CHROMIUM REDUCTION BY ZERO-VALENT IRON AND BACTERIA

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ABSTRACT

A study of alternative chromium reduction methods was performed for wastewater or contaminated water. Two existing chromium reduction treatment methods were tested on the wastewater samples: treatment with (1) zero-valent iron, and (2) bacteria cultures. We found that both methods can reduce chrome. However, the chrome reduction process using bacteria is considerably slower than that using iron powder.

When iron powder was used to reduce hexavalent chromium to trivalent chromium, we found that (a) when the sample containing low levels of total chromium (< 20 mg/liter) was mixed properly with a sufficient amount of iron powder at a pH of 4 to 8, 70% to 90% of total chromium could be reduced in 2 to 4 hours; and (b) the chrome adsorption-reduction efficiency is limited by the transport process of Cr(VI) from the bulk of the wastewater to the surface of the iron powder. We also found that both pH and conductivity of the sample gradually increased while the chromium concentration decreased. In a leaching test of used iron powder filtered from the treated wastewater, we found that most of the chromium adsorbed on the iron powder was very stable, and only low levels of Cr(VI) were detected in the leachate.

When hexavalent chrome samples were treated with mixed bacteria cultures (methanol-enriched) or the *Bacillus cereus* strain, we found that (a) the presence of low chromium concentrations (between 0.6 and 3.1 mg/liter) did not inhibit bacterial growth, and (b) the initial chromium reduction rates for the mixed cultures and *Bacillus cereus* were comparable (0.05 ± 0.03 mg/liter/hr for the first 24 hours). However, when the sample containing higher chromium concentrations (e.g., 8.9 mg/liter) was treated using the mixed bacteria culture, the initial bacterial growth was inhibited, but was not completely suppressed, by the chromium.

INTRODUCTION

Chromates (CrO_4^{2-}) or chromic acid are commonly used in plating and metal surface cleaning processes and are also used frequently in cooling towers as a corrosion inhibitor. Since hexavalent chromium, or Cr(VI), is very soluble in water and highly toxic, wastewater generated from these facilities containing chromates or groundwater contaminated with chromates near some industrial sites must be treated before discharge or reuse. The conventional treatment process generally involves two steps: (a) a detoxification process that reduces Cr(VI) to Cr(III), and (b) precipitation or removal of chromium or other heavy metals from the contaminated water.

Under oxic conditions, Cr(VI) can exist as bichromate ($HCrO_4^-$) or chromate (CrO_4^{2-}), depending on the pH of the aqueous system. These oxyanions are readily reduced to trivalent forms when the electron donors (reducing reagents) exist in aqueous solution. The reduction rate increases as the pH

decreases. Trivalent chromium, Cr(III), species are very stable with respect to the oxidation-reduction potential. They can react with particulates and form metal salts in the form of $Cr(OH)_3$ that are less soluble in water when the pH is 8 to 10 or higher.

Methods of treating water contaminated by chromium or chromates have been studied extensively. For example, chromium reduction can be coupled with oxidation of various reducing reagents, including sodium metabisulfite [1], hydrogen sulfide [2], divalent iron [1, 3, 5–8], Fe(II)-bearing minerals [4], zero-valent iron [1, 9–13], organic compounds (e.g., thios or thiols) [14, 15], or via biotic pathways with certain bacteria species [7, 16].

After chromium reduction, it is essential to follow certain precipitation procedures to destabilize and remove the metal complex from the water. In aqueous solution, free metal ions are coordinated with water molecules (hydrolysis) containing free pairs of electrons to achieve stabilization [17]. Thus the complexes would remain in suspension in solution.

When some chelating ligands, such as humic acid or ethylenediaminetetraacetic acid, are present in the solution, a ligand with multiple electron-donor groups will attach to a metal ion and form a stable chelated metal complex [18, 19]. In order to precipitate metal ions as salts from contaminated water, the metal complexes must be destabilized. Factors influencing destabilization include type and dosages of coprecipitant and flocculant, pH, chemical composition of the water, and mixing conditions of the treatment process [20–22].
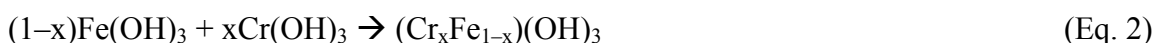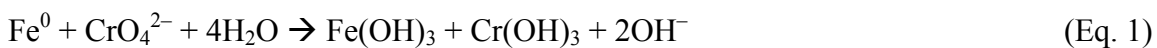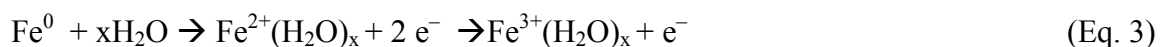
REVIEW OF CHROME REDUCTION METHODS

