

## Adsorption Studies of Chromium(VI) and Molybdenum(VI) Through Soil Static Phase

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**Abstract:** Adsorption of chromium(VI) and molybdenum(VI) by six types of soil beds was examined using soil thin layer chromatography. The effects of decomposition of soil organic matter by 30% H<sub>2</sub>O<sub>2</sub>, cation saturation (K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>), size of the soil particles, soil pH, sewage sludge, sample pH and surfactants (cationic, nonionic and anionic) were investigated. On the basis of differential migration, optimum conditions for the separation of Cr(VI) from Cr(III) and from Mo(VI) on soil thin layer plates were identified. The mobility (or R<sub>F</sub> value) of Cr(VI) and Mo(VI) through all soils follows the order: Cr(VI) > Mo(VI) > Cr(III). The R<sub>F</sub> values of Cr(VI) and Mo(VI) were found to depend upon the soil parameters such as soil organic matter, clay content of soil, cation exchange capacity of soil, cation saturation, size of soil particles, soil pH, sewage sludge content and the nature of surfactant (cationic, anionic or nonionic) in the mobile phase. The obtained results have been explained on the basis of adsorption behavior of Cr(III), Cr(VI) and Mo(VI) on soil colloids.

**Key words:** Adsorption, metal ions, soil parameters, sewage sludge, surfactants, soil thin layer chromatography.

### INTRODUCTION

The occurrence of heavy metals in soils may be beneficial or toxic to the environment. Generally chromium(VI) and molybdenum(VI) are found in soil at low concentrations as a result of contamination by agricultural activities, sewage sludge, industrial wastes and waste water. Molybdenum occurs naturally as well. Both metals have many physical and chemical similarities and belong to the same (group VI) of the periodic table. These metals when applied to soil may transport through soil and can react with organic and inorganic compounds to form soluble or insoluble compounds or get adsorbed onto soil colloids (Epstein and Chaney, 1978; Wetterhahn and Hamilton, 1989; Bradl, 2004). The availability and effectiveness of heavy metals (e.g. chromium and molybdenum) in soils are largely governed by several factors such as (a) the nature and percentage of clay minerals, (b) nature of exchangeable cations, (c) pH, and (d) organic matter (Dube et al., 2001; Yang et al., 2001; Bradl, 2004). The distribution and mobility of chromium in soil is basically controlled by three important factors, including oxidation-reduction, precipitation-dissolution and sorption-desorption reactions (Saleh et al., 1989). Chromium(VI) exists in solution as hydrochromate, chromate and dichromate ions. In strongly basic or neutral solutions, it exists as chromate and in acidic solution hydrochromate predominates (Rai, 1989). The toxicity of chromium varies principally according to its oxidation state. Thus hexavalent chromium is more toxic than trivalent chromium (Murti et al., 1989; ATSDR, 1993; Katz and Salem, 1994; Fendorf, 1995; James et al., 1997). This may be due to the fact that chromium(VI) penetrates mammalian cells more readily than chromium(III) (Wetterhahn and Hamilton, 1989). Chromium(VI) causes skin irritation resulting in ulcer formation and dermatitis. Overexposure to chromium(VI) leads to liver damage, pulmonary congestion and edema (Nethercott et al., 1994; ITCC, 2000; Chandra and Kulshrestha, 2004). Therefore, the presence of chromium(VI) in water, soil and wastewater has been of great concern. On the other hand, molybdenum in soil solution occurs predominately as MoO<sub>4</sub><sup>2-</sup>, HMoO<sub>4</sub><sup>-</sup> and H<sub>2</sub>MoO<sub>4</sub><sup>0</sup>. The concentration of MoO<sub>4</sub><sup>2-</sup> and HMoO<sub>4</sub><sup>-</sup> in solution increases with increasing soil pH (Lindsay, 1979). Plants absorb molybdenum as MoO<sub>4</sub><sup>2-</sup>. The most important factors affecting molybdenum availability are soil pH and the amount of Al and Fe oxides in the soil (Lindsay, 1979; McBride and Cherney, 2004). Molybdenum availability varies with soil type in the following decreasing order: organic soil > clay soil > sandy soil. Excessive amounts of molybdenum are toxic, especially to grazing cattle or sheep. Molybdenum toxicity causes stunted growth and bone deformation in the animal.

