



## Conversion of Cr (VI) in water and soil using rhamnolipid

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### ABSTRACT

Batch experiments were performed to evaluate the feasibility of using rhamnolipid for the removal and reduction of hexavalent chromium from contaminated soil and water. The rhamnolipid can reduce 100% of initial Cr (VI) in water at optimum conditions (pH 6, 2% rhamnolipid concentration, 25°C) if the concentration is low (10 ppm). For higher initial concentrations (400 ppm), it takes 24 h to reduce Cr by 24.4% in one day. In the case of soil, rhamnolipid only can remove the soluble part of the chromium present in the soil. The extraction increased with an increase in the initial concentration in soil but decreased slightly with the increase of temperature above 30°C. A sequential extraction study was used on soil before and after washing to determine from what fraction the rhamnolipid removed the chromium. The exchangeable and carbonate fractions accounted for 24% and 10% of the total chromium, respectively. The oxide and hydroxide portion retained 44% of chromium present in the soil. On the other hand, 10% and 12% of the chromium was associated with the organic and residual fractions. Rhamnolipid can remove most of the exchangeable (96%) and carbonate (90%) portions and some of the oxide and hydroxide portion (22%) but cannot remove chromium from the other fractions. This information is important in designing the appropriate conditions for soil washing.

### RÉSUMÉ

Des expériences en batch ont été réalisées afin d'évaluer la faisabilité d'utiliser le rhamnolipide pour l'enlèvement et la réduction de chrome hexavalent provenant de sols contaminés et d'eau. Le rhamnolipide peut réduire la quantité de Cr(VI) initiale par 100% dans l'eau à des conditions optimales (pH 6, concentration de 2% du rhamnolipide, 25°C), si la concentration est faible (10 ppm). Pour de plus grandes concentrations initiales (400 ppm), il faut attendre une période de 24 h pour réduire le Cr par 24,4% dans une seule journée. Dans le cas des sols, le rhamnolipide ne peut pas supprimer la partie dissous du chrome présent dans le sol. L'extraction a été améliorée avec une augmentation de la concentration initiale dans le sol, mais a légèrement diminué avec l'augmentation de la température supérieure à 30°C. Une étude de l'extraction séquentielle a été utilisée sur le sol avant et après le lavage afin de déterminer la fraction du rhamnolipide qui enlève le chrome. Les fractions du carbonate, et échangeables représentaient 24% et 10% du chrome total, respectivement. Les oxydes et hydroxydes partie étaient de 44% de chrome présents dans le sol. D'autre part, 10% et 12% du chrome a été associé aux fractions organique et résiduelle. Le rhamnolipide peut supprimer la plupart des échangeables (96%) et le carbonate (90%) et de certaines portions de l'oxyde et d'hydroxyde de partie (22%), mais ne peut pas supprimer le chrome de l'autre des fractions. Cette information est importante pour l'élaboration des conditions appropriées pour le lavage des sols.

### 1 INTRODUCTION

Chromium is one of the most widely used metals in industry and chromium contamination of the environment is extensive resulting in large quantities of it being discharged into the environment (Bartlett, 1991). Hexavalent chromium [Cr (VI)] and trivalent chromium [Cr (III)] are the two main forms of chromium present in the soils. Cr (VI) is of great concern as it has highly toxic and carcinogenic properties and also for its potential for the contamination of groundwater due to its greater mobility in soils and in the aquatic environment. Therefore, to protect the public health and the environment, the remediation of chromium contaminated sites is a top priority (Reddy et al., 1997).

Major sources of chromium include the metal finishing industry, petroleum refining, leather tanning, iron and steel industries, production of inorganic chemicals, textile manufacturing, dyes, electroplating, metal cleaning,

plating, photography, wood treatment and pulp production (Laxman et al., 2002; Xu et al., 2004). Since hexavalent chromium is a very soluble and mobile species, highly toxic and mutagen and carcinogen, it is considered as a priority pollutant for soils and natural wastes (Erdem et al., 2004). Cr (VI) is toxic to humans, animals, plants and microorganism and is associated with the development of various chronic health disorders including organ damage, dermatitis and respiratory impairment. In the environment, Cr (VI) does not readily precipitate or become bound to components of soil. Therefore, Cr (VI) can move through the sediment into aquifers to contaminate groundwater and other sources of drinking water (Xu et al., 2004).