In this study, we focus on the reduction reaction of Cr(VI) with zero-valent iron powder and with bacteria cultures for wastewater samples collected from a metal surface cleaning facility. We examine the reduction efficiencies of these alternative treatment methods. A brief review of these abiotic or biotic methods is presented below.

1. **Chrome or chromate reduction by zero-valent iron (Fe^o).**

   Lately there has been considerable interest in using zero-valent iron to treat halogenated organic chemicals or inorganic chemicals [e.g., 23, 24] in contaminated aqueous solutions. Many types of reactive barriers or permeable walls have been constructed for groundwater remediation sites or landfill leachate treatments [9–13]. Laboratory and field tests for the iron-filling treatment process have proved to be effective.

   The thermodynamic instability of iron can drive redox reactions when an electron acceptor is present in the aqueous system. For water contaminated with chromate, iron is the electron donor and chromate is the electron acceptor. In an aqueous solution containing chromate, several reactions can occur:

   $$Fe^0 + CrO_4^{2-} + 4H_2O \rightarrow Fe(OH)_3 + Cr(OH)_3 + 2OH^- \qquad\qquad \text{(Eq. 1)}$$

   $$(1-x)Fe(OH)_3 + xCr(OH)_3 \rightarrow (Cr_xFe_{1-x})(OH)_3 \qquad\qquad \text{(Eq. 2)}$$

$$Fe^0 + xH_2O \rightarrow Fe^{2+}(H_2O)_x + 2\ e^- \rightarrow Fe^{3+}(H_2O)_x + e^- \qquad \text{(Eq. 3)}$$

$$3Fe^{+2} + Cr^{+6} \rightarrow 3Fe^{+3} + Cr^{+3} \qquad \text{(Eq. 4)}$$

Reactions (1) and (2) mainly occur on the solid surface of iron powder. As reactions (1) or (2) suggest, when reduced, chromium can be precipitated by adjusting the pH as chromium–iron hydroxide solid solution. Earlier studies [9–11] indicated that the removal of Cr(VI) by Fe^0 is through chrome reduction and the subsequent precipitation of the Fe(III)-Cr(III) hydroxide, (oxy)hydroxide phase, or $(Cr_xFe_{1-x})(OH)_3$.

Compared to reactions (1) or (2), reaction (3) may be slower or insignificant but is a continuous process when the water is in the aerobic system and when the solution pH is increased [3]. Although ferrous ions can also reduce Cr(VI) to Cr(III), our previous studies [1] have indicated that reaction (1) or (2) dominates the overall process of chrome reduction-absorption, and reaction (3) or (4) is secondary.

2. Biotic Chromate Reduction.

Biological reduction of Cr(VI) can occur under anaerobic or aerobic conditions. Several bacterial species have been studied for Cr(VI) reduction [7, 16, 25–28]. They include the *Bacillus* strain, sulfate-reducing bacteria, the *Shewanella alga* strain, the *Pseudomonas* strain, and some other unspecified anaerobic or aerobic bacteria identified from contaminated and noncontaminated sites.

Earlier studies [16, 25] using a Cr(VI)-reducing species, *Bacillus* sp., in various reactors found that the *Bacillus* sp. cells may produce a soluble reductase that complexes with Cr(VI) in an enzymatic reaction in which hexavalent chromium receives electrons to form trivalent chromium.

In other studies of chromium-reducing anaerobes isolated from contaminated and noncontaminated sites [26], bacterial growth inhibition by Cr(VI) was observed for all anaerobic bacteria cultures. However, Cr(VI) did not completely arrest the growth, and Cr(VI) reduction correlated with bacterial growth. This study also demonstrated the advantages of selecting indigenous bacteria from the contaminated zone or media for bioremediation rather than using pure cultures. Several other bacteria strains were also studied for their ability to reduce Cr(VI) [27]. Chromate reduction via a biotic-abiotic pathway under iron-reducing conditions was also examined [7]. The results indicated that direct bacterial reduction is considerably slower than reduction by ferrous ions.