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The use of soil as static phase in the study of separation and adsorption of metal ions by thin layer chromatography is simple, rapid and inexpensive. It provides an opportunity to examine the uptake and translocation of metal ions through soil. Most reported soil thin layer chromatographic methods involve the use of mixed organic solvent systems, chemical fertilizers, anions and surfactants as mobile phase (Khan, 1982; Khan et al., 1983; Khan et al., 1991; Sanchez-Camazano et al., 1995; Mohammad and Jabeen, 2003). A few studies have also reported on the use of soil layers mixed with surfactants, silica gel, alumina, kieselguhr or cellulose to examine the mobility of metal ions (Sanchez-Camazano et al., 1995; Mohammad and Jabeen, 2003). Some studies have been conducted to evaluate the mobility of metal ions through soil saturated with different cations ( $H^+$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ) (Khan et al., 1983; Khan et al., 1982).

Literature survey revealed that no work has been reported on the adsorption of chromium(VI) and molybdenum(VI) through soil static phase by thin layer chromatography, in spite of the fact that the presence of these metal ions in soil offers significant influence on the growth of plants.

In view of the above mentioned facts, the present study was undertaken to examine the influence of several factors such as decomposition of soil organic matter, exchangeable cations, size of soil particles, soil pH, addition of sewage sludge, variation of sample pH, and the nature of surfactants on the adsorption of chromium(VI) and molybdenum(VI) through soil static phase with the aid of thin layer chromatography. The mutual separations of Cr(VI) from Cr(III) and Mo(VI) were also achieved.

## MATERIALS AND METHODS

Six natural uncultivated soil samples were collected from the surface horizon (depth of 0-30 cm) at different places of Aligarh district (India). The physico-chemical properties including pH (1:2, soil: water ratio), organic matter (Walkely and Black, 1947), clay (Piper, 1950), cation exchange capacity (Jackson, 1973), exchangeable cations (Jackson, 1973) and base saturation were determined.

### 2.1. Apparatus:

A TLC applicator (Toshiniwal, India), glass plates (20 cm  $\times$  3.5 cm), glass jars (24 cm  $\times$  6 cm) with cover, dropper, 100 mesh sieve (BSS), digital pH meter (Elico, 181E, India) and mechanical shaker were used.

### 2.2. Chemicals and Reagents:

Calcium chloride, potassium chloride, ammonium chloride, hydrochloric acid and sodium hydroxide (CDH, India);  $H_2O_2$  30% (Qualigens, India); methanol, ethanol and cetyltrimethylammonium bromide (CDH, India); Triton X-100 (Loba Chemie, India) and sodium dodecyl sulphate (BDH, India) were used. All other reagents were Analytical reagent grade.

Aqueous solutions (0.05M) of chromium chloride, potassium dichromate and sodium molybdate were used for Cr(III), Cr(VI), and Mo(VI) respectively.

Ethanol solution of haematoxyline(0.5%) was used for the detection of all cations.

### 2.3. Preparation of Soil TLC plates:

For the preparation of soil TLC plates, soil samples were dried, grounded and sieved through 100 mesh (BSS) to get uniform particle size. Soil thin layer plates were prepared by mixing soil with double distilled water in a 1:2 ratio. The resultant slurry was mechanically shaken for 5 min and then it was spread (20 x 3.5 cm<sup>2</sup>) TLC glass plates with the aid of TLC applicator to get uniform layers of 0.5 mm thickness. The plates were air dried at room temperature (30  $\pm$  1 °C) and stored in air tight chamber until used.

### 2.4. Procedure:

Two lines were drawn at 3 and 13 cm from the base, so that a 10 cm distance could be used for development of plates. About one drop (5  $\mu$ L) of each metal ion (0.05 M) was spotted at the base line on separate TLC plates in a single application with the help of micropipette. The plates were then allowed to develop (up to the upper line of the plates) in closed chromatographic glass chambers (24 cm long and 6 cm wide) using distilled water or aqueous surfactants as mobile phase by ascending technique. To prevent disintegration of soil in contact with developer, wet strips of filter paper about 2.5 cm wide were wrapped around the bottom of the plate before the development. The developed plates were air dried at 60 °C in an oven. Finally, the positions of Cr(VI) and Mo(VI) on TLC plates were located by spraying 0.5% (w/v) ethanolic solution of haematoxyline. The violet spots of Cr(VI) and Mo(VI) complexes with haematoxyline appeared on TLC plates were found to be stable for several hours.

The retardation factor ( $R_F$  value) of Cr(VI) and Mo(VI) was determined using the following equation:

$$R_F = 0.5 (R_L + R_T)$$

Where  $R_L$  = Leading distance moved by Cr(VI) and Mo(VI) from the starting line.

