break through points of the amounts of Cr as influenced by alkylbenzenesulphonate in soil columns, Cr concentrations 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 experiment. The breaks through curves (BTCs) were plotted using relative concentration (C/C_0) versus fractional volume (V/V_0), 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' contents of the two soils were not high (Table 1) and were within the average range of organic contents of the agricultural soils in Chittoor district. The total Cr contents in sandy loam soil of Merlapaka village and clay loam soil of Ramchandrapuram village were 13.8 mg kg^{-1} and 24.8 mg kg^{-1} respectively which are higher than the average Cr content (6.28 mg kg^{-1}) in the soils of Chittoor district. Water soluble Cr was not detected in both the soils. However, appreciable amounts of Al - Cr, Fe- Cr and Ca-Cr were found in both the soils but clay loam soil of Ramachandrapuram village had higher concentrations than sandy loam soil of Merlapaka village (Table 1). 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 $\text{Fe} > \text{Al} > \text{Mn}$. Moreover, the non-crystalline form 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 (Table 1).

The effect of Alkylbenzenesulphonate surfactant on Cr 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 Cr from clay loam soil of Ramachandrapuram village is shown in Figure 1. Concentration of Cr in the effluents of soil columns treated with 0.01M KCl, and 0.01M KCl in 0.01% alkylbenzenesulphonate, and 0.01 M KCl in 0.05% alkylbenzenesulphonate was almost the same up to near 6 pore volumes ($V/V_0 \approx 6$) (Figure 1). However, from the beginning of 6 pore volumes, Cr concentration in the effluent of 0.01 M KCl in 0.05% alkylbenzenesulphonate treatment was higher than that of 0.01% alkylbenzenesulphonate treatment which was a little higher than that of control (0.01M KCl

treatment). Moreover, after 13 pore volumes, significant difference in concentration of Cr in effluents between 0.01M KCl in 0.05% alkylbenzenesulphonate treatment, 0.01M KCl in 0.01% alkylbenzenesulphonate treatment and 0.01 M KCl treatment was observed with higher concentration of chromium in the effluent of 0.01 M KCl in 0.05% alkylbenzenesulphonate treatment than with the other two treatments (Figure 1).

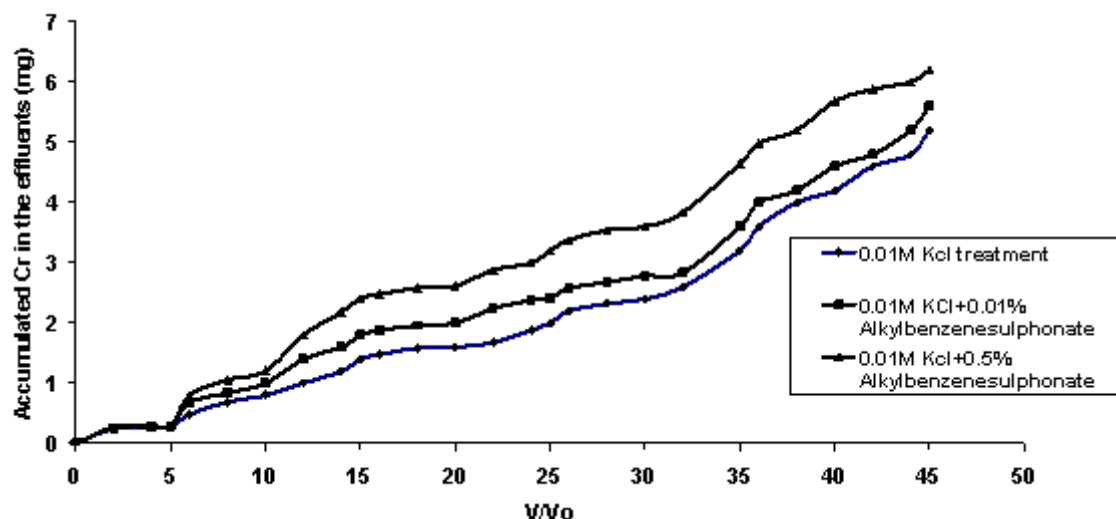


Figure-1: The accumulated Cr in the effluents of clay loam soil column leached with 0.01M KCl in absence, in the presence of alkylbenzene sulphonate

