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Reduction of Chromium in Water and Soil using a Rhamnolipid Biosurfactant

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ABSTRACT: Hexavalent chromium is of great concern as it is highly toxic and carcinogenic. The objective of this study is the reduction of hexavalent chromium to trivalent chromium using the biosurfactant rhamnolipid in both water and soil media. Rhamnolipid is readily biodegradable with a very low environmental impact. Batch experiments were performed to evaluate the feasibility of using rhamnolipid for the removal and reduction of hexavalent chromium from contaminated soil and water. Rhamnolipid concentration, pH and temperature were evaluated and found to affect the reduction efficiency. At a low concentration of Cr (10 ppm), 100% of initial Cr (VI) in water at optimum conditions was reduced., whereas at a higher concentration (400 mg/L) the reduction was lower (*24.4%).* In the case of soil, rhamnolipid, the reduction trend of the extracted chromium is the same as in water media.

KEYWORDS: Remediation, Chromium, Biosurfactant, Rhamnolipid

1. INTRODUCTION

Chromium can be readily found in the environment as it is one of the most widely industrial used metals, resulting in large quantities of it being discharged into the environment (Bartlett, 1991).It is one of the most frequently found contaminant at National Priority List (NPL) sites (USEPA, 2004). Although chromium is present in the hexavalent chromium [Cr (VI)] or trivalent chromium [Cr (III)] forms, Cr (VI) is of greatest concern due to its toxicity and carcinogenic properties. There is also the potential for the contamination of groundwater due to its greater mobility in soils and in the aquatic environment. 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. Therefore, to reduce the risk to the public health and the environment, the remediation of chromium contaminated sites is highly desirable (Reddy et al., 1997; Erdem et al., 2004).

Major sources of chromium include the following industries: metal processing, 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). In 2011, more than 24 million metric tons of chromium were produced (Papp, 2012). The heavy metal pollution of soil results in negative environmental impacts including groundwater contamination. The percolation of rainwater through soil causes the slow extraction of metals which may reach aquifers (Arnfalk et al., 1996). The improper storage or burial of production residues from different industrial or commercial sites leads to the toxic heavy metal contamination of soil and subsequent groundwater contamination. Sometimes leaking or mishandling during the transportation of different hazardous materials cause the contamination. The soil contamination contributes not only to pollution of groundwater but also results in restricted utilization of the site and in some cases, a complete prohibition on cultivation or other potential use of the area (Abumaizar et al., 1999). In the environment, Cr (VI) does not readily precipitate or become bound to components of soil. Therefore, Cr (VI) is highly mobile 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, wastes and sediments (Dahl et al., 2013). The speciation of the contaminants and other site-specific characteristics are among the criteria for selection of a specific technology for treatment of a contaminated site. Another important consideration is that the selected method does not leave toxic residues (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).

Soil flushing and washing has various advantages such as a short treatment time and the possibility of extracting metals from the washing effluents (Dermont et al., 2008). Mechanisms for metal removal include ion exchange, solubilization of metals and solubilization of mineral components containing the contaminants. Reduction of Cr(VI) to Cr(III) via chemical means is an additional mechanism for chromium.

Biological products called biosurfactants which are produced from bacteria and yeasts have the potential for environmental remediation of heavy metals from soil and sediments (Mulligan et al., 2001a). As biosurfactants solubilize and disperse contaminants during soil washing, they are a potential solution for heavy metal removal. They can be produced from readily available and renewable substrates such as sugars and food grade oils or even waste materials. 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 an anionic rhamnolipid which is from the glycolipid group produced by *Pseudomonas aeruginosa.* There are four types of rhamnolipids. Rhamnolipids type I and type II are suitable for soil washing and heavy metal removal due to their carboxylic functional groups, hydrophobic and hydrophilic portions. The biosurfactant JBR210 which was used in this study is an aqueous solution of 10% rhamnolipid containing two major rhamnolipids, RLL (R1) and RRLL (R2). JBR210 is a readily biodegradable surfactant with a very low environmental impact. Its toxicity is very low as a commercial surfactant and also it has low skin irritation at use (Mulligan, 2009).

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 to investigate the factors influencing the reduction efficiencies.