$R_T$  = Trailing distance moved by Cr(VI) and Mo(VI) from the starting line.

### **2.5. Adsorption by Organic Matter-Free Soil:**

In order to study the effect of soil organic matter as suggested by Jackson (1973), organic matter free soil was also used to prepare TLC plates and the chromatography of Cr(VI) and Mo(VI) on these plates was performed as described above.

### **2.6. Effect of Exchangeable Cations:**

To study the effect of exchangeable cations of soil on the adsorption of Cr(VI) and Mo(VI), soil samples saturated with  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $NH_4^+$  were prepared by equilibrating the soil with 1N chloride solutions of the respective cations. Excess salts were removed by washing the treated soil with aqueous methanol (MeOH + water, 4:1v/v) followed by final washing with distilled water. Soil samples treated with exchangeable cations were coated on the plates for use of the static soil phase to examine the mobility of Cr(VI) and Mo(VI) using distilled water as developer.

### **2.7. Effect of Particle Size:**

To study the effect of particle size, the soils were passed through standard sieves of 100, 150 and 300 mesh sieve (BSS) and used as the static phase and distilled water as the developer.

### **2.8. Effect of Soil pH:**

The effect of pH on the adsorption of Cr(VI) and Mo(VI) was studied using the soil samples at various pH values (4.0, 5.0, 6.0, 10.0, adjusted with 0.1N HCl or 0.1N NaOH) as layer material in combination with distilled water as developer.

### **2.9. Effect of Sewage Sludge:**

Sewage sludge was mixed with soil in different proportions (sewage sludge : soil, 1:4, 1:2, and 3:4, w/w).. The mixtures were slurried with distilled water in 1:2 ratios by shaking for 5 min and then it was coated as a 0.5 mm thick layer over TLC plates for use as the static phase while distilled water was used as developer.

### **2.10. Effect of Sample pH:**

To study the effect of pH of sample on the adsorption, the pH values of Cr(VI) and Mo(VI) solutions were adjusted by adding 0.1N HCl or 0.1N NaOH into sample solution.

### **2.11. Effect of Surfactants:**

In order to study the effect of surfactants (cationic, nonionic and anionic) listed in Table 1, aqueous solutions of CTAB, Triton X-100 and SDS (near CMC and above CMC) were used as a developer and natural soils used as static phase.

### **2.12. Separation:**

For separation, aqueous solutions of Cr(VI) and Cr(III) (1:2 ratio) and Cr(VI) and Mo(VI) (1:1 ratio) were mixed and 5  $\mu$ L of the resultant mixtures was loaded on the TLC plates at the point of application. The plates were developed with distilled water and the resolved spots were detected by spraying haematoxyline on TLC plates.

## **RESULTS AND DISCUSSION**

The results of this study are summarized in Tables 1-7 and Figs. 1-5. The adsorption behavior of Cr(VI) and Mo(VI) was examined on soil thin layer plates prepared from six different types of soil ( $S_1$ - $S_6$ ). Table 2 lists the physico-chemical parameters of soil samples used. The mutual separations of Cr(VI) and Cr(III) as well as Cr(VI) and Mo(VI) were realized during the present study.

An examination of results listed in Table 3, shows that the mobility of Cr(VI) and Mo(VI) in all soils ( $S_1$ - $S_6$ ) followed the order Cr(VI) > Mo(VI). The mobility of these metal ions is controlled by their adsorption capability on soil colloids.

**Table 1:** Some Typical Surfactants, Nature, Chemical Structure, Molecular Weight and Their CMC Values

| Surfactants                                     | Nature   | Chemical structure   | Molecular weight | CMC value at 25°C       |
|---|----------|--|------------------|-------------------------|
| Cetyltrimethylammonium bromide (CTAB)           | Cationic | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> Br <sup>-</sup>                    | 364              | 9.2×10 <sup>-4</sup> M  |
| t-octylphenoxydecaethoxy ethanol (Triton X-100) | Nonionic | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> C <sub>6</sub> H <sub>4</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>10</sub> OH | 646              | 2.05×10 <sup>-4</sup> M |
| Sodium dodecyl sulphate (SDS)                   | Anionic  | C <sub>12</sub> H <sub>25</sub> O SO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>   | 288              | 8.1×10 <sup>-3</sup> M  |

