INNOVATIVE TREATMENT FOR CHROMIUM CONTAMINATED SITES

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ABSTRACT

Hexavalent chromium Cr(VI) is a common environmental pollutant that is treated by reduction to trivalent form Cr(III) which can be oxidized again to the toxic form, Cr(VI). A study is being conducted on the removal of Cr(III) to eliminate the hazard imposed by its presence in soil. The effect of addition of negatively charged biosurfactants (rhamnolipids) on chromium contaminated soil was studied. Results showed that the rhamnolipids have the capability of extracting a portion of the stable form of chromium; Cr(III) from the soil. The removal of hexavalent chromium was also enhanced using a solution of rhamnolipids. Results from sequential extraction procedure showed that rhamnolipids remove chromium from the carbonate, and oxide/hydroxide portions of the soil.

RÉSUMÉ

Chrome hexavalent Cr(VI) est un pollutant commun qui est traité par la réduction à la forme trivalent Cr(III) qui peut être oxydé encore au forme toxique; Cr(VI). Une étude sera dirigée sur l'enlèvement de Cr (III) pour éliminer le danger imposé par sa présence dans le sol. L'effet de biosurfactants négativement chargé (rhamnolipides) sur le sol contaminé avec du chrome a été étudié. Les résultats ont démontré que les rhamnolipides ont la capacité d'extraire une portion de la forme stable du chrome; connu sous le nom de chrome trivalent. L'enlèvement du chrome hexavalent a été amélioré en utilisant la solution de rhamnolipides. Les résultats de la procédure d'extraction séquentielle ont démontré que les rhamnolipides enlèvent le chrome des fractions de carbonate, d'oxyde et d'hydroxyde du sol.

1. INTRODUCTION

Chromium is the 7th most abundant element in the earth. It exists in 9 different oxidation states, however, only trivalent and hexavalent forms are common in nature (chromium(III) and chromium(VI), respectively). Hexavalent chromium Cr(VI), is carcinogenic, mutagenic, toxic, highly soluble and mobile; therefore it is considered as a hazardous contaminant. On the other hand, trivalent chromium Cr(III), is an essential trace element for humans and is relatively stable and immobile because of low solubility and propensity to sorb to natural solids (USEPA 1995).

Through history, chromium has many industrial uses, typical industries that deal with chromium are: wood preservative and treatment, tanning and leather working, metal plating and stainless steel production, and pigmentation (Barnhart 1997, Katz et al. 1994). Those industries are the main reason for chromium contamination in soil and groundwater.

As of October 2003, there are 69 chromium contaminated sites in the province of Quebec according to the Ministry Of Environment (2003). These sites have to be treated or rehabilitated for further development.

The presence of chromium in soil is controlled by the following reactions; oxidation-reduction reactions (Redox), precipitation-dissolution reactions, and sorption-desorption reactions (Zayed and Terry 2003). Cr(VI) can be reduced chemically and biologically under both aerobic and anaerobic conditions. Ferrous iron (Eary and Rai 1988), elemental iron (steel wool) (James 1994), hydrogen peroxide (Pettine et al. 2003), hydrogen sulfide (Thornton and Amonette 1999), as well as many other chemicals such as: ferrous sulfate, ferrous ammonium sulfate, sodium sulfite, sodium hydrosulfite, sodium bisulfite, and sulfur dioxide (Higgins et al. 1997) are the well-known compounds capable of the chemical reduction of hexavalent chromium. On the other hand, many bacterial cultures (mixed or pure bacteria) are also capable of reducing the hexavalent form of chromium, such as; Streptomyces griseus (Laxman and More 2002), Entrobacter cloacae strain H01 (Rege et al. 1997), Bacillus subtilis (Garbisu et al. 1998), Pseudomonas mendocina (Salunkhe et al. 1998), Thiobacillus ferrooxidans (Quintana 2001), iron-reducing bacteria (Wielinga et al. 2001), sulphate reducing bacteria (Türick and Apel 1997) and many more.