EXPERIMENTAL MATERIALS AND METHODS

Wastewater samples were prepared by diluting the solution taken directly from the chromate-solution tank of the metal cleaning facility with water or media. The solution used in the process tank normally contains 30 g/liter of chromate and trace amounts of several other heavy metals (mainly copper, nickel, and zinc). The initial pH of our samples was between either 4 and 5 or 7 and 8.

Iron powders were obtained from the machine shop next to the surface cleaning facility of the research institute. The sizes of these powders were about 1 mm by 3 mm. Treatment tests of wastewater samples were conducted in 500 ml glass beakers. The tests were always conducted at room temperature in aerobic conditions. When iron powder was used, a shaker or a manual mixer was used at a speed equivalent to 100 to 400 rpm.

Biological reduction tests were always performed with duplicates. Wastewater samples were prepared by diluting the stock solution containing 30 g/liter of chromic acid with deionized water and media. Each sample flask contained either 100 or 200 ml of liquid sample.

Two types of bacteria cultures were used: mixed bacteria enriched by methanol, and the *Bacillus cereus* strain. Approximately 3 to 5 ml of bacteria cultures was added to each flask. Each flask containing the methanol-enriched mixed bacteria was fed with 0.2 to 0.3 ml of methanol (as a carbon source). When the *Bacillus cereus* strain was used in the test, the media also contained glucose and yeast, and methanol was not added. Wastewater samples were mixed on a stirrer plate with stir bars at 200 to 350 rpm. The tests were conducted at room temperature in aerobic conditions.

Media Preparation: The media used for the methanol-enriched mixed cultures contained the following: 2,000 mL distilled water; KH_2PO_4, 2.00 g; Na_2HPO_4, 1.72 g; NH_4Cl, 2.00 g; $MgSO_4 \cdot 7H_2O$, 0.24 g; $CaCl_2 \cdot 2H_2O$, 0.12 g. The media used for the *Bacillus cereus* culture consisted of the following: K_2HPO_4, 60 mM; KH_2PO_4, 45 mM; $(NH_4)_2SO_4$, 15 mM; $MgSO_4$, 10 mM; Na-citrate, 2.4 mM; glucose, 0.2% (w/v); and yeast extract, 0.2% (w/v).

Analysis: Wastewater samples were analyzed before and after treatment using a HACH DR/4000 spectrophotometer. Several batches of samples were also analyzed before and after treatment by a commercial analytical laboratory, following standard EPA methods (EPA 7196 for dissolved hexavalent chromium and EPA 6010 for total chromium). A gas chromatograph (HP6890N) with a flame ionization detector was used for organic chemical analysis (methanol). Bacteria growth was measured as optical density or light absorbance with a spectrometer (Perkin Elmar EZ210).

RESULTS AND DISCUSSIONS

Tests with zero-valent iron powder.

Several sets of tests were performed for samples with a wide range of chromium concentrations, using various amounts of iron powder. The first set of samples, containing 5.6 ± 1.0 mg/liter of total chromium (120 ml per sample; original pH ~8.5), was treated with 1 gram of iron powder. The sample flasks were sealed and placed on a shaker set at 200 rpm. Within 5 to 6 hours, the chromium concentration gradually decreased to 2.9 ± 0.6 mg/liter. (The initial reduction was ~50%.) When the iron powder was left in the sample for 24 hours (on the shaker), the total chromium concentration was further reduced to 1.2 mg/liter. Figure 1 shows the results of this test.
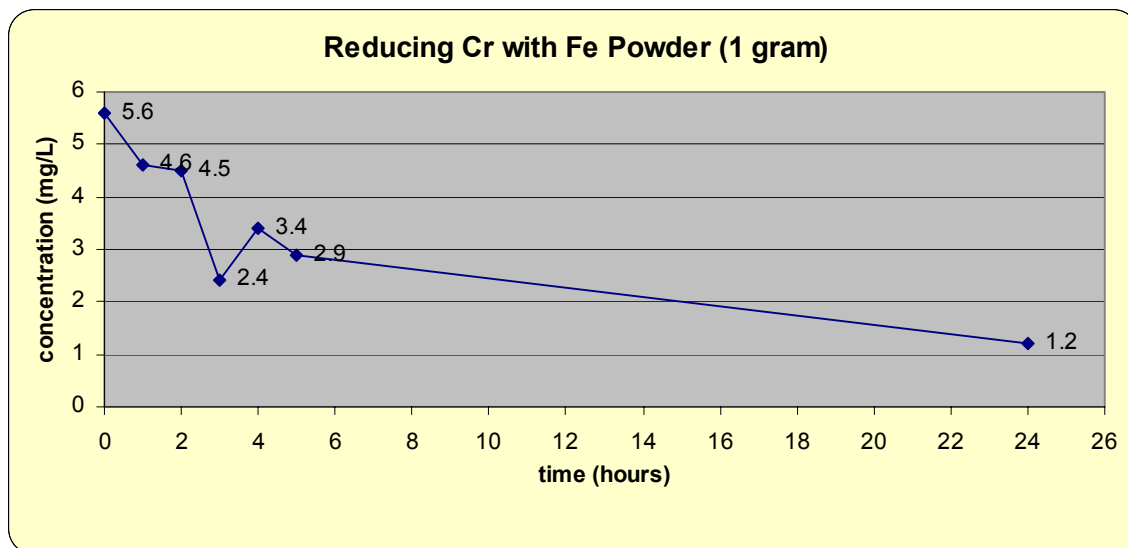
Reducing Cr with Fe Powder (1 gram)