**Table 2:** Physico-chemical Properties of Six Soils Studied

| Soil           | pH (1:2, soil: water) | Organic matter (%) | Clay (%)   | Cation exchange capacity (cmol <sub>c</sub> kg <sup>-1</sup> ) | Exchangeable cations (cmol <sub>c</sub> kg <sup>-1</sup> ) |                |                  |                  |
|----------------|-----------------------|--------------------|------------|--|--|----------------|------------------|------------------|
|                |                       |                    |            |  | Na <sup>+</sup>  | K <sup>+</sup> | Mg <sup>2+</sup> | Ca <sup>2+</sup> |
| S <sub>1</sub> | 8.10±0.41             | 0.56±0.03          | 5.90±0.30  | 11.90±0.60   | 1.59±0.08  | 0.79±0.04      | 1.50±0.08        | 5.80±0.29        |
| S <sub>2</sub> | 8.60±0.43             | 0.65±0.03          | 13.87±0.69 | 16.32±0.82   | 0.86±0.04  | 0.38±0.02      | 0.51±0.03        | 5.66±0.28        |
| S <sub>3</sub> | 8.20±0.41             | 0.68±0.03          | 10.70±0.54 | 13.45±0.67   | 0.99±0.05  | 0.31±0.02      | 0.70±0.04        | 7.12±0.36        |
| S <sub>4</sub> | 7.40±0.37             | 0.51±0.03          | 9.20±0.46  | 11.95±0.60   | 0.58±0.03  | 0.77±0.04      | 1.45±0.07        | 5.50±0.28        |
| S <sub>5</sub> | 7.90±0.40             | 0.55±0.03          | 8.60±0.43  | 13.00±0.65   | 0.51±0.03  | 0.51±0.03      | 1.21±0.06        | 7.10±0.36        |
| S <sub>6</sub> | 8.00±0.40             | 0.75±0.04          | 14.07±0.70 | 18.50±0.93   | 0.91±0.05  | 1.15±0.06      | 0.21±0.01        | 5.54±0.28        |

**Table 3:** Effect of Organic Matter and Exchangeable Cations on the Mobility of Cr(VI) and Mo(VI) Through Soil Static Phase

| Soil           | R <sub>f</sub> values    |                             | R <sub>f</sub> values for different exchangeable cations |                           |                       |                                   |
|----------------|--------------------------|-----------------------------|--|---------------------------|-----------------------|-----------------------------------|
|                | Soil with organic matter | Soil without organic matter | K <sup>+</sup> soil                                      | Mg <sup>2+</sup> soil     | Ca <sup>2+</sup> soil | NH <sub>4</sub> <sup>+</sup> soil |
| S <sub>1</sub> | 0.97±0.05 (0.91±0.05)    | 0.96±0.05 (0.83±0.04 T)     | 0.95±0.05 (0.95±0.05)                                    | 0.95±0.05 (ND)            | 0.95±0.05 (ND)        | 0.93±0.05 (ND)                    |
| S <sub>2</sub> | 0.89±0.04 (0.72±0.04)    | 0.91±0.05 (0.81±0.04)       | 0.96±0.05 (0.91±0.05)                                    | 0.93±0.05 (ND)            | 0.92±0.05 (ND)        | 0.86±0.04 (ND)                    |
| S <sub>3</sub> | 0.87±0.04 (0.84±0.04)    | 0.94±0.05 (0.86±0.04)       | 0.96±0.05 (0.94±0.05)                                    | 0.92±0.05 (0.90±0.04)     | 0.86±0.04 (ND)        | 0.76±0.04 (0.71±0.05)             |
| S <sub>4</sub> | 0.93±0.05 (0.89±0.04)    | 0.94±0.05 (0.89±0.04)       | 0.76±0.04 T (0.86±0.04)                                  | 0.96±0.05 (0.91±0.05)     | 0.86±0.04 (ND)        | 0.83±0.04 (0.73±0.04)             |
| S <sub>5</sub> | 0.95±0.05 (0.89±0.04)    | 0.97±0.05 (0.92±0.05)       | 0.95±0.05 (0.92±0.05)                                    | 0.92±0.05 (0.89±0.04)     | 0.89±0.04 (ND)        | 0.85±0.04 (0.83±0.04)             |
| S <sub>6</sub> | 0.82±0.04 (0.78±0.04)    | 0.91±0.05 (0.56±0.03 T)     | - (-)  | 0.83±0.04 T (0.80±0.04 T) | 0.74±0.04 T (ND)      | 0.68±0.03 T (0.56±0.03 T)         |

R<sub>f</sub> values of Mo(VI) are given in parenthesis; T = Tailed spots; ND = Not detected