Beside the bacterial reduction of hexavalent chromium, different plants such as vascular aquatic plants (i.e. Bacopa monnieri, Scirpus lacustris, Phragmites karka and nymphaea alba) (Chandra et al. 1997), marine algae (i.e. Pachymeniopsis sp. and Pelvetia sp.) (Lee et al. 2000), and wetland plants (E. crapssipes) (Lytle 1998) are capable of Cr(VI) reduction under different levels of chromium accumulation. Soil’s natural components have also the ability to reduce Cr(VI) to Cr(III). Some examples of these components are natural organic matter (NOM) such as: fulvic acid (Wittbrodt and Palmer 1995) and humic acid (Wittbrodt and Palmer 1996).

According to Ross et al (1981), trivalent chromium pollution problems would arise if it becomes mobilized by any means of its solubilization such as its oxidation to the hexavalent form or its complexation with naturally occurring ligands. Therefore it should not be assumed that Cr(III) is harmless when added to soil. Bartlett and James (1979) have found that trivalent chromium can be oxidized within the soil naturally by manganese (hydr)oxides which have a high.
adsorption capacity for metal ions, and the oxidation increased with decreasing pH in old, dried, sieved soil.

Another oxidant of aqueous Cr(III) is dissolved oxygen, but the oxidation rate is too slow to be considered a significant factor for Cr(III) oxidation (Eary and Rai 1987). They also found that the amount of oxidized trivalent chromium in a specific soil represents the "Oxidative Capacity of the Soil", which was very high in clay and very low in sandy soil. Quite recently, Zhang and Bartlett (1999) found a light-induced oxidation of aqueous Cr(III) to Cr(VI) in the presence of ferric iron Fe(III) under acidic conditions.

Chinthamreddy and Reddy (1999) stated that Cr(III) oxidation depends on the soil pH that which depends on the buffering capacity of the soil. In low-buffering soils, significant oxidation of trivalent chromium can occur. The soil type also has an effect on the oxidation of trivalent chromium, in peaty soil; Cr(III) cannot be oxidized even in the presence of manganese oxides due to the high concentration of organic matter that is capable of reducing hexavalent chromium to the trivalent form (Kozuh 2000). Oxidation also is limited by Cr(III) complexation (or chelation) with organic ligands and compounds. James and Bartlett (1983a) stated that the complexation of Cr(III) with fulvic acid rendered it mobile in soil and prevented its precipitation.

It should be noted that the Ministry of Environment in Quebec (2003) has regulated the concentration of total chromium in both water and soil as 50 $\mu$g/L for water and a concentration of 250 mg/kg for residential areas and 800 mg/kg for commercial and industrial areas.

The word "surfactant" is an abbreviation for "Surface Active Agent". Surfactants are amphiphilic compounds (containing both hydrophobic and hydrophilic portions) (Lang and Wagner 1987). In solutions; the surfactants tend to concentrate at the air/water interface where the hydrophilic part can be hydrated in the water while the hydrophobic part does not disrupt the hydrogen-bond structure of the water by being immersed in the aqueous phase. At that concentration on the air/water interface the surfactants are capable of reducing the free energy of a system by replacing the bulk molecules of higher energy at an interface, hence increasing its solubility.

Based on hydrophilic groups and charge type, surfactants have four classifications; amphoteric or zwitterionic (bi-charged), anionic (positively charged), cationic (negatively charged) and non-ionic (no charge). Each one of these surfactants is used for a specific purpose.

Surfactants have a unique character, which is the "Critical Micelle Concentration" (CMC), which can be defined as the minimum concentration necessary to initiate micelle formation, and beyond this level of surfactant concentration the surface tension remains constant (Mulligan and Gibbs 2004). The CMC is influenced by the surfactant’s structure, the concentration of solutes, pH, temperature and ionic strength. It should be noted that the lower the CMC the more efficient are the surfactants.