Fig. 1. Chromium Reduction Using 1 Gram of Iron Powder.

During the test, we also monitored the variations of pH and conductivity of the sample. In the first 4 to 5 hours, the solution pH increased slightly from 8.5 to about 8.7. It then gradually increased to 9.2 over 24 hours as the chromium concentration decreased. The pH increase agrees well with reaction equation (1). The solution conductivity remained constant, with minor deviations in the first 3 to 4 hours, and then gradually increased over 24 hours as the chromium concentration decreased further. This is probably due to the reaction (3) was becoming the dominant process in the solution when the chromium concentration was 80% below the initial concentration.

The details of chromium reduction-adsorption (reaction (1) or (2)) and iron-oxidation (reaction (3) or (4)) processes in solution are complicated. They occur simultaneously with different rates and might be influenced by multiple factors, such as initial chromium concentration, the presence of other heavy metals in the solution, the redox potential of each ion, the pH, the mixing conditions, the available fresh adsorption sites on iron powder, and the dissolved oxygen in the solution.

Another set of samples containing 14 mg/liter of total chromium or 12 mg/liter of hexavalent chromium (200 ml per sample; pH 7 to 7.3) was treated with 3 or 4 grams of iron powder. It was found that for the sample treated with 4 grams of iron powder, the hexavalent chromium was reduced to 3.3 mg/liter (while total chromium was 4.2 mg/liter) in the first 2 hours. For the sample treated with 3 grams of iron powder, the total chromium concentration in the sample was reduced to 2.9 ± 0.3 mg/liter within the first 4 hours. These samples were periodically agitated with a manual mixer at approximately 100 rpm for 15 minutes each hour.

The above results indicate that the iron powder used in the study (3–4 grams) can effectively reduce 70% of the chromium within the first 2 hours, or 80% within 4 hours. when the samples were mixed periodically. However, when the iron powder (3 grams) was left in the sample for another 20 hours without agitation, the total chromium concentration was reduced only to 2.1 ± 0.3 mg/liter (see Table I).

In the third set of tests, we found that when the samples containing 8 mg/liter of total chrome content (6.8 ± 0.3 mg/liter of hexavalent chromium) were mixed vigorously with 4 grams of iron powder using a manual mixer at approximately 400 rpm for 30 minutes each hour, the total chromium in the treated wastewater sample (at pH 4 to 5) could be reduced to 1 mg/liter within 3 to 4 hours. Our results (EPA Method 7196) showed that the majority of the remaining chromium in the treated solution was Cr(VI), and its concentration was 0.99 mg/liter (Table I). This result suggests that most of the chromium (~90%) was reduced and adsorbed on the iron powder surface within 3 to 4 hours.

The above three sets of tests indicate that when the chromium concentration is low (8 to 14 mg/liter), iron powder can reduce 70% to 90% of chromium in the sample within 2 to 4 hours if sufficient iron powder and proper mixing are provided.

Table I Summary of chrome reduction tests using iron powder (zero-valent).