**Table 4:** Effect of Surfactants (As Mobile Phase) on the Mobility of Cr(VI) and Mo(VI) Through Soil Static Phase

| Soil           | CTAB                             |  |   | Triton X-100   |   | SDS   |  |
|----------------|----------------------------------|--|---|--|---|---|--|
|                | Distilled water(M <sub>i</sub> ) | Near CMC (9.2×10 <sup>-3</sup> M)(M <sub>i</sub> ) | Above CMC (9.2×10 <sup>-3</sup> M)(M <sub>i</sub> ) | Near CMC (2.05×10 <sup>-3</sup> M) (M <sub>i</sub> ) | Above CMC (2.05×10 <sup>-3</sup> M) (M <sub>i</sub> ) | Near CMC (M <sub>i</sub> ) (8.1×10 <sup>-3</sup> M) | Above CMC (8.1×10 <sup>-3</sup> M) (M <sub>i</sub> ) |
| S <sub>1</sub> | 0.97±0.049 (0.91±0.046)          | 0.96±0.048 (ND)                                    | 0.92±0.046 (ND)                                     | 0.92±0.046 (0.91±0.046)                              | 0.95±0.048 (0.93±0.047)                               | 0.92±0.046 (0.88±0.044)                             | 0.79±0.040 (0.88±0.044)                              |
| S <sub>2</sub> | 0.89±0.045 (0.72±0.036)          | 0.98±0.049 (0.44±0.022 T)                          | 0.92±0.046 (0.60±0.030 T)                           | 0.94±0.047 (0.88±0.044)                              | 0.85±0.043 (0.81±0.041)                               | 0.82±0.041 (0.76±0.038)                             | 0.71±0.036 (0.64±0.032)                              |
| S <sub>3</sub> | 0.87±0.044 (0.84±0.042)          | 0.93±0.047 (0.95±0.048)                            | 0.88±0.044 (0.83±0.042)                             | 0.91±0.045 (0.88±0.044)                              | 0.76±0.038 (0.78±0.039)                               | 0.79±0.040 (0.85±0.043)                             | 0.75±0.038 (0.81±0.041)                              |
| S <sub>4</sub> | 0.93±0.047 (0.89±0.045)          | 0.94±0.047 (0.90±0.045)                            | 0.89±0.045 (0.88±0.044)                             | 0.97±0.049 (ND)                                      | 0.88±0.044 (ND)                                       | 0.94±0.047 (0.82±0.041)                             | 0.86±0.043 (ND)                                      |
| S <sub>5</sub> | 0.95±0.048 (0.89±0.045)          | 0.95±0.048 (0.91±0.045)                            | 0.83±0.042 (0.79±0.040)                             | 0.94±0.047 (0.88±0.044)                              | 0.84±0.017 (0.82±0.041)                               | 0.75±0.038 (0.79±0.040)                             | 0.92±0.048 (0.73±0.037)                              |
| S <sub>6</sub> | 0.82±0.041 (0.78±0.039)          | 0.93±0.047 (0.85±0.043)                            | 0.80±0.040 (0.77±0.039)                             | 0.84±0.042 (0.80±0.040)                              | 0.78±0.039 (0.76±0.038)                               | 0.80±0.040 (0.72±0.036)                             | 0.81±0.041 (0.69±0.035)                              |

T= Tailed spots; ND = Not detected

**Table 5:** Mutual Separation of Cr(VI) from Cr(III) by Soil Thin Layer Chromatography

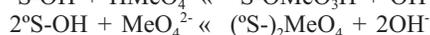
| Soil           | Cr (VI)    | Cr (III)   |
|----------------|------------|------------|
| S <sub>1</sub> | ND         | ND         |
| S <sub>2</sub> | 0.97±0.049 | 0.01±0.001 |
| S <sub>3</sub> | 0.87±0.044 | 0.01±0.001 |
| S <sub>4</sub> | 0.88±0.044 | 0.03±0.002 |
| S <sub>5</sub> | 0.79±0.040 | 0.02±0.001 |
| S <sub>6</sub> | 0.79±0.040 | 0.01±0.001 |

ND = Not detected.