Biosurfactants are also surface active agents produced by bacteria, yeast and fungi, during cultivation on various carbon sources, in particular during growth on hydrophobic substrates such as hydrocarbons. Recently, they are getting more attention due to their anionic nature, low toxicity, high surface active properties and most importantly their biodegradability (Lang and Wagner 1987, Mulligan et al. 2001). They are classified as glycolipids, lipopeptides, phospholipids, fatty acids, neutral lipids, polymeric and particulate. Most of these biosurfactants are either cationic or neutral, however some anionic biosurfactants such as surfactin (which contains amine groups) from a bacteria called Bacillus subtilis can also be found commercially.

A type of anionic biosurfactant; rhamnolipids, specifically, will get more attention in this paper due to its effectiveness and well-studied properties. Rhamnolipids (RL) are negatively charged biosurfactants from the glycolipid group made by the Pseudomonas aeruginosa bacteria (Gruber et al. 1993). Four types of rhamnolipids can be found, type I and II are used for soil washing and heavy metal removal, on the other hand, type III is used for paper processing and lubricants, finally type IV is used in food and agricultural industries, building and construction, paints, inks and food (Tsuji 1998, Jeneil Biosurfactant Co.) Figure 1 provides two examples of rhamnolipids (type R1 or RLL and type R2 or RRLL) and Table 1 shows some properties of rhamnolipids.

The objective of this study is to examine the effect of rhamnolipids on the mobility of chromium (trivalent and hexavalent) in soil. Time, soil to solution ratio, rhamnolipids concentrations, and the solution pH were also studied.
2. MATERIALS AND METHODS

Two chemicals; potassium dichromate (K₂Cr₂O₇) and chromium chloride hexahydrate (CrCl₃·6H₂O), were purchased from Fisher Scientific Canada Ltd. Rhamnolipids (JBR215) (15% concentration) were obtained from Jeneil Biosurfactant Co. LLC. Soil (kaolinite) was obtained from the structure and material engineering laboratory at Concordia University and the distilled water was also prepared in the environmental engineering laboratory at Concordia University.

A Perkin-Elmer model “AAnalyst 100” atomic absorption (AA) spectrometer was used to determine the chromium concentration. The analytical wavelength used was 357.9 nm with a slit width of 0.7 nm. Standards for the calibration curve were used by making the following solutions of chromium (Cr(VI) and Cr(III) separately): [0, 1, 5, 25 ppm] diluted with 5% nitric acid.

Table 1. Some Properties of Rhamnolipids*

<table>
<thead>
<tr>
<th>Property</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Dark reddish-brown</td>
</tr>
<tr>
<td>Odor</td>
<td>Soapy</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.03-1.05</td>
</tr>
<tr>
<td>pH</td>
<td>6.5-7.5</td>
</tr>
<tr>
<td>Boiling point</td>
<td>100 °C</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>soluble</td>
</tr>
<tr>
<td>Surface tension</td>
<td>29 mN/m</td>
</tr>
<tr>
<td>Interfacial tension</td>
<td>0.3 mN/m</td>
</tr>
<tr>
<td>Volatility</td>
<td>Not volatile</td>
</tr>
<tr>
<td>Micelle diameter</td>
<td>5 nm</td>
</tr>
<tr>
<td>CMC</td>
<td>25-60 mg/L</td>
</tr>
</tbody>
</table>

* (Dahr Azma 2002, Jeneil Biosurfactant Co.)

Soil contamination

The soil was first washed with distilled water for 1 hour, then oven dried at 110 °C for 48 hours. Then a known amount (1.5 g) of chromium chloride hexahydrate was added to 200 ml of distilled water then the mixture was added to 25 g of kaolinite in a plastic Erlenmeyer flask, pH adjusted to 7, and placed on an orbital shaker for two weeks.