Treatment	Initial Cr[#] conc., mg/liter	Chemicals added	Final pH	Effluent total Cr conc., mg/liter	Comments
Zero-valent iron #1 (Fe^0)	14	3 g Fe^0	7.6	2.9	Fe^0 mixed in the sample for 4 hours (~100 rpm) Initial pH 7–7.3
Zero-valent iron #2	Following the iron test #1	3 g Fe^0	7.6	2.1 (4.04×10^{-5})	Following the above test for another 20 hours (no agitation)
Zero-valent iron #3	14 $(Cr^{6+} \simeq 12)$	4 g Fe^0	7.5	4.2 $(Cr^{6+} \simeq 3.3)$	Fe^0 mixed in the sample for 2 hours (~100 rpm) Initial pH 7–7.3
Zero-valent iron #4	8	4 g Fe^0 (4 hr)	4–5	1.0 $(Cr^{6+} \simeq 0.99)$	Fe^0 mixed in the sample Vigorously (~400 rpm) Initial pH: 4–5

We also conducted a set of leaching tests of iron powder filtered from a treated wastewater sample that originally contained 20 mg/liter chromium. The filtered iron powder was dried and then divided into three batches (1 gram each). Each batch of iron powder was washed with 75 ml of water at a preselected pH range. We found the following:

(a)   When the filtered iron powder was rinsed with acidic (2 < pH < 3) or caustic (10 < pH <11) water, a small fraction (< 4%) of adsorbed chromium was redissolved into the acidic water, or less than 0.1% into the caustic water. Less than 0.02% of adsorbed chromium was released into the rinsewater with a pH between 6 and 7. Most of the redissolved or released chromium from the iron powder was Cr(VI).

(b)   Because of (a), we believe that most chrome reduction occurred on the surface of the iron powder, and probably most of the chromium adsorbed on the iron powder was trivalent chromium, which is much less soluble in water than hexavalent chromium.

Tests with bacteria cultures

Four sets of biological chrome-reduction tests were performed. Mixed bacteria culture enriched by methanol and a *Bacillus cereus* strain of bacteria were used for the tests. Wastewater samples containing 8.9, 3.0, and 0.6 mg/literiter of chromium were prepared by diluting the stock solution containing 30 g/liter of chromic acid with deionized water and media. Each sample flask contained either 100 or 200 ml of sample. Approximately 3 to 5 ml of bacteria cultures and 0.2 to 0.3 ml of methanol (as a carbon source) were added to each flask containing the methanol-enriched mixed bacteria. In the *Bacillus cereus* strain tests, the media contained glucose and yeast, and methanol was not added.

Figure 2 shows the results of two chrome-reduction tests using the methanol-enriched mixed culture. The original chromium concentrations were 3.1 ± 1 and 0.65 ± 0.1 mg/liter, respectively. The total chromium concentrations in the supernatants (after spinning at 4,200 rpm for 30 minutes) were greatly reduced to 0.58 and 0.25 mg/liter, respectively, within one day. The initial chrome-reduction rates were estimated at 0.08 and 0.02 mg/liter/hr, respectively, for the first 24 hours. This indicates that most of the chromium in the solution (40% to 80%) was absorbed or reduced by the mixed bacteria.
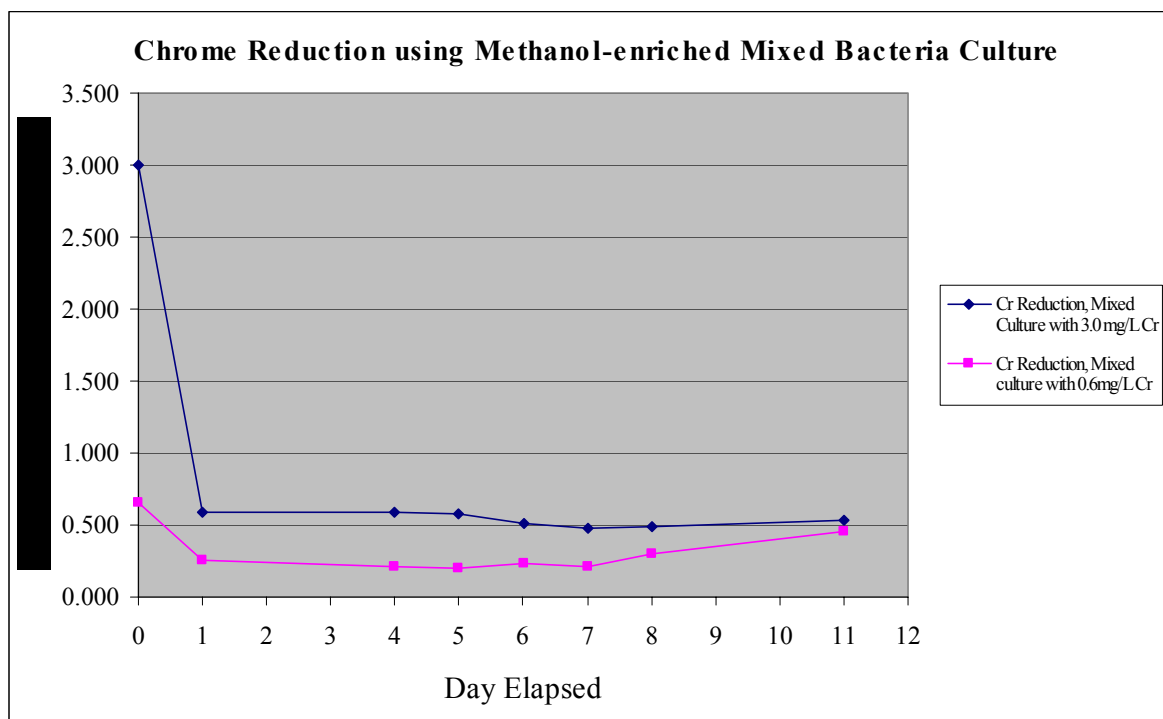