To decrease costs, various technologies have been developed and implemented for the remediation of contaminated water, soil and sediments. An important consideration is that the selected method does not leave toxic residues which must be subsequently removed (Roundhill, 2001). The reduction of highly toxic and

mobile Cr (VI) to less toxic and less mobile Cr (III) is likely to be useful for the remediation of the contaminated waters and soils (Palmer and Wittbrodt, 1991).

Bioremediation has the potential for the remediation of heavy metal contaminated sites. It has been established that biosurfactants which are produced from bacteria and yeasts have the potential for environmental remediation of heavy metals from soil and sediments (Mulligan et al., 2001). As biosurfactants solubilize and disperse contaminants as a soil washing technique, they are a potential solution for heavy metal removal. An attractive characteristic is that they can be produced from readily available and renewable substrates such as sugars and food grade oils. Other advantages include effectiveness at extreme temperatures, pH and salt concentrations, low critical micelle concentration (CMC) values and high degrees of effectiveness in lowering the surface tension (Mulligan and Gibbs, 1993). Therefore, biosurfactants present effective and nontoxic candidates for the remediation of contaminated sites.

The biosurfactant used in this study is called rhamnolipids which is from the glycolipid group and made by *Pseudomonas aeruginosa*. There are four types of rhamnolipids. Rhamnolipids type I and type II are suitable for soil washing and heavy metal removal which is the concern of this study. The biosurfactant JBR210 which was used in this study is an aqueous solution of 10% rhamnolipid containing two major rhamnolipids, RLL (R1) and RRL (R2). JBR210 is a readily biodegradable surfactant with a very low environmental impact. Its toxicity is very low as a commercial surfactant.

The objectives of this research were to determine the feasibility of using biosurfactant (Rhamnolipid JBR210) to enhance the removal and reduction of hexavalent chromium in water and soil media and also to investigate the factors influencing the reduction efficiencies.

## 2 MATERIALS AND METHODS

### 2.1 Materials

Potassium dichromate ( $K_2Cr_2O_7$ ) was purchased from Fisher Scientific Canada Ltd. Rhamnolipids (JBR210) was obtained from Jeneil Biosurfactant Co LLC. Soil was collected from Parc Jean Drapeau, Montreal. Distilled water was prepared in the Environmental Engineering laboratory at Concordia University.

### 2.2 Procedure for batch tests: water part

Potassium dichromate ( $K_2Cr_2O_7$ ) was used as a source of hexavalent chromium. A stock solution of 2000 ppm of Cr (VI) was prepared by dissolving  $K_2Cr_2O_7$  in distilled water. The working solutions were prepared by diluting the stock solution with distilled water. Batch studies were performed by varying pH, surfactant concentrations, Cr (VI) concentrations, temperatures and contact time. Samples were taken after 24 h shaking to ensure that equilibrium has been reached and then centrifuged. The supernatant was then analyzed by Perkin Elmer 'Lambda 40' UV/VIS spectrometer for Cr (VI) concentration by a colorimetric method. A purple color was generated with

1,5-diphenylcarbazide complexation agent (DPC) at a visible wavelength of 540 nm according to the procedure of U.S.EPA (1992). The initial Cr (VI) concentration was also measured the same way. Then the percentage of Cr (VI) reduction was determined by the Eq. 1.

$$\% Cr (VI)_{reduction} = \frac{[Cr (VI)_{initial} - Cr (VI)_{final}]}{Cr (VI)_{initial}} \times 100 \% \quad [1]$$

### 2.3 Soil spiking procedure

The required amount of predissolved potassium dichromate ( $K_2Cr_2O_7$ ) was added to the air dried uncontaminated soil. A ratio of 1 g of soil per 10 mL of solution (2000 mg/L) was used. The soil was left in the solution over one week. The soil was shaken on a reciprocating orbital shaker for 24 hours and then removed by centrifugation (3000 rpm, 20 min) and oven dried. To obtain different concentrations in soil, the soils were left in the solutions (2000 mg/L and 4000 mg/L) for 3, 7 and 10 days. For most experiments, the soil was used with a contamination level of 1040 mg/kg (of soil) which was obtained by keeping a 2000 mg/L solution in soil for one week. Other concentrations were 880 mg/kg, 1480 mg/kg, 1820 mg/kg and 2040 mg/kg. The experiments were performed 2.5 months after contaminating the soil.