**Table 6:** Mutual Separation of Cr(VI) and Mo(VI) on Soil pH (4.0 ± 0.1) by Thin Layer Chromatography

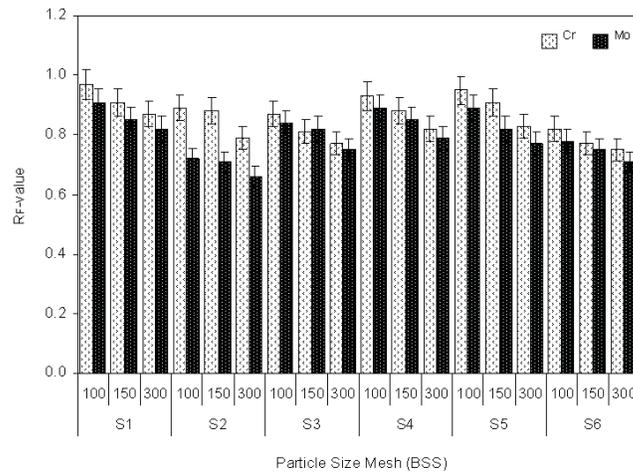
| Soil           | Cr (VI)    | Mo (VI)    |
|----------------|------------|------------|
| S <sub>1</sub> | 0.81±0.041 | ND         |
| S <sub>2</sub> | 0.84±0.042 | 0.31±0.016 |
| S <sub>3</sub> | 0.57±0.029 | ND         |
| S <sub>4</sub> | 0.86±0.043 | 0.59±0.030 |
| S <sub>5</sub> | 0.90±0.045 | 0.63±0.032 |
| S <sub>6</sub> | 0.76±0.038 | 0.21±0.011 |

ND = Not detected.

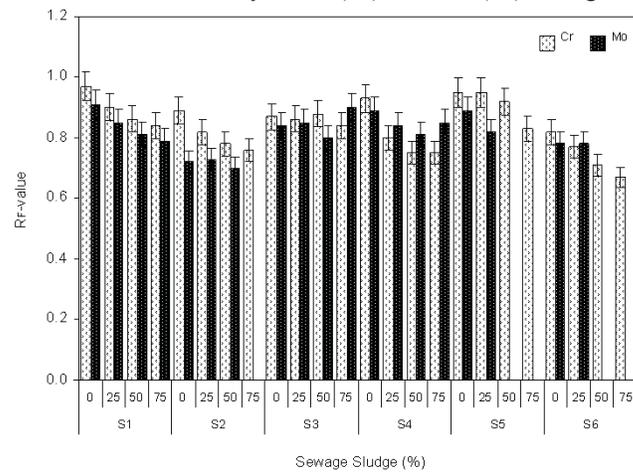


Where <sup>o</sup>S-OH represents hydrous oxides of Al or Fe; Me represents Cr or Mo.

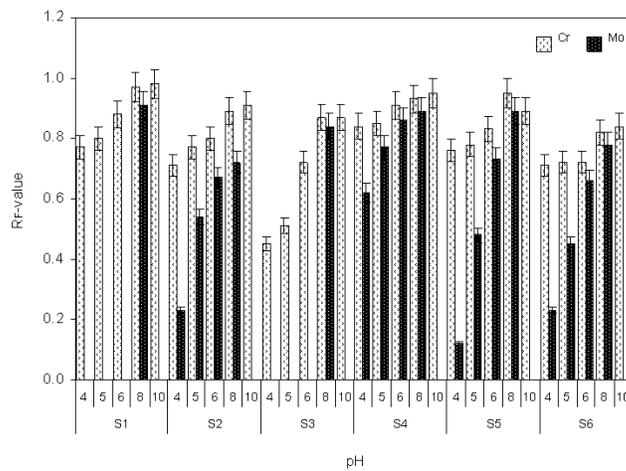
It appears that Mo(VI) is strongly adsorbed by soil constituents (e.g. Fe and Al oxides) in comparison to the adsorption of Cr(VI) and hence Mo(VI) shows lower R<sub>f</sub> value on all soil layers.



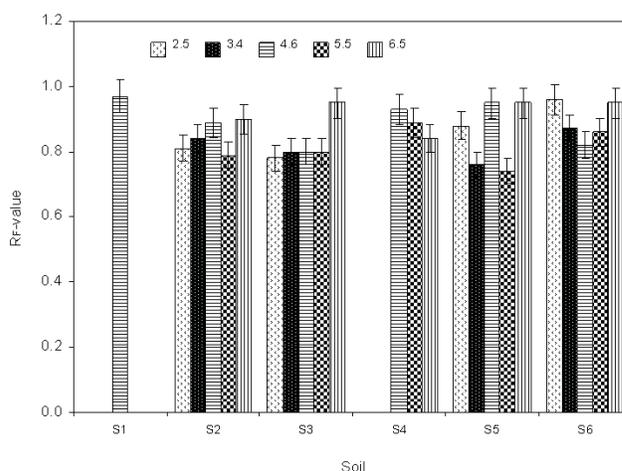
**Fig. 1:** Effect of particle size on the mobility of Cr (VI) and Mo (VI) through soil static phase