Fig. 2. Chrome Reduction Using Methanol-enriched Mixed Bacteria Culture. Our results also showed that the chromium concentrations in the solutions remained at these levels for 10 days.

Figure 3 shows the bacteria growth (measured as the increase of light absorbance at 590 nm) during these 10 days. We found that the presence of a low initial concentration of chromium did not inhibit the growth of mixed bacteria. Two sets of analyses of these samples were conducted for dissolved hexavalent chromium (EPA method 7196) and total chromium (EPA method 6010). Results of the

samples taken prior to spinning (i.e., with biomass) showed that only 2% to 7% of the chrome was Cr(VI) in solution, which means more than 90% of the chromium was reduced and absorbed by the bacteria. When the samples were centrifuged and biomasses were removed from the solutions, Cr (VI) was not detected in the supernatants (detection limit: 0.002 mg/liter). These results suggest that the methanol-enriched mixed culture can reduce Cr(VI) to Cr(III). Table II shows these results.
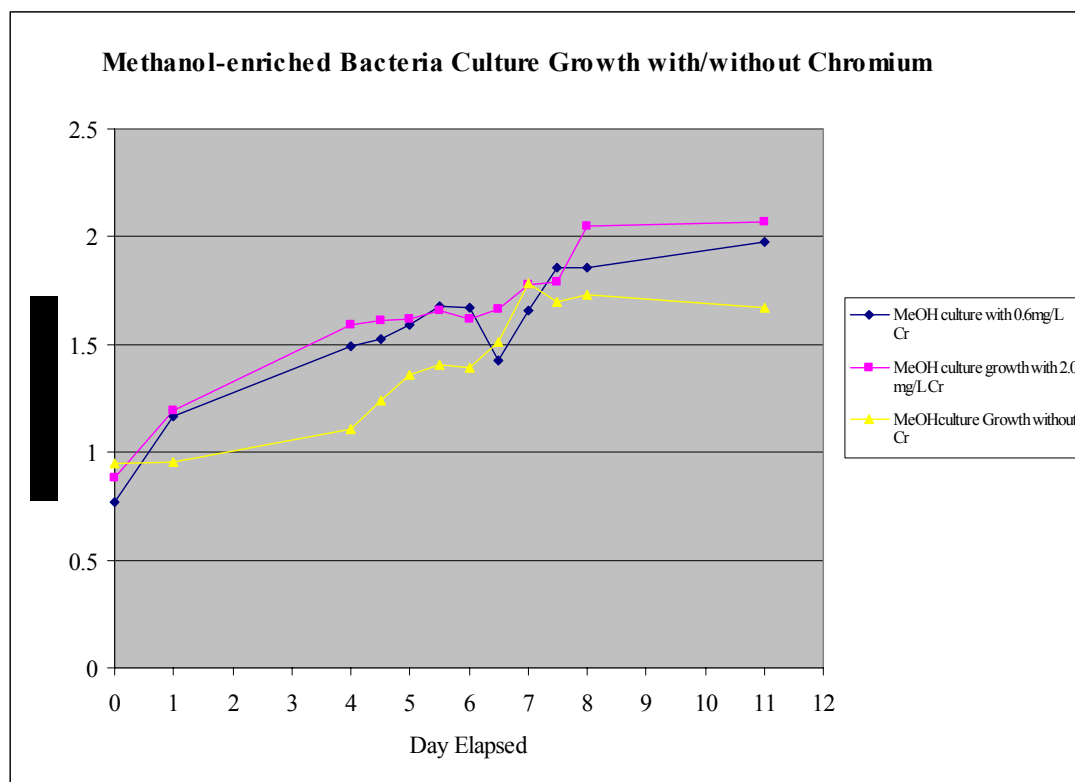