2. MATERIALS AND METHODS

2.1 Materials

Natural soil used in this study was collected from a park. The soil was free from contamination. It was contaminated artificially and then used for the experiments. The soil sample was characterized using standard EPA or ASTM methods before contaminating it. Cation exchange capacity (CEC) was determined using the method proposed by Chapman (1965) and obtained value was 11.2 cmoles/kg. Particle size distribution was performed according to the standard method for soil ASTM D422-63 (ASTM, 1998). The grain size distribution of the soil indicates a sandy soil. Approximately 80.8% was finer than 2 mm and 1.8% passed through a 0.075 mm sieve. Loss on ignition (LOI) was another parameter chosen to estimate the organic content in the soil. According to the ASTM D2974-00 method (ASTM, 2000), oven dried soil samples (105°C) were placed in a furnace at 550°C for 4 hours. After the soil was cooled in a desiccator and the weight (w) was measured, loss on ignition (%) in each sample was calculated. The obtained organic matter content was 5.5%. To check the heavy metals content in the soil, it was digested by the method recommended by Environment Canada (1990). There was a negligible amount of chromium in the soil and low levels of Pb (5 mg/kg), Zn (70 mg/kg), Cu (70 mg/kg) and Ni (45 mg/kg) were found. Soil pH was determined by using a 1:10 soil to water ratio (EPA sw 846 method 9045D) which was 7.3. The measured soil moisture content was 9.2%. Carbonate content was measured by following the procedure of Mulligan et al. (2001) and the obtained carbonate content was 3.5%. Soil specific gravity was determined by using the standard method ASTM D854 – 98.

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

2.2 Procedures for batch water tests

Potassium dichromate ($K_2Cr_2O_7$) was used as a source of hexavalent chromium. A stock solution of 2000 mg/L of Cr (VI) was prepared by dissolving $K_2Cr_2O_7$ in distilled water. The stock solution was diluted with distilled water to prepare the required solutions as required. 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 Method 7196A (1992). The initial Cr (VI) concentration was also measured the same way. Then the percentage of Cr (VI) reduction was determined by the equation:

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

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. For different concentrations in soil, the soils were left in the solutions (2000 mg/L, 4000 mg/L) for 3, 7 and 10 days. For most experiments, the soil was used with a Cr contamination level of 1040 mg/kg (of soil) which was obtained by keeping 2000 mg/L solution in soil for one week. Other Cr concentrations were 880 mg/kg, 1480 mg/kg, 1820 mg/kg and 2040 mg/kg. The experiments were done 2.5 months after contaminating the soil to ensure stronger Cr bonding to 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. Analyses were performed using a Perkin Elmer Atomic Absorption Analyst 100 Spectrophotometer. Chromium (357.9 nm) was analyzed after preparing the standards, blanks and samples according to standard methods (APHA-AWWA-WPCF, 1980).Then the initial Cr concentrations in the soil were measured.

2.5 Critical micelle concentration measurement

One of the most widely used indices for evaluating surfactant activity is the critical micelle concentration (CMC). CMC is the minimum surfactant concentration required to reach the lowest interfacial or surface tension values. The CMC was found by determining the variation of surface tension with biosurfactant concentration. The surface tension of rhamnolipid solution at different concentrations was measured with a Fisher Scientific Surface tensiometer. The duNouy ring method was used, where the ring was pulled through the rhamnolipid solution until it broke through the surface. The value of the surface tension at that point was recorded. The surface tension was measured at various dilutions and CMC was determined. The CMC is the point at which the surface tension abruptly increases (Mulligan et al., 2001a). Hence, concentrations above the CMC were used for the experiments in order to ensure the formation of micelles.

2.6 Soil washing procedure

Batch soil washing studies were performed by varying 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 adsorption spectrophotometer and for Cr (VI) by a UV/VIS spectrometer. Cr (VI) concentration was measured by Perkin Elmer 'Lambda 40' UV/VIS spectrometer by a colorimetric method. 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 Method 7196A (1992). The soil washing efficiency is presented as percent Cr removal which is the mg Cr extracted in the supernatant compared to the initial mg content in the soil.

The biosurfactant rhamnolipid 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.

2.7 Sequential extraction procedure

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 according to Yong et al. (1993). The soil samples were washed using rhamnolipid solution and control and then dried prior to sequential extraction. The most available metals were found in the water soluble and exchangeable fractions by adding 8 ml of 1 M $MgCl_2$, pH 7, to 2 g dried soil sample with shaking for 1 hour at room temperature (23°C). Metals associated with carbonate were extracted by adding 8 ml of sodium acetate, pH adjusted to 5 with acetic acid, with 5 hours shaking at room temperature. Metals bound to Fe-Mn oxides and hydroxides were removed by adding 20 ml of 0.04 M $NH_2OH.HCl$ in 25% (v/v) acetic acid at 96°C in a water bath for 6 hours. To extract metals from organic and sulphide matter, 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 (pH 2) were added at 85°C for 2 hours, followed by 3 ml of 30% H_2O_2 (pH 2) at 85°C for 3 hours. Finally 5 ml of 3.2 M ammonium acetate in 20% (v/v) HNO_3 were added and then diluted to 20 ml at room temperature for 30 minutes. The last fraction is called the residual fraction and soil samples were digested in order to remove heavy metals in this fraction by applying a diluted aqua regia (50 ml HCl + 200 ml HNO_3 + 750 ml deionized water) for 3 hours at 96°C. After each extraction step the suspensions were centrifuged at 3500 rpm for 20 minutes. Each of the fractions was collected and the concentrations of chromium were measured in each fraction by atomic absorption spectrometry and then the amounts of chromium were calculated.