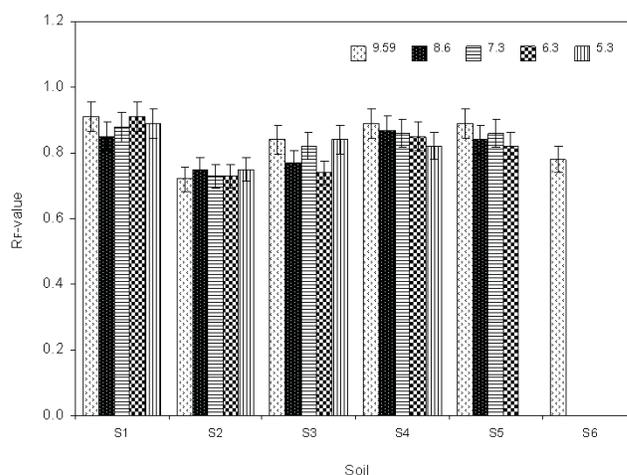
**Fig. 2:** Effect of sewage sludge on the mobility of Cr (VI) and Mo (VI) through soil static phase



**Fig. 3:** Effect of pH on the mobility of Cr (VI) and Mo (VI) through soil static Phase



**Fig. 4:** Effect of change of Cr (VI) pH on their mobility through soil static phase



**Fig. 5:** Effect of change of Mo (VI) pH on their mobility through soil static phase

The data of Table 3, also reveal that the oxidation of soil organic matter (with 30% H<sub>2</sub>O<sub>2</sub>) results in the slight increase in R<sub>F</sub> value or decrease in compactness of spot of both Cr(VI) and Mo(VI) ions in all the cases (S<sub>1</sub>-S<sub>6</sub>). The enhanced mobility or decreased in spot compactness on organic matter free soil layers may be attributed to the reduction in complex forming capacity of soil (Schnitzer, 1982).

From Table 3, the R<sub>F</sub> values of Cr(VI) and Mo(VI) obtained on soil (S<sub>1</sub>-S<sub>6</sub>) layers saturated with different cations (K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and NH<sub>4</sub><sup>+</sup>) were found to follow the order K<sup>+</sup> soil > Mg<sup>2+</sup> soil > Ca<sup>2+</sup> soil > NH<sub>4</sub><sup>+</sup> soil, with the exception of Mg<sup>2+</sup> soil (S<sub>1</sub> and S<sub>2</sub>), Ca<sup>2+</sup> soil (S<sub>1</sub>-S<sub>6</sub>) and NH<sub>4</sub><sup>+</sup> soil (S<sub>1</sub> and S<sub>2</sub>) where Mo(VI) was not detected. This mobility pattern is in reverse order of the adsorption magnitude of calcium, magnesium and potassium (i.e. adsorption order: Ca<sup>2+</sup> > Mg<sup>2+</sup> > K<sup>+</sup>) on soil (Tisdale et al., 2003). The strongest adsorption (or lowest mobility) of Cr(VI) and Mo(VI) on NH<sub>4</sub><sup>+</sup> treated soil is in consonance with the finding of earlier work (Tisdale et al., 2003). Both metal ions were found to produce compact spots on layer prepared from S<sub>3</sub> (NH<sub>4</sub><sup>+</sup> soil). On the other hand Cr(VI) and Mo(VI) produced tailed spots on layers prepared from S<sub>6</sub> (saturated with Mg<sup>2+</sup>, Ca<sup>2+</sup>, and NH<sub>4</sub><sup>+</sup>). The layer prepared from S<sub>6</sub> (K<sup>+</sup> soil) gets cracked during development in distilled water and hence S<sub>6</sub> is not suitable for thin layer chromatography.

Fig. 1, clearly demonstrate that the R<sub>F</sub> values of Cr(VI) and Mo(VI) decreased with the decrease in particle size of the soil, because of higher adsorption capacity of the smaller particles (Ryan et al., 1985). Furthermore, more compact and well-formed circular spots were realized on layers prepared from soils of smaller particle size.