### 2.4 Initial contamination measurement

Contaminated dry soil samples were digested with concentrated nitric acid and the samples were prepared for Atomic Absorption Spectrophotometer analysis. Then initial Cr concentrations in the soil were measured.

### 2.5 Procedure for batch tests: soil part

Batch soil washing studies were performed by varying the pH, soil solution ratios, surfactant concentration, initial Cr (VI) concentration, temperatures and contact time. Samples were taken after 24 hours shaking to ensure that equilibrium has been reached and then centrifuged. The supernatant was then analyzed for total Cr concentration by atomic absorption spectrophotometer and for Cr (VI) by a UV/VIS spectrometer. The rhamnolipid biosurfactant was used to determine its capability in removing Cr (VI) from the soil. Distilled water alone was used as a control to account for the removal of contaminants by physical mixing. All results are the average of duplicate experiments and are presented as % Cr removal.

$$\%Cr \text{ removal} = \frac{mg \text{ Cr in supernatant}}{mg \text{ Cr in original soil}} \times 100\% \quad [2]$$

$$\%Cr(VI) \text{ reduction} = \frac{\text{Total extracted Cr} - Cr(VI)}{\text{Total extracted Cr}} \times 100\% \quad [3]$$

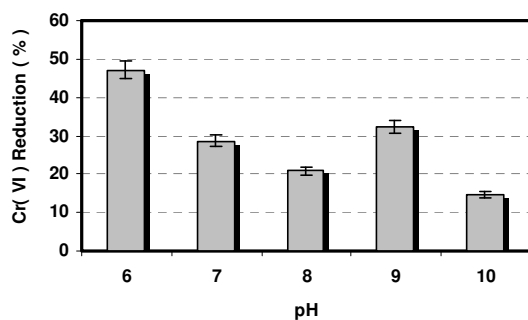
## 2.6 Sequential extraction procedure

Sequential extraction of heavy metals includes several steps to determine each portion of the metal component in the soil (Mulligan, 1998). Sequential extractions of soils were done before and after the soil washing. Soil samples of one gram were washed with the biosurfactant solution and control and then dried prior to sequential extraction. Each of the fractions was collected and the concentration of Cr was determined in each of the fractions by AA analysis. The amounts of Cr extracted from the soil by each of the extractants were then calculated.

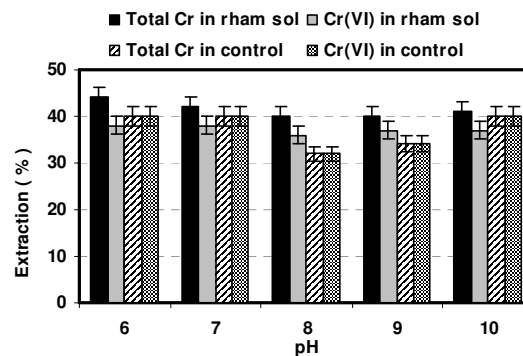
## 3 RESULTS AND DISCUSSION

### 3.1 Effect of pH

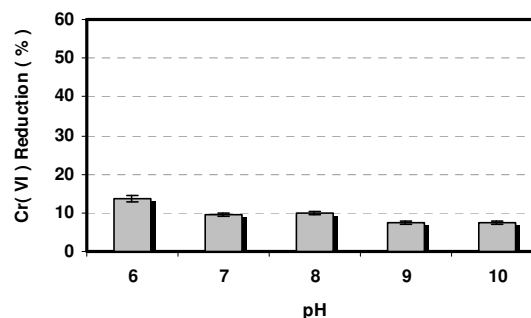
The effect of pH was investigated by treating 10 ppm of Cr (VI) solution with 0.5% rhamnolipid at 25°C for 24h in water media and in case of soil the experiment was done taking one gram of soil (initial contamination level of 1040 ppm) and 10 mL of 0.5% rhamnolipid solution at 25°C.