3. RESULTS AND DISCUSSION

3.1 Water experiments

3.1.1 Effect of pH

The first experiment was done varying the pH to see its effect on the reduction of Cr (VI). As the rhamnolipid precipitates below pH 5.5 (Dahrazma, 2005), pH values of 6 to 10 were studied. The effect of pH was investigated by treating 10 ppm of Cr (VI) solution with 0.5% rhamnolipid at 25°C for 24h. This mixture of solutions were obtained taking 10 ml of 50 ppm $K_2Cr_2O_7$ solution, 25 ml of 1% rhamnolipid solution and 15 ml of distilled water to have the final volume of 50 ml. Figure 1 shows the reduction of Cr (VI) at different pH values studied. The reduction of Cr (VI) by the rhamnolipid with carboxlic functional groups appeared to decrease with the increase of pH. Reduction of chromium by organic compounds with carboxyl, carbonyl and hydroxyl functional groups is more rapid at low pH. The result was also in accordance with previous research performed on reduction of hexavalent chromium by ascorbic acid (Xu et al., 2004) where increasing the pH resulted in lower rates of reduction of Cr (VI) .

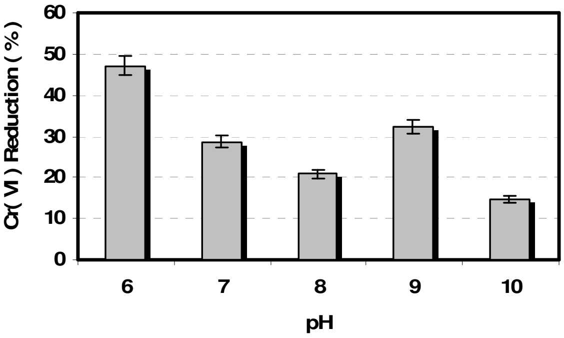

Figure 1 Effect of pH on the reduction of Cr (VI) using 10 ppm Cr (VI) solution & 0.5% rhamnolipid solution

The maximum reduction efficiency (47.1%) was obtained at pH 6 and this result agrees with the research performed on reduction of hexavalent chromium by *Streptomyces griseus* (Laxman & More, 2002) where maximum conversion of hexavalent to trivalent form was observed in the pH range of 6-7. At pH 10, a small amount (about 15%) of Cr (VI) was reduced.

3.1.2 Effect of concentration of rhamnolipid

This experiment was performed with 10 mg/L of Cr (VI) solution with various rhamnolipid concentrations. The pH was 6, temperature was 25°C and time was 24h. 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% of rhamnolipid concentration which was chosen as the optimum concentration.

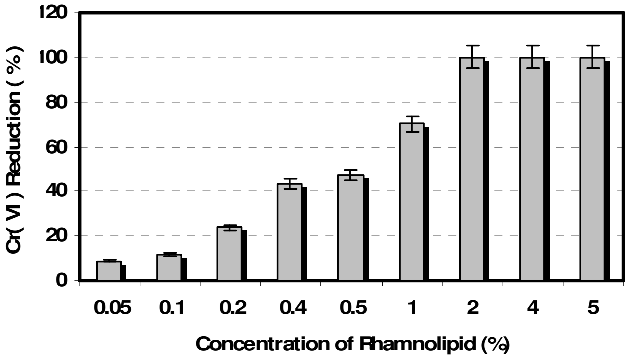

Figure 2 Effect of concentration of rhamnolipid on Cr (VI) reduction using 10 ppm Cr (VI) solution

With the increase of rhamnolipid concentration, the concentration of Cr (VI) decreased when the concentrations of rhamnolipid were in the range of 0.05 to 2% (20000 mg/L). At a rhamnolipid concentration of 2% and higher, the concentrations of Cr (VI) in the solution were negligible. Therefore, the amount of rhamnolipid for the reduction of 10 mg/L hexavalent chromium is 20000 mg/L. Hence, the molar ratio of rhamnolipid required for the reduction of Cr (VI) was 1:180.

3.1. 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. The percentage reduction of Cr (VI) was determined at different initial metal ion concentrations ranging from 10 to 400 mg/L. An increase in Cr (VI) concentration from 10 to 400 mg/L resulted in a decreased reduction of Cr (VI). This confirms the previously determined optimal molar ratio of 1:180.

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 mg/L. The amount of Cr (VI) reduced was increased with an initial Cr (VI) concentration and maximum reduction value of 100 mg/L was observed at 400 mg/L. Erdem et al. (2004) also showed that the amount of Cr (VI) reduced decreases with increasing the initial chromium concentration.

3.1.4 Effect of temperature

The temperature dependence of Cr (VI) reduction by rhamnolipid was studied in the range of 10-50°C taking 10 mg/L Cr (VI) solution at pH 6 and 2% rhamnolipid concentration. Figure 3 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 increase in the solubility and mobility of Cr (VI) ions with temperature (Malkoc and Nuhogldu, 2007). The solubility of rhamnolipid also increases with temperature and consequently so does the reduction capacity.