Fig. 3. Mixed Bacteria Growths in Solutions with and without Chromium.

The third set of tests, with 8.9 mg/liter chromium in the sample, was also conducted using mixed bacteria culture enriched by methanol. The total chromium concentration was reduced to 5.2 ± 0.3 mg/liter within one day (or 45% reduction in 24 hours), and then was maintained at that level for 5 days. During these 5 days, no bacteria growth (measured as light absorbance) was observed in the sample. In order to stimulate bacteria growth, an additional 3 ml of methanol was added to the sample. After the addition, bacteria growth increased, and the chromium concentration decreased (Figure 4). These results suggest that bacteria growth might be inhibited, but not completely arrested, by chromium when its initial concentration is relatively high.

We also examined the chrome-reduction effectiveness of the *Bacillus cereus* strain (data not shown). It was found that this bacteria strain is capable of reducing the chromium concentration from 2.4 mg/liter to 1.3 mg/liter within one day. The initial chrome-reduction rate was about 0.05 mg/liter/hr (or 45% reduction in 24 hours), which is similar as that of the mixed bacteria culture. These results suggest that the *Bacillus cereus* strain can reduce Cr(VI) to Cr(III).

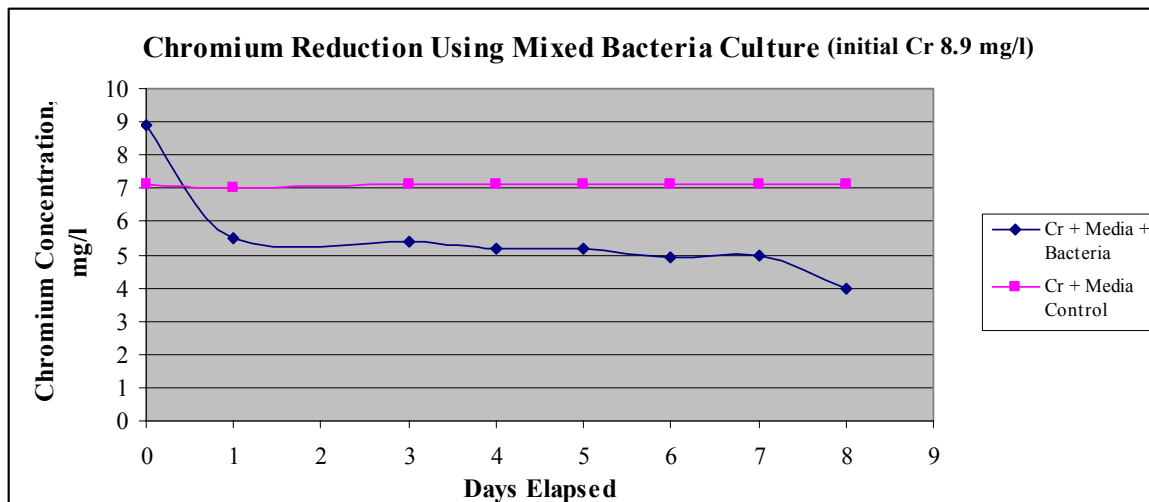**Chromium Reduction Using Mixed Bacteria Culture** (initial Cr 8.9 mg/l)

Fig. 4a. Chromium Reduction and Mixed Bacteria Growth.
Note: The pink square Cr + Media is the control, which
indicates that the media did not reduce chromium.