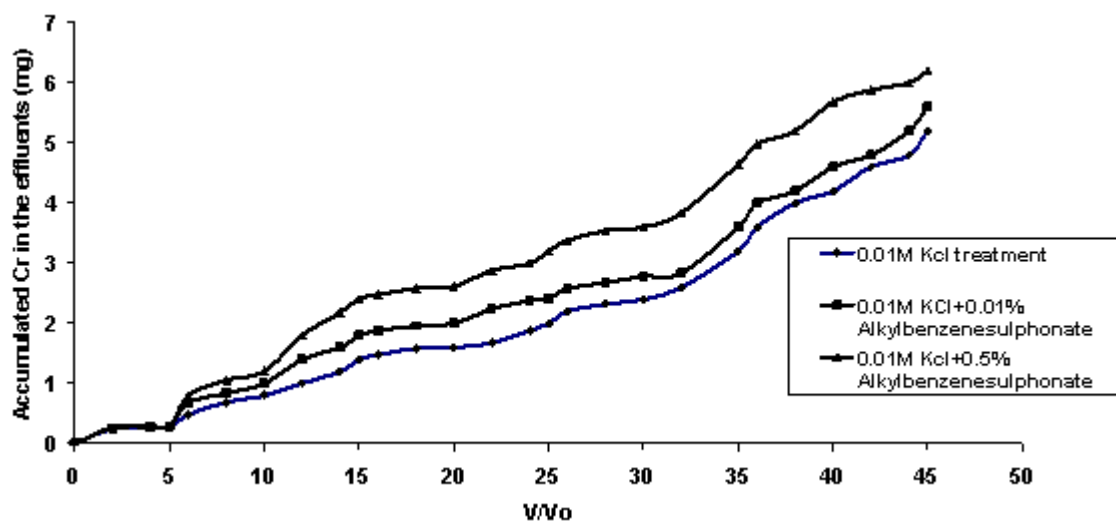


Figure-2: The accumulated Cr in the effluents of sandy loam soil column leached with 0.01M KCl in absence and in the presence of alkylbenzene sulphonate surfactant

The changes in the trends of accumulated Cr in the effluents of sandy loam soil columns of Merlapaka village leached with 0.01 M KCl or 0.01M KCl in 0.05% alkylbenzenesulphonate or 0.01 M KCl in 0.01% alkylbenzenesulphonate were different from those of clayloam soil columns of Ramachandrapuram village (Figures 2 and 1). From the beginning of 6 pore volumes, Cr concentration in the effluent of 0.01 M KCl in 0.05% alkylbenzenesulphonate was higher than that of 0.01M KCl in 0.01% alkylbenzenesulphonate treatment which was little higher than that of control (Figure 2). For the leached pore volumes around 10 to 22 significant difference in the

amount of Cr accumulated between the two soil columns leached with 0.01 M KCl, 0.01M KCl in 0.05 % alkylbenzenesulphonate and 0.01M KCl in 0.01 % alkylbenzenesulphonate were observed. From near 32 pore volumes, the Cr concentration in the effluent of 0.01 M KCl in 0.05% alkylbenzenesulphonate was significantly higher than in the effluent of 0.01M KCl in 0.01% alkylbenzenesulphonate which was a little higher than control (Figure 2). These results clearly indicated that the input of the surfactant alkylbenzenesulphonate increased the mobility of Cr in soil. Further as the concentration of alkylbenzenesulphonate increased, the mobility of Cr in soil also increased.

In the presence of alkylbenzenesulphonate surfactant, the mobility of Cr in the soils increased because that the alkylbenzenesulphonate anions and Cr which exists as chromate anion can compete for adsorption sites in the soils, thereby decreasing the adsorption of Cr and increasing its mobility in soil.

The adsorption of Cr by the two soils and the mobility of Cr in the soil columns were analysed by the breakthrough curves (BTCs) of Cr in soil columns. The Cr BTCs of the two soils showed that the added Cr in influent can be retained by soil components to some extent. For both soils, the added Cr was leached out in effluents, when the influent used was above 10 pore volumes (Figures 3 and 4). The Cr breakthrough point ($C/C_0=1$) for clay loam soil of Ramachandrapuram village when treated with the influent of 50 mg L^{-1} Cr and 0.01M KCl in 0.05% alkylbenzenesulphonate was 24 pore volumes, and when treated with the influent of 50 mg L^{-1} Cr and 0.01 M KCl in 0.01% alkylbenzene sulphonate was 26 pore volumes, while the C/C_0 was only 0.5 at near 26 pore volumes for soil column when treated with the influent of 50 mg L^{-1} Cr in 0.01M KCl (Figure 3). This is attributed to the added alkylbenzenesulphonate in promoting the desorption of Cr from soil components. Correspondingly, in the absence of Cr in the influent of both 0.01M KCl and 0.01 M KCl in 0.05% alkylbenzenesulphonate, and 0.01M KCl in 0.01% alkylbenzenesulphonate, the concentration of Cr in the effluents of soil columns at the same pore volumes described above were not comparable and very low (not shown).