Xu et al. (2004) and Erdem et al. (2004) also showed that reduction percentage of the Cr (VI) increases by increasing the temperature of the solution, by ascorbic acid and siderite, respectively, for the reduction of Cr (VI) in aqueous solutions.

The maximum reduction (100%) was obtained at 25°C and after that temperature, the reduction was the same. At low temperatures, reduction decreases because the temperature might be below the Krafft point (the temperature at which the solubility of an ionic surfactant becomes equal to the CMC of the surfactant) of the surfactant components which can cause the surfactant concentration to drop below the CMC, thereby rendering the surfactant useless (West & Harwell, 1992).

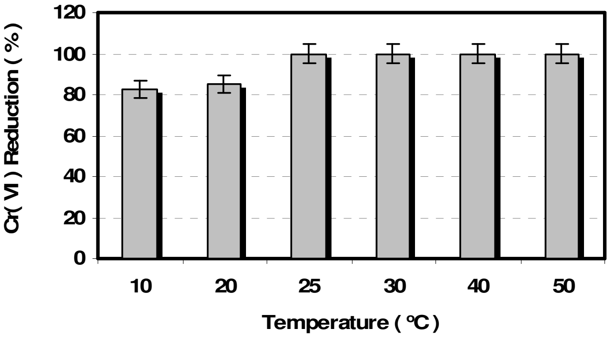

Figure 3 Effect of temperature on Cr (VI) reduction using 10 ppm Cr (VI) solution & 2% rhamnolipid solution

3. 1.5 Effect of time

The results of the reduction of Cr (VI) by rhamnolipid over time are presented in Figure 4. This experiment was performed taking 10 mg/L of Cr (VI) solution at optimum condition (pH 6 and 2% rhamnolipid concentration) at 25°C. The reduction rate of Cr (VI) was very fast initially and about 77% of the initial Cr (VI) was reduced within the first 30 minutes and about 93% reduction within the first hour but after that the reduction rate decreased over the reaction time. Deng (1995) showed that the reduction of chromium(VI) by organic compounds such as ascorbic acid at neutral pH could take months to years for 50% reduction to occur.

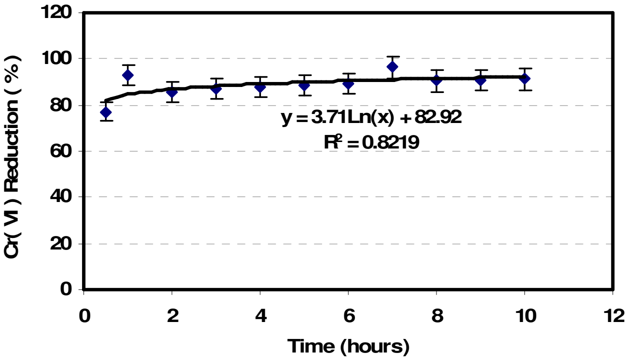

Figure 4 Effect of time on Cr (VI) reduction using 10 mg/L Cr (VI) solution & 2% rhamnolipid solution

As the curve does not show any local maximum, a time at which the slope of the curve becomes less than 1% reduction per hour was considered as the optimum time. This was at 4 hours.

3.2 Soil experiments

3.2.1 Effect of pH

Soil washing experiments were performed at various pH values to determine their effects on Cr extraction and also on the reduction of Cr (VI). The initial Cr contamination level of soil was 1040 mg/kg for this experiment. The experiment was done with one gram of soil and 10 mL of 0.5% rhamnolipid solution at 25°C.

The maximum total Cr was removed at pH 6 which is 44% of initial total Cr concentration in soil (Figure 5). Although the control (distilled water) can extract a good percentage of Cr (VI) which is very soluble in water, the amount was less than by the rhamnolipid. However as the control showed that the total Cr was the same as Cr(VI) , this means that the control cannot reduce the Cr (VI) in this solution. This was not the case for the rhamnolipid solutions, where at all pH values, the amount of Cr(VI) was less than the total Cr. This decrease of Cr (VI) in the rhamnolipid solution indicates the reduction of Cr (VI) to trivalent form by the rhamnolipid.

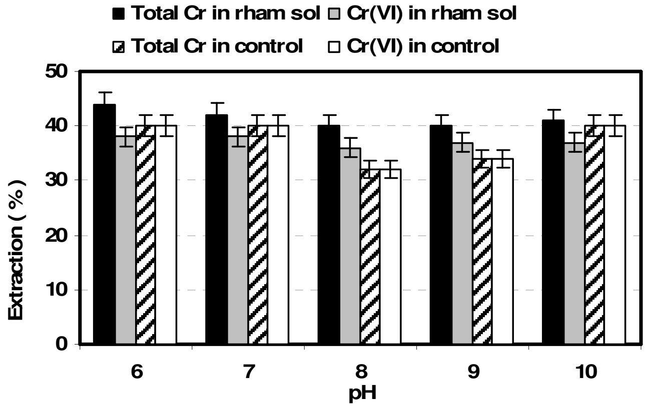

Figure 5 Removal of Cr (VI) at different pH from 1040 mg/kg contaminated soil & 0.5% rhamnolipid solution

Figure 6 shows the reduction of Cr (VI) at different pH values for the rhamnolipid solutions. Maximum reduction was obtained at pH 6 which is 13.6% of extracted Cr. As maximum reduction was obtained at pH 6, this pH was selected as the optimum pH and all other experiments were performed at this pH.