(a)



(b)



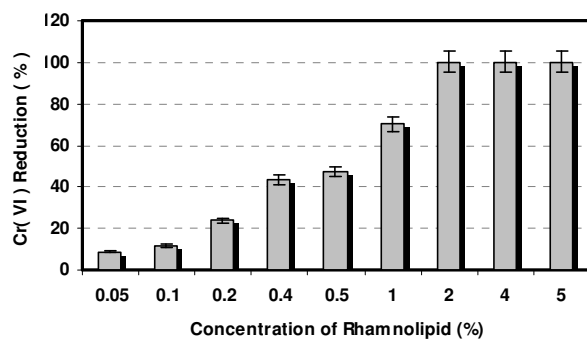
(c)

Figure 1. Effect of pH on the extraction (b) and reduction of Cr (VI) (a) in water and (c) in soil

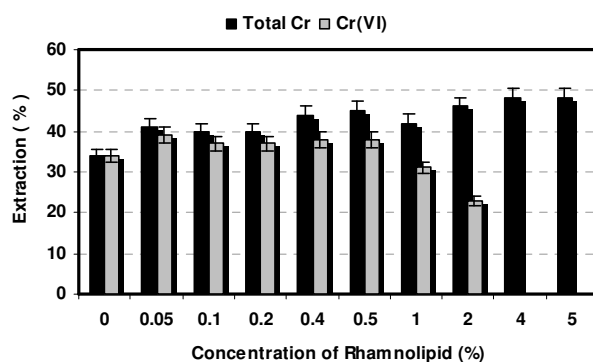
The maximum reduction was obtained at pH 6 both in water and soil (Figure 1: a, c) but the reduction was 47.1% of initial Cr (VI) concentration in water and 13.6% of extracted Cr (0.44 mg) in the soil. The reduction of Cr (VI) appeared to decrease with the increase of pH. The result was in accordance with previous research performed on reduction of hexavalent chromium by ascorbic acid in aqueous solutions (Xu et al., 2004) where increasing the pH resulted in more Cr (VI) remaining in aqueous solutions.

### 3.2 Effect of concentration of biosurfactant

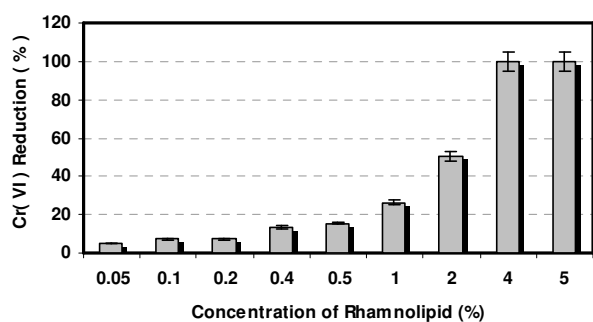
This experiment was done taking 10 ppm of Cr (VI) solution for water media and one gram of 1040 ppm contaminated soil in the case of soil media with various rhamnolipid concentrations such as 0.05%, 0.1%, 0.2%, 0.4%, 0.5%, 1%, 2%, 4% and 5%. The pH was 6, temperature was 25°C and time was 24h.



(a)



(b)



(c)

Figure 2. Effect of concentration of rhamnolipid on the extraction (b) and reduction of Cr (VI) (a) in water and (c) in soil

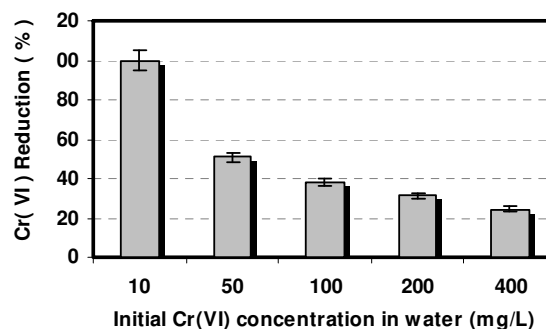
Figure 2 shows the results which indicate that the reduction efficiency increases with the increase of the concentration of rhamnolipid. The maximum reduction (100%) was achieved by a 2% rhamnolipid concentration which was chosen as the optimum concentration.