The concentration of trivalent chromium in kaolinite was 7500 mg/kg (the concentration was found by microwave digestion of 1g of contaminated kaolinite with 10 ml of nitric acid). Due to the high solubility of hexavalent chromium, the maximum contamination that was obtained was 500 mg/kg.

Parameters variations

Experiments took place through a batch test at room temperature (1 gram of contaminated soil in contact with rhamnolipid solution in a 50 ml centrifuge tube). After each experiment, each sample was centrifuged for 20 minutes at 3000 rpm to two phases, and the chromium concentration was measured for each phase.

To study the time effect on the extraction of chromium from the soil the following periods of time were studied (1, 2, 3, 4, 6, 8, 11, 14 days). The following values for the pH variations were used (6, 7, 8, 9, 10). It should be stated here that the rhamnolipids precipitate at pH < 5.5 therefore the minimum value of pH was 6. Soil to solution ratio was varied according to the following ratios: (1g: 20ml, 1:25, 1:30, 1:35, and 1:40). Finally, different concentrations of rhamnolipids were examined on the soil; (0.25, 0.5, 0.75, 1, 1.5, 2, 3, 4, 5%).

Sequential extraction

The fractions of chromium in soil are categorized as five groups: soluble, exchangeable, organic, oxide, and residual. For each group a special treatment is necessary. Table 2 shows the sequential extraction steps.

Quality control

All experiments were done in triplicate. A mass balance was performed between the soil’s and solution’s chromium (to assure the extraction of chromium to the solution phase). Due to the different behavior between hexavalent and trivalent chromium in the atomic absorption measurements, some random samples of Cr(III) were oxidized to Cr(VI) using potassium permanganates, and then measured to give the same results of the original. It should be noted that control samples were made for both solutions (rhamnolipid and water) by adding (1 g) of clean soil with both solutions separately.

Table 2. Steps for sequential extraction (adapted from Mulligan 1998).

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Chemical Reagents</th>
<th>Soil fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Extraction of Cr</td>
<td>Soluble</td>
</tr>
<tr>
<td></td>
<td>(1.5 g of soil)</td>
<td>by rhamnolipid and distilled water for 24 hrs with 15 ml of solution.</td>
</tr>
<tr>
<td>2</td>
<td>Extraction of Cr</td>
<td>Exchangeable</td>
</tr>
<tr>
<td></td>
<td>with 8 ml of 1 M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>magnesium chloride</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(pH 7) for 1 hour.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Extraction of Cr</td>
<td>Carbonates</td>
</tr>
<tr>
<td></td>
<td>with 8 ml of 1M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sodium acetate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>adjusted to pH 5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>with acetic acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>for 5 hours</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Extraction of metals with 20 ml of 0.04 M</td>
<td>Oxides and hydrides</td>
</tr>
<tr>
<td></td>
<td>hydroxylamine</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hydrochloride in 25% (v/v) acetic acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH 2.5 at 96 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>for 6 hours</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Extraction with 3 ml of 0.02 M</td>
<td>Organic matter</td>
</tr>
<tr>
<td></td>
<td>nitric acid and 5 ml of 30% hydrogen</td>
<td></td>
</tr>
<tr>
<td></td>
<td>peroxide (pH 2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>for 2 hours</td>
<td></td>
</tr>
<tr>
<td></td>
<td>at 85 °C, followed by 3 ml of 30% hydrogen peroxide (pH 2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>for 3 hours at 85 °C and then 5 ml of 3.2 M</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ammonium acetate in 20% (v/v) nitric acid diluted to 20 ml at room temperature for 30 minutes with distilled water.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Digestion for 3 hours at 80 °C with 25 ml of dilute aqua regia (5 ml of hydrochloric acid, 20 ml of</td>
<td>Residual fraction</td>
</tr>
<tr>
<td></td>
<td>nitric acid and 75 ml of distilled water).</td>
<td></td>
</tr>
</tbody>
</table>
3. RESULTS AND DISCUSSION

**Time optimization**

Shaking results (1g of soil and 30 ml of rhamnolipid (0.5%) at pH = 7 for different time periods) showed that a three day period of contact time was a reasonable contact time between the rhamnolipid and the Cr(III) contaminated kaolinite, (as shown in Figure 2). It should be stated that water had a negligible extraction of trivalent chromium.