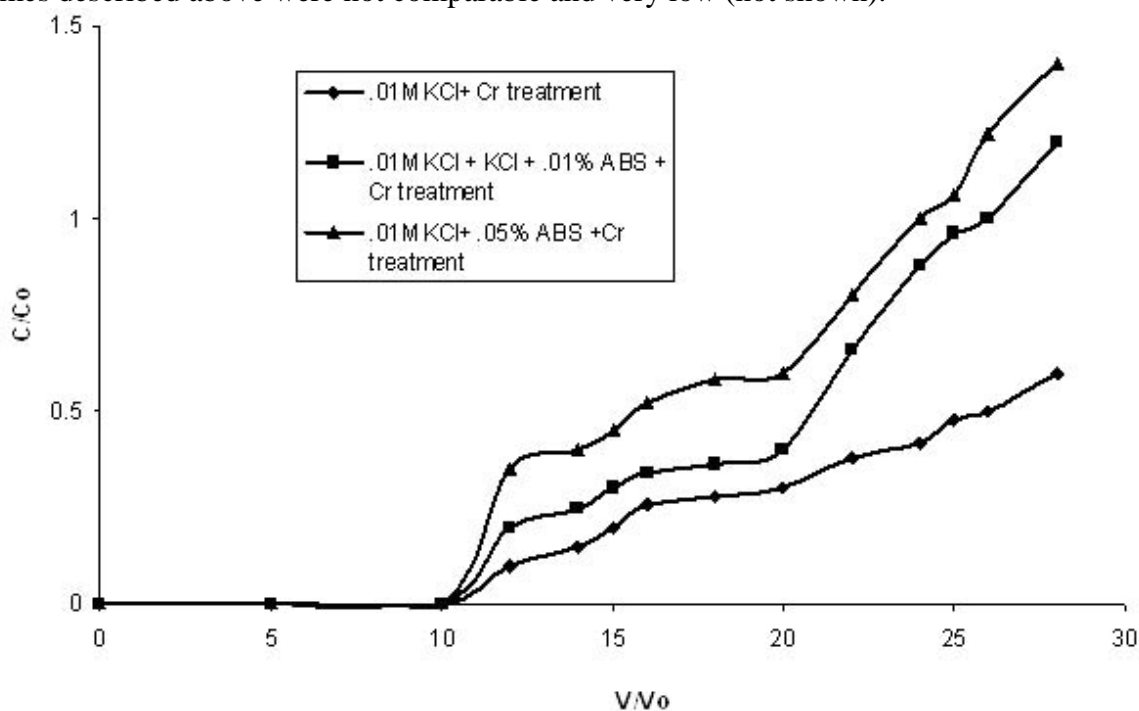


Figure-3: The Cr breakthrough curves of clay loam soil column treated with 0.01% and 0.05% concentrations of alkylbenzene sulphonate influent