In the case of soil, both the extraction of Cr and the reduction of Cr (VI) increase with an increase in the rhamnolipid concentration. The maximum extraction is 48% of initial concentration which was obtained at 4% and 5% rhamnolipid concentrations. However, the 4% and 5% concentrations are viscous and hard to work with. On the other hand, 2% rhamnolipid concentration gave a

46% extraction which was chosen as the optimum rhamnolipid concentration.

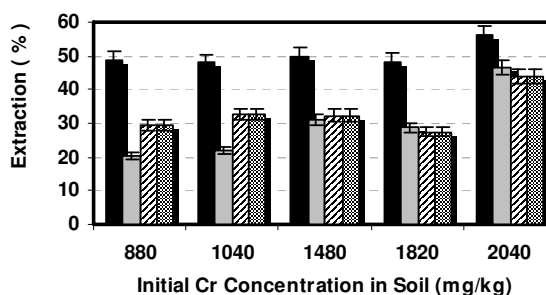
### 3.3 Effect of initial concentration of Cr (VI)

To determine the effect of different initial metal ion concentrations on the reduction of Cr (VI), an experiment was performed using various initial concentrations of Cr (VI) at optimum pH (6) and rhamnolipid concentration (2%) at 25°C for 24 h. Figure 3 (a, c) shows the percentage reduction of Cr (VI) at different initial metal ion concentrations (a) in water ranging from 10 to 400 ppm and (c) in soil. An increase in Cr (VI) concentration from 10 to 400 ppm resulted in a decreased reduction of Cr (VI). The percent reduction of Cr (VI) decreased by increasing initial Cr (VI) concentrations in the solutions with complete reduction at 10 ppm and only 25% reduction of 400 ppm. The amount of Cr (VI) reduced increased with an initial Cr (VI) concentration and maximum reduction of 100 ppm was observed at an initial concentration of 400 ppm. Erdem et al. (2005) also showed that the amount of the Cr (VI) reduced increases with an increasing initial chromium concentration.

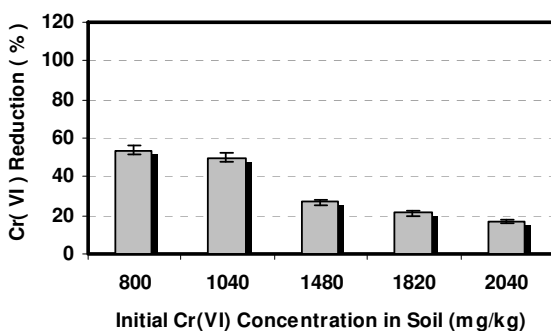


(a)

■ Total Cr in rham sol □ Cr(VI) in rham sol  
▨ Total Cr in control ▩ Cr(VI) in control



(b)



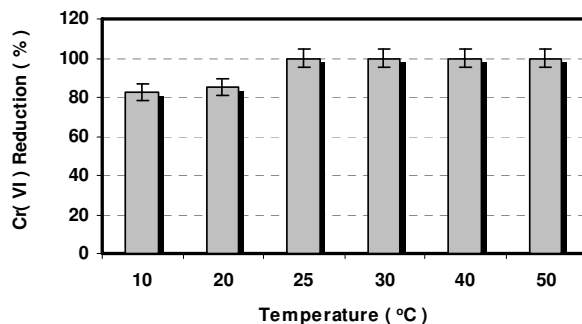
(c)

Figure 3. Effect of initial concentration of Cr (VI) on the extraction (b) and reduction of Cr (VI) (a) in water and (c) in soil