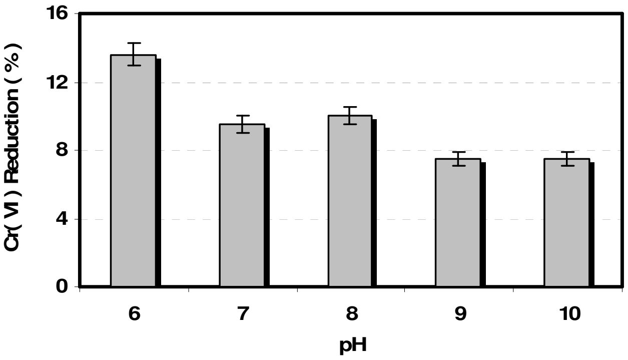

Figure 6 Effect of pH on Cr (VI) reduction by rhamnolipid

3.2.2 Effect of surfactant to soil ratio

This experiment was performed by taking one gram of contaminated soil (1040 mg/kg) with various volumes of 0.5% rhamnolipid solutions at pH 6 and 25°C. The rhamnolipid volumes were 10, 20, 30, 40 and 50 mL. Figure 7 shows the extraction of Cr at various volumes of rhamnolipid washing solution.

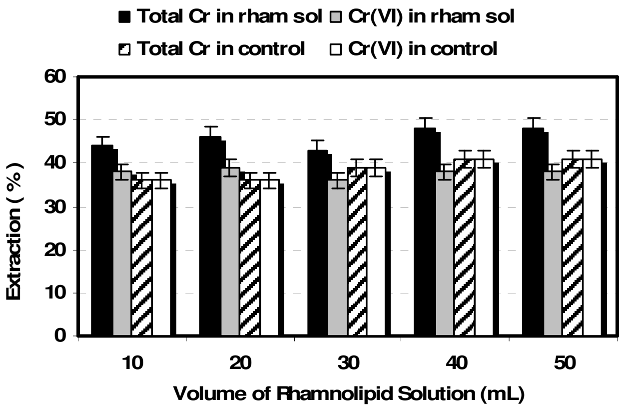

Figure 7 Removal of Cr (VI) at various surfactants to soil ratios from 1040 mg/kg contaminated soil & 0.5% rhamnolipid solution

The Cr removal from the soil increases with the increased volumes of rhamnolipid solutions but not by a large amount. Therefore, as using larger volumes of surfactant solutions will not be economic, 20 mL was chosen for all other experiments.

The reduction of Cr (VI) also increases with the increase of rhamnolipid solutions. Figure 8 shows the reduction of Cr (VI) at various surfactant volumes. The maximum reduction is 20.8% of extracted Cr which was obtained at 40 and 50 mL of rhamnolipid solutions. Around 15% reduction was obtained at 20 mL solution which is not that different from the maximum reduction obtained.

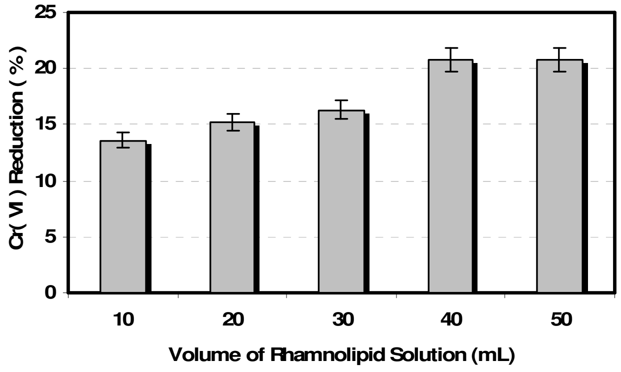

Figure 8 Effect of various rhamnolipid to soil ratios on Cr (VI) reduction

3.2.3 Effect of concentration of rhamnolipid

The washing experiment in this step was performed with one gram of contaminated soil (1040 mg/kg) and using different percentages of rhamnolipid concentrations at pH 6 and 25°C.

Both the removal of Cr and the reduction of Cr (VI) increases with an increase in the rhamnolipid concentration. Figure 9 shows the removal of Cr at various rhamnolipid concentrations. 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% removal which was chosen as the optimum rhamnolipid concentration.