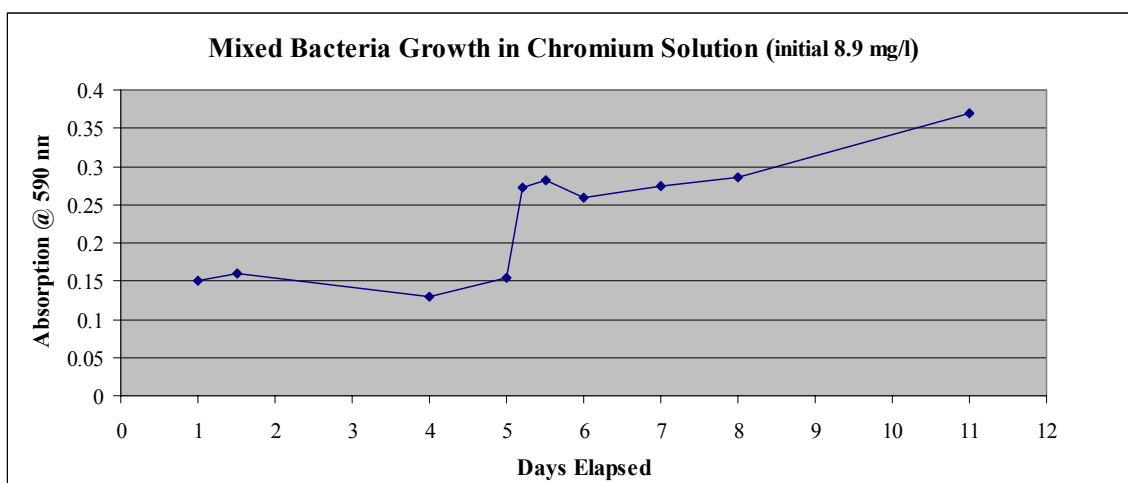**Mixed Bacteria Growth in Chromium Solution** (initial 8.9 mg/l)

Fig. 4b Chromium Reduction and Mixed Bacteria Growth.
Note: An additional 3 ml of methanol was added into
the sample after the fifth day.

Table II. Chromium-Reduction Results of Methanol-enriched Mixed Bacteria Culture.

Cr tests	Conditions	Mixed culture with 0.6 mg/liter Cr	Mixed culture with 3.0 mg/liter Cr	Mixed culture without Cr
Total Cr	Unspinned w/biomass	0.53$\pm$0.1	3.1$\pm$1.0	ND
Hexavalent Cr	Unspinned w/biomass	0.04	0.064	ND
Total Cr	Spinned no biomass	0.25	0.68	ND
Hexavalent Cr	Spinned no biomass	ND	ND	ND

SUMMARY

(1)   Wastewater samples with a wide range of chromium concentrations (0.6 to 22 mg/liter) were prepared for treatment tests using zero-valent iron powder or two types of bacteria cultures. We found that both the zero-valent iron powder and bacteria (including the mixed culture and the *Bacillus cereus* strain) can reduce Cr (VI) to Cr(III). However, iron powder is more efficient than bacteria cultures in chrome reduction.

(2)   When iron powder is used to reduce hexavalent chromium to less soluble trivalent chromium, the chrome absorption-reduction efficiency is limited by the transport or diffusion process of Cr(VI) from the bulk of the wastewater to the fresh surface of the iron powder. This indicates that proper mixing and sufficient retention time of the iron powder in the solution are crucial in achieving higher chrome-removal results.

(3)   We also found that when there is sufficient iron powder in the sample and the mixing condition is proper, chromium reduction can be effective. For example, in one sample containing 14 mg/liter of total chromium that was treated with 4 grams of iron powder, the iron powder effectively reduced 70% of the chromium within the first 2 hours when the sample was mixed periodically. However, when the iron powder was left in the sample for another 20 hours without agitation, the total chromium concentration was only reduced by another 5%. In another sample containing 8 mg/liter of total chromium, when mixed frequently with 4 grams of iron powder, 90% of the total chromium was reduced in 3 hours.

(4)   The leaching test of iron powder filtered from the treated wastewater indicated that most of the chromium absorbed on the iron powder (probably trivalent chrome) was very stable. When the iron powder was rinsed with either acidic (2 < pH < 3) or caustic (10 < pH < 11) water, less than 4% of the absorbed chromium was redissolved into the acidic water, and less than 0.1% was redissolved in caustic water, almost all of it hexavalent chromium.

(5)   We found that both pH and conductivity of the sample gradually increased as the chromium concentration decreased over 24 hours. The increase