Surprisingly, the rhamnolipids had an effect also on Cr(VI) contaminated soil. Extraction of 90% of Cr(VI) was accomplished compared with 60% extraction using water (results not shown). A possible explanation of the extraction of negatively charged anions (hexavalent chromium) by a negatively charged biosurfactant (rhamnolipids) is the ion-exchange phenomena.

![Figure 2. Effect of time on the extraction of Cr(III).](image)

**Soil-solution ratio optimization**

Results (Figure 3) of 1g of soil in contact with rhamnolipid solution (0.5%) with different soil to solution ratio (pH = 7) showed no large variations. However a 20 ml of solution with 1 g of soil gave the largest extraction. On the other hand, extraction of hexavalent chromium was increasing with an increase in the solution volume (results not shown).

![Figure 3. Effect of soil to solution ratio on the extraction of Cr(III).](image)

**Rhamnolipid concentration optimization**

A concentration of 1 to 1.5% showed a good level of extraction (even though the extraction was highest with a concentration of 4%). It should be noted here that the concentration of trivalent chromium in the liquid phase for the samples with a rhamnolipid concentration above 2% was estimated by subtracting the concentration of chromium in soil after contact with rhamnolipids from the concentration of chromium in the same soil before contact with rhamnolipids. Figure 4 provides the results for different concentrations of rhamnolipid. By increasing the concentration of rhamnolipids the extraction of hexavalent chromium increased (results not shown).

![Figure 4. Effect of rhamnolipid concentration on the extraction of Cr(III).](image)

**pH optimization**

The effect of pH with 1g of soil and 30 ml of rhamnolipid (1.5%) showed that the lower the pH (to a certain extent) the better the extraction. pH = 7 was optimal for this case as stated in Figure 5. pH variations on the Cr(VI) contaminated soil had no effect (results not shown).

A possible explanation for that is that trivalent chromium tends to precipitate with high pHs (higher than pH 5), unlike the highly soluble, hexavalent chromium which does not precipitate under extreme pHs.

![Figure 5. Effect of pH on the extraction of Cr(III).](image)

**Sequential extraction**

The sequential extraction study shows that carbonate, oxide and hydroxide, and organic matter fractions are the major sources of chromium in the soil and the rhamnolipid is able to extract chromium from these portions. As shown in Figure 6 the exchangeable portion of chromium was not detected.
which means that chromium contamination cannot be treated by the ion or cation exchange treatment.

4. SUMMARY

Rhamnolipids showed potential for extracting both types of chromium from the carbonates, oxides and hydroxides portions of soil. The optimal conditions for extracting trivalent chromium were as the following:
- Contact time: 3 days
- pH: 7
- Soil to solution ratio: 1g to 20 ml
- Rhamnolipids concentration: 1 to 1.5%

As mentioned earlier, due to its high solubility hexavalent chromium did not require optimization of all the stated parameters. However the presence of the rhamnolipids in solution enhanced its extraction.

![Fraction of Cr(III) in the contaminated kaolinite from the sequential extraction experiments.](image)

Figure 6. Fractions of Cr(III) in the contaminated kaolinite from the sequential extraction experiments.

5. FUTURE WORK

More experiments will be conducted with different types of soil, the effect of foaming will be studied, a multiple wash of soil with rhamnolipids will be examined, and a continuous flow (column experiments) will take place in the laboratory. The same experiments will be conducted on actual contaminated soil (from contaminated sites).

ACKNOWLEDGEMENTS

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Session 1A
Page 40