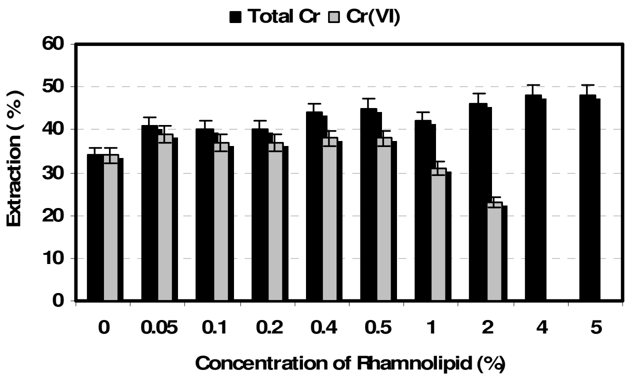

Figure 9 Removal of Cr (VI) at various rhamnolipid concentrations from 1040 mg/kg contaminated soil

Figure 10 shows the reduction of Cr (VI) at various rhamnolipid concentrations. The extracted Cr (VI) was fully reduced at 4% and 5% concentrations of rhamnolipid whereas a 2% rhamnolipid concentration reduced 50% of the extracted Cr.

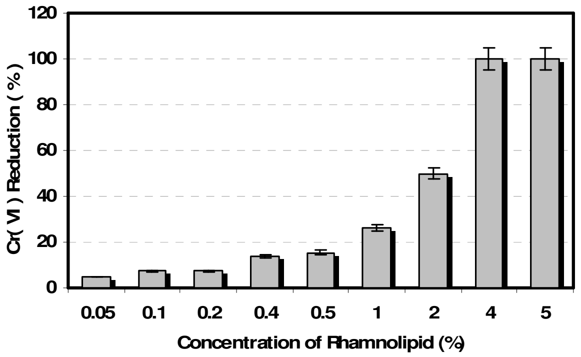

Figure 10 Effect of various rhamnolipid concentrations on Cr (VI) reduction

3.4 Effect of initial concentration of Cr (VI)

The effect of initial Cr concentration was also investigated to determine how it affects removal efficiency. The concentrations were 880, 1040, 1480, 1820 and 2040 mg/kg.

The experiment was performed using 2% rhamnolipid at pH 6 and 25°C. Figure 11 shows that 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.

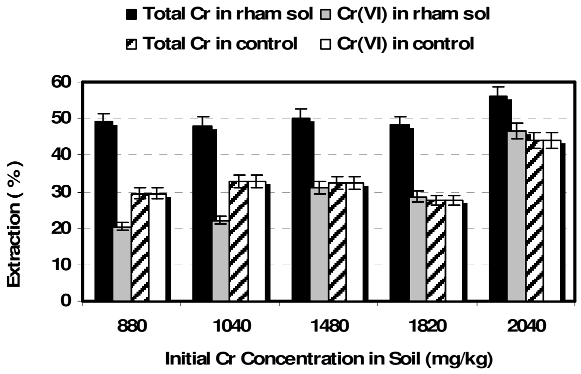

Figure 11 Removal of Cr (VI) at various initial concentrations in soil using 2% rhamnolipid solution

Figure 12 shows that the percentage 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 is 53.8% of 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 extracted Cr.

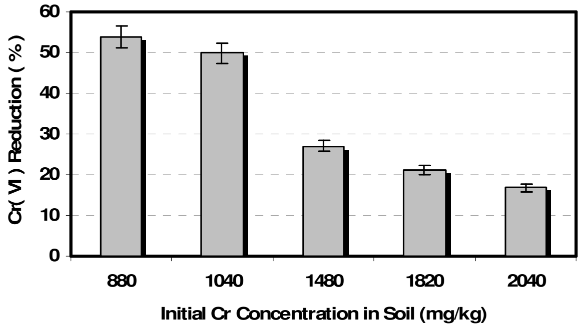

Figure 12 Effect of different initial Cr (VI) concentrations on reduction of Cr(VI)

3.2.5 Effect of temperature

This experiment was performed to evaluate the effect of temperature on the extraction and the reduction of Cr (VI). One gram of soil (1040 ppm) was washed using 2% rhamnolipid solutions at pH 6 at temperatures from 10 to 50°C.

The considered temperatures were 10, 20, 25, 30, 40 and 50°C. The extraction of Cr fluctuates with temperatures without any trend with temperatures. The maximum extraction was observed at 25°C which is 46% of the initial concentration. The extraction decreases at temperatures of 30 to 50°C.

On the other hand, Figure 13 shows that reduction of Cr (VI) increases with temperature. Maximum extraction was at 25°C but at this temperature Cr (VI) was reduced 50% of extracted Cr. Rhamnolipid is adsorbed or precipitated onto soil surface for which the effective concentration of rhamnolipid is reduced and consequently it reduces the removal efficiency. The complete reduction of extracted Cr was observed at 40 and 50°C. The reason is the solubility of both Cr (VI) and rhamnolipid increases with temperature which was discussed earlier.