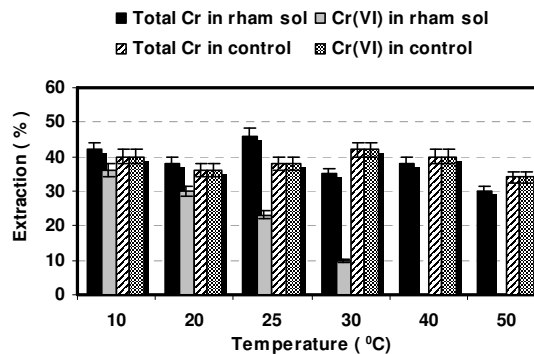
In the case of soil the initial concentrations were 880, 1040, 1480, 1820 and 2040 ppm. The extraction of Cr increases with the increase of initial Cr concentration in soil. The maximum removal value of 56% was observed at an initial concentration of 2040 mg/kg of soil. The reduction of Cr (VI) decreases with the increase of extraction of Cr. In other words, the percentage reduction decreases with higher initial Cr concentration in soil. The maximum reduction percentage was 53.8% of the extracted Cr which corresponds to an initial concentration of 880 mg/kg of soil. The minimum reduction percentage was observed for an initial concentration of 2040 mg/kg of soil which is 16.8% of the extracted Cr.

### 3.4 Effect of temperature

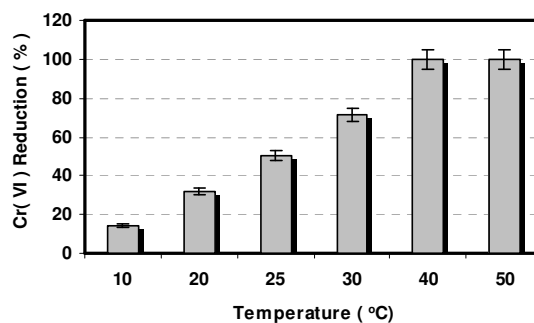
Cr (VI) reduction by rhamnolipid was studied in the range of 10-50°C taking 10 ppm Cr (VI) solution at pH 6 and 2% rhamnolipids concentration. For the soil part, one gram of soil (1040 ppm) was used and all other conditions were the same as in the water tests.



(a)



(b)



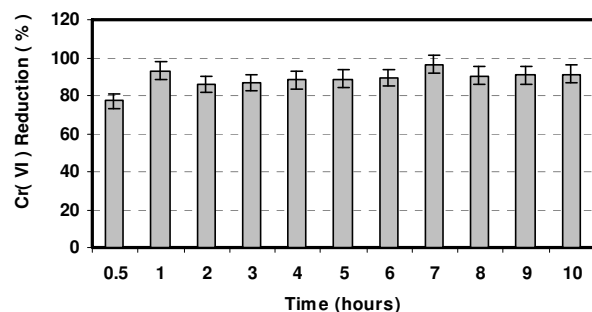
(c)

Figure 4. Effect of temperature on the extraction (b) and reduction of Cr (VI) (a) in water and (c) in soil

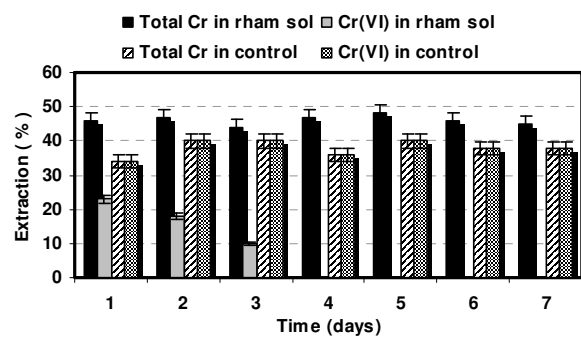
Figure 4 (a, c) shows the percentage of the reduction of Cr (VI) as a function of temperature which indicates that reduction percentage of the Cr (VI) is enhanced with the increase of temperature. This may be a result of the increase in the solubility and mobility of Cr (VI) ions with temperature (Malkoc and Nuhoglu, 2007). The solubility of rhamnolipid also increases with temperature and consequently so does the reduction capacity.