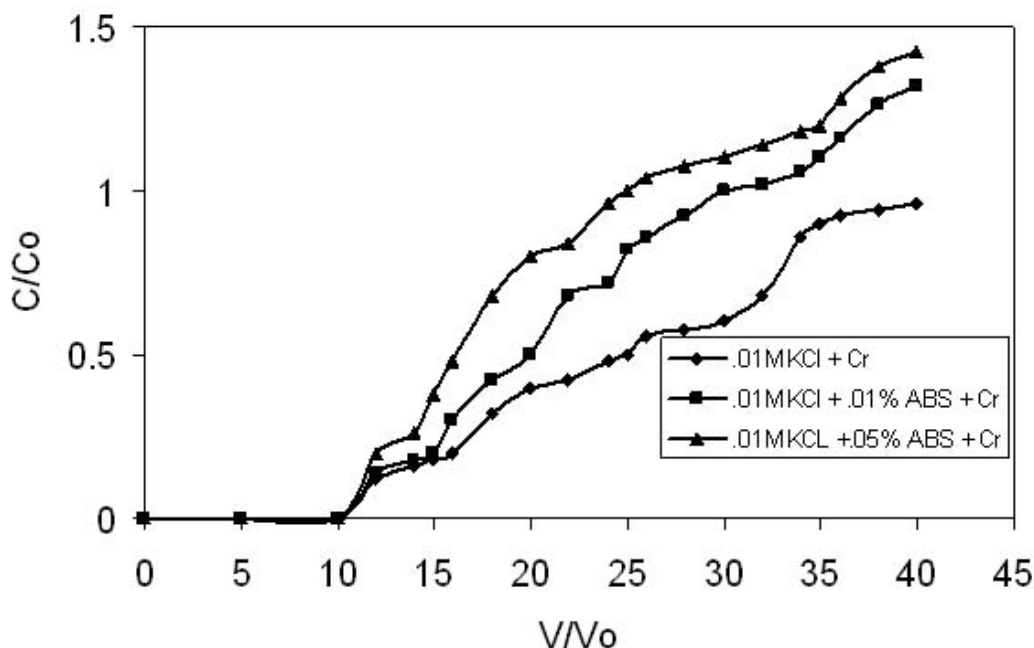


Figure-4: The Cr breakthrough curves of sandy loam soil column treated with 0.01% and 0.05% concentrations of alkylbenzene sulphonate influent

The Cr break through point ($C/C_0=1$) was near 30 pore volumes for sandy loam soil of Merlapaka village, when treated with the influent of $50 \text{ mg L}^{-1}\text{Cr}$ and 0.01 M KCl in 0.01% alkylbenzenesulphonate, and was near 25 pore volumes for sandy loam soil of Merlapaka village when treated with influent of 0.01M KCl in 0.05% alkylbenzenesulphonate, while the C/C_0 was only 0.5 even at near 25 pore volumes for the soil treated with $50 \text{ mg L}^{-1}\text{Cr}$ in 0.01 M KCl (Figure 4). Similarly the Cr concentrations in the effluents of soil columns treated with the influents of both 0.01M KCl and 0.01M KCl in 0.05% alkylbenzenesulphonate and 0.01M KCl in 0.01% alkylbenzenesulphonate, were also not comparable and very low (not shown). This thus indicates the substantial influence of alkylbenzenesulphonate in competing with Cr adsorption by soil components and in subsequent mobility of Cr in soil profile.

At the breakthrough points for the adsorption of Cr by soil components, the amount of Cr and alkylbenzenesulphonate in the influent computed from the pore volumes and their respective pore volume numbers used for leaching the two soil columns were very close (Figures 3 and 4) although the related characteristics in governing the adsorption of Cr by soil components of the two soils were different (Table1). This shows that the amount of alkylbenzenesulphonate used in the study was more important than related soil characteristics in influencing the desorption of Cr and its subsequent mobility in soil environment. However the related characteristics of the two soils in governing the adsorption of Cr by soil components played role in affecting the adsorption as well as desorption processes of Cr by the two soils (Figures 3 and 4). The discrepancy in C/C_0 on BTCs of Cr adsorption by clay-loam soil column of Ramachandrapuram village treated with the influents containing $50 \text{ mg L}^{-1}\text{Cr}$ and 0.01M KCl in 0.05% alkylbenzenesulphonate, 0.01M KCl in 0.01% alkylbenzenesulphonate, and $50 \text{ mg L}^{-1}\text{Cr}$ in 0.01M KCl started at near 23 pore volumes (around 600 ml effluent) (Figure 3), while that sandy loam soil of Merlapaka village started at 21 pore volumes (around 520 ml effluent) (Figure 4). The tendencies of the BTCs for the adsorption as well as desorption of Cr by soil components of the two soils were quite different (Figures 3 and 4). This clearly indicates that characteristics of the two soils also substantially affected the adsorption as well as desorption processes of Cr by soil components as influenced by alkylbenzenesulphonate surfactant.

CONCLUSION

The soil column leaching experiments showed that the addition of alkylbenzenesulphonate in the influent increased the Cr concentrations in the effluents of the two soil columns. Moreover the Cr BTCs showed that less 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 ($C/C_0=1$). The results obtained thus implicate the risk of ground water contamination by Cr originated from Cr containing soils in the presence of alkylbenzenesulphonate surfactants released from urban waste water.

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