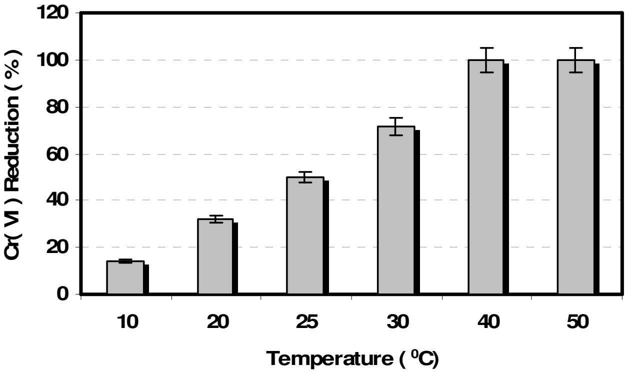

Figure 13 Effect of temperature on Cr (VI) reduction

3.2.6 Effect of time

This experiment was to determine how time affects the extraction of Cr and on the reduction of Cr (VI). One gram of soil (1040 mg Cr/kg) was washed with 2% rhamnolipid solution at pH 6 and 25°C.

The experiment was carried out for 7 days and no significant changes in Cr extraction were observed. The extraction (Figure 14) was almost the same every day which varies from 45 to 48% of the initial Cr concentration.

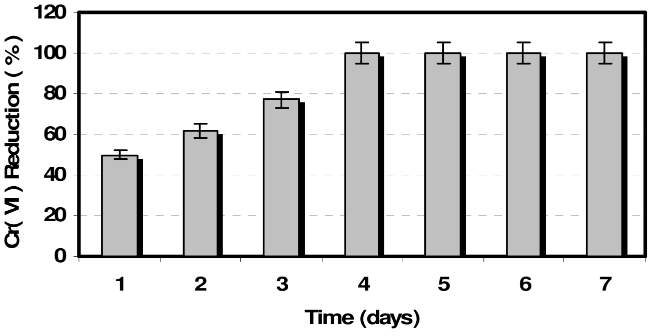

Figure 14 Removal of Cr (VI) over time from 1040 mg/kg contaminated soil & 2% rhamnolipid solution

Although the extraction did not vary over time, the reduction of Cr (VI) increased with time. Figure 15 shows the reduction of Cr (VI) with time. After one day the reduction of Cr (VI) was 50% of the extracted Cr. After 4 days Cr (VI) was completely reduced. Massara et al. (2007) also showed that hexavalent chromium was reduced by the rhamnolipid over time where they used chromium contaminated kaolinite. They found that rhamnolipid has the capability of reducing almost 100% of the extracted Cr (VI) to Cr (III) over a period of 24 days and the reduction of Cr (VI) to Cr (III) was initiated after a three-day period. In the case of soil, the rhamnolipid may have sorbed more to the soil than to kaolinite, thus decreasing the efficiency of the rhamnolipid.

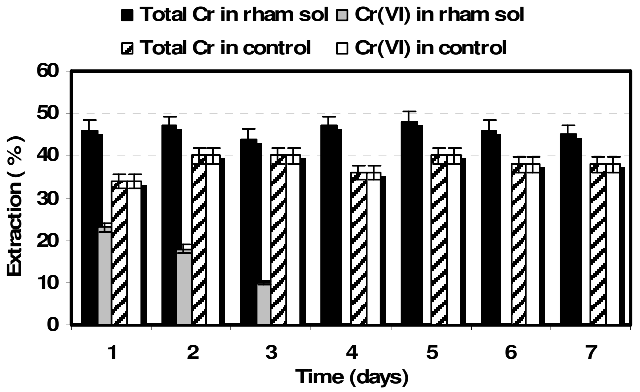

Figure 15 Effect of contact time on Cr (VI) reduction

3.2.7 Sequential extraction experiment

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. Figure 16 shows the sequential extraction of Cr Prior to washing, it was determined that the chromium was found mainly in the exchangeable and oxide fractions with lower amounts in the carbonate, organic and residual fractions. 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.