### 3.5 Effect of time

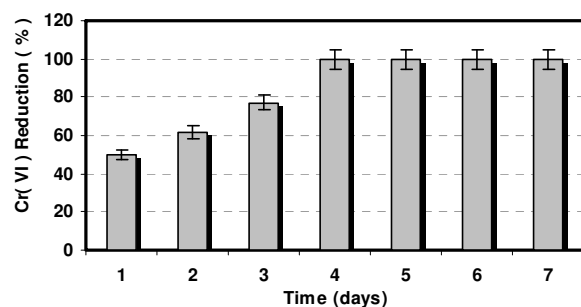
The results of the reduction of Cr (VI) by rhamnolipid over time are presented in Figure 5. This experiment was performed taking 10 ppm of Cr (VI) solution for water media and one gram (1040 ppm) of soil at optimum conditions (pH 6 and 2% rhamnolipid concentration) at 25°C. The reduction rate of Cr (VI) was very fast initially in water media and about 77% of the starting Cr (VI) was reduced within the first 30 minutes and about 93% reduction occurred within the first hour but after that the reduction rate decreased over the reaction time.



(a)



(b)



(c)

Figure 5. Effect of time on the extraction (b) and reduction of Cr (VI) (a) in water and (c) in soil

For the soil part, the experiment was carried out for 7 days and no significant changes in Cr extraction were observed. The extraction was almost the same for each day which varied from 45 to 48% of the initial Cr concentration. Although the extraction was the same each day, the reduction of Cr (VI) increased with time. After one day the reduction of Cr (VI) was 50% of the extracted Cr. After 4 days, Cr (VI) was completely reduced.

### 3.6 Selective sequential extraction

Selective sequential extraction experiments were performed on the soil without soil washing or pH adjustment prior to the procedure and also following soil washing to determine which fractions were removed by the surfactants. The soil was washed using 2%

rhamnolipid solution at pH 6 and distilled water was used as control. The fraction removed by the rhamnolipid or control is designated as the soluble fraction. Figure 6 shows the sequential extraction of Cr. It can be seen that the exchangeable and carbonate fractions of Cr are 24% and 10% respectively whereas the oxide fraction accounted for 44% of Cr present in the soil. The organic fraction made up about 10% of the Cr. The residual amount is about 12% of the Cr present in the soil.

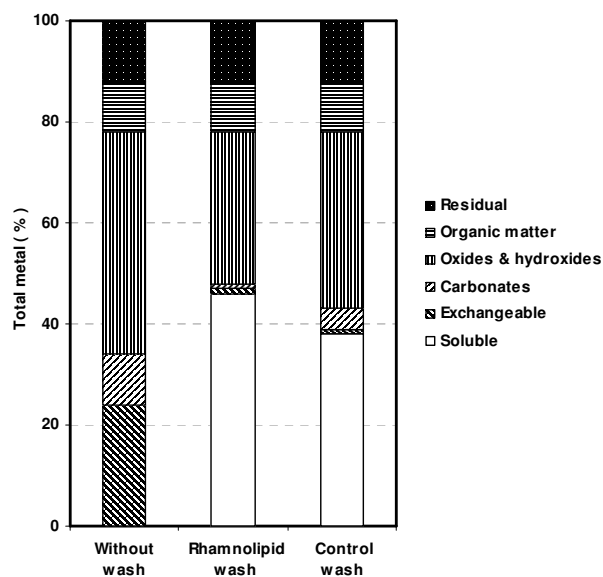


Figure 6. Sequential extraction of Cr (VI) contaminated soil

## 4 CONCLUSIONS

This research was performed to evaluate the feasibility of using rhamnolipid for the reduction of hexavalent chromium both in water and soil media. The study dealt with several factors involved in reduction of Cr (VI) to find the optimum conditions. The parameters were pH, concentration of biosurfactant, initial Cr concentration, temperature and contact time. pH, initial Cr concentration and rhamnolipid concentration have a significant effect on the reduction of Cr (VI).

The reduction trend of Cr (VI) both in water and soil media was the same but the reduction efficiency was better in water than soil although the experimental conditions were the same in both cases. The main reason for this is that soil adsorbs rhamnolipids, thereby lowering the reduction capacity of rhamnolipid.

## ACKNOWLEDGEMENTS

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