From Fig. 2, it is clear that the  $R_F$  values of Cr(VI) and Mo(VI) were found to decrease with the decrease in pH of soil ( $S_1$ - $S_6$ ) used as static phase with the exception of Mo(VI), which was not detected on layers prepared from  $S_1$  and  $S_3$  (pH  $6.0 \pm 0.1$  to  $4.0 \pm 0.1$ ). The decrease in mobility (or  $R_F$  value) at lower pH of soil may be attributed to the increase in the number of positively charged sorption sites on the phyllosilicate and oxide minerals on the soil environment (Aide and Cummings, 1997; Goldberg et al., 2008). However, no significant change in the mobility of Cr(VI) was observed when the pH of soil was increased from 8 to 10. On soil layers ( $S_1$ - $S_6$ , pH  $10 \pm 0.1$ ) Mo(VI) could not be detected likely due to its precipitation.

From the results shown in Fig. 3, it is evident that there is a reduction in the mobility of Cr(VI) and Mo(VI) with the increase of amount of sludge in soil samples ( $S_1$ - $S_6$ ). This decrease in mobility (or  $R_F$  value) of Cr(VI) and Mo(VI) may be attributed to the decrease in pH (range  $\sim 7.8$ - $7.1$ ) of sludge amended soil.

There was no pronounced effect of variation of sample pH of Cr(VI) (pH, range 2.5-6.5) and Mo(VI) (pH, range 5.3-9.59) on their mobility (Figs. 4 and 5). The original sample pH values of Cr(VI) and Mo(VI) were 4.6 and 9.59 respectively.

To examine the influence of the concentration of surfactants (cationic, nonionic and anionic) on the  $R_F$  values of Cr(VI) and Mo(VI), chromatography was performed on different types of soil layers ( $S_1$ - $S_6$ ). The  $R_F$  values of Cr(VI) and Mo(VI) obtained in pure water (i.e., zero surfactant concentration,  $M_1$ ) and in aqueous solutions of surfactants at various concentration levels ( $M_2$  –  $M_7$ ) are presented in Table 4. The mobilities of Cr(VI) and Mo(VI) are slightly modified in the presence of surfactants at all concentration levels. The significant effect on the mobility of both ions was observed with  $M_7$  where SDS (an anionic surfactant) concentration is above CMC value. In this case Cr(VI) and Mo(VI) showed strong retention towards soil and hence their  $R_F$  values are lower compared to  $R_F$  values obtained with  $M_1$  (i.e., distilled water). It appears that SDS micelles provide an entirely different microenvironment for the increased retention of Cr(VI) and Mo(VI) on soil surfaces. It is therefore, concluded that anionic surfactant (SDS) is more effective than cationic (CTAB) and nonionic (Triton X-100) surfactants to check the mobility of Cr(VI) and Mo(VI) through soil bed.

Except  $S_1$ , (where Cr(VI) and Mo(VI) were not detected). Cr(VI) was clearly separated from Cr(III) on soil thin layer plates prepared from ( $S_2$ - $S_6$ ) using distilled water as mobile phase (Table 5). Similarly, with this mobile phase, Cr(VI) can be separated from Mo(VI) on soil thin layer plates prepared from  $S_2$ ,  $S_4$ ,  $S_5$  or  $S_6$  (pH  $4.0 \pm 0.1$ ). Mo(VI) except  $S_1$  and  $S_3$  layers (Table 6).

### **Conclusions:**

Our results demonstrated that the adsorption of Cr(VI) and Mo(VI) was influenced by organic matter, clay content, and cation exchange capacity of the soil. The soil with higher organic matter, clay content, and cation exchange capacity generally had higher adsorption capacity for Cr(VI) and Mo(VI). The Cr(VI) and Mo(VI) adsorbed by clay minerals and organic matters become unavailable to plants. Among parameters studied, the most important parameter affecting the adsorption of Cr(VI) and Mo(VI) is the soil pH. The adsorption was higher at low pH value. The mobility (or adsorption) of Cr(VI) and Mo(VI) vary with nature and concentration of surfactants used in mobile phase, which demonstrated that surfactant play an important role in the mobilization of heavy metals [Cr(VI) and Mo(VI)] through soil phase. The present study is useful to assess the bioavailability of Cr(VI) and Mo(VI) to plants. The higher  $R_F$  values are indicative of low adsorption of metal ions through soil static phase facilitating their availability to plants. Conversely, lower  $R_F$  values (strongest adsorption) demonstrate the restricted mobility of metal ions through soil bed (i.e., strong retention by soil).

### **ACKNOWLEDGEMENT**

The author's are thankful to the Chairman, Department of Applied Chemistry, Aligarh Muslim University, Aligarh (India). One of author (Abdul Moheman) is grateful to university grant commission (New Delhi, India) for providing financial assistance.

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