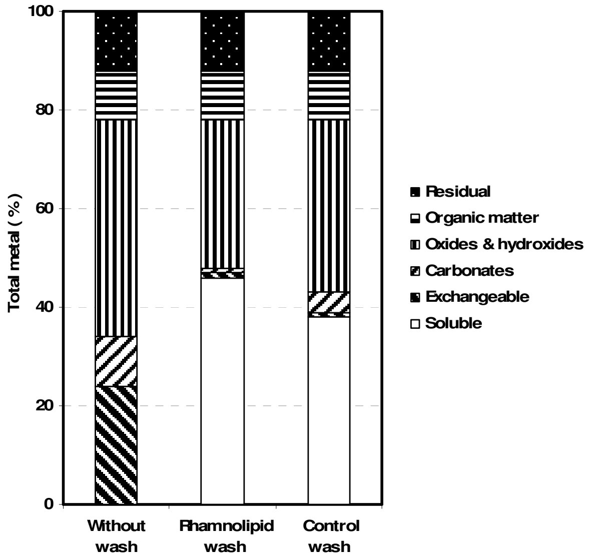

Figure 16 Sequential extraction of Cr (VI) contaminated soil

The soil was then washed using 2% rhamnolipid solution at pH 6 and distilled water was used as control. The main fraction removed by the rhamnolipid or control was from the exchangeable and carbonate fractions. The control removed lower amounts from the oxide and carbonate fractions than the rhamnolipid. The more strongly bound residual and organic fractions were not affected by the washing processes. The study shows the exchangeable portion in the soil is 24% and rhamnolipid can remove 96% of this portion. Therefore, ion exchange plays an important role in the chromium extraction process by rhamnolipid due to the anionic nature of the biosurfactant. The carbonate portion is lower (10%), but rhamnolipid can remove 90% of the carbonate portion. The study shows that Cr is mainly retained in oxides and hydroxides portion (44%). The organic and residual fractions retained 10% and 12% of chromium. Rhamnolipid can remove through solubilization some (22%) of the oxides and hydroxides portion but it cannot remove the organic and residual portions. Under acidic conditions, the oxide phase containing chromium could be released but rhamnolipid precipitates under acidic conditions (pH below 5). So, it would be difficult to remove chromium from the oxide part. The chromium associated with the organic part can be removed by rhamnolipid under basic conditions. The residual fraction is difficult to remove. The same trends were shown by a study by Parthasarathi and Sivakumaar (2011) where 48%, 60% and 29% of the exchangeable, carbonate and oxide fractions, respectively, could be removed by a 0.5% concentration of biosurfactant with less than 10% from the organic and residual fractions. Chen et al. (2011) showed that for chromium in the residual and oxide fractions, a solution of 0.5M HCl solution was necessary to remove chromium from these fractions but this leads to potential disruption of the soil structure.

4. CONCLUSIONS

Distilled water was used to determine the behavior of hexavalent chromium in water media. $K_2Cr_2O_7$ was mixed with distilled water to prepare the Cr (VI) solution. The objective of this work was to evaluate the capability of biosurfactant to reduce or convert the Cr (VI) and to determine what parameters affect the reduction of Cr (VI). The removal mechanism from soil for Cr(VI) by the biosurfactant was a combination of solubilization of the various constituents and ion exchange in combination with reduction to Cr(III).

The pH is an important factor for the reduction of Cr (VI). Maximum reduction was observed at pH 6 since both Cr (VI) and rhamnolipid are more soluble at this pH compared to other pHs at which the experiment was performed. Higher concentrations of rhamnolipid showed higher reduction rates than did lower concentrations. Although the percentage reduction of Cr (VI) decreases with the increase of initial Cr (VI) concentration, the amount of Cr (VI) reduced increased with the increase of initial Cr (VI) concentrations in the solution. Even the temperature has a positive effect on the reduction of Cr (VI). Below 25°C the reduction is a little lower but can reduce the major percentage of Cr (VI). The temperature of groundwater usually varies from 10-20°C. In that case, more time would then be needed to complete reduction of Cr (VI) or a higher concentration of rhamnolipid would be needed. The optimum time for the reduction of Cr (VI) from water was obtained by 4 hours but for higher concentrations of Cr (VI), more time is needed.

The pH of groundwater varies from 5 to 9. As rhamnolipid works well at pH 6 and at 2% concentration, rhamnolipid can be used to remediate the groundwater at optimum conditions to obtain effective results.

Soil contaminated with hexavalent chromium was used in this study. The objective of this work was to evaluate the capability of rhamnolipid in enhancing the removal of Cr (VI) from the soil and in reducing the Cr (VI). The objective also included determining what parameters affect the extraction and reduction of Cr (VI).

From the soil washing experiments at different conditions, it has been observed that the amount of extracted Cr was almost the same for all conditions. The extracted Cr ranges from 40-48% of the initial Cr concentration. Although Cr (VI) is very soluble in water not all Cr (VI) is removed when rhamnolipid or water is added to the contaminated soil. Rhamnolipid can remove only the soluble part (40-48%). Even water can extract 40% as Cr (VI) is very soluble. The extraction of chromium is almost the same in all conditions as rhamnolipid can extract only the soluble part present in the soil. The extraction increases with an increase of initial Cr concentration in the soil. The reason is that the soluble part is more there. Extraction decreased slightly at a temperature of 30-50°C. This might occur as rhamnolipid can reduce Cr (VI) to Cr (III) quickly above 30°C. Therefore, some of the soluble part of Cr (VI) in the soil might be converted to Cr (III) before it is extracted by the rhamnolipid solution.

The purpose of the sequential extraction test on soil which has been previously washed with rhamnolipid was to determine from what fraction rhamnolipid removed the metals and potential mechanisms for removal. This information can then be used to determine if soil washing by rhamnolipid is useful or effective. The sequential extraction study gives important information to design the appropriate conditions for soil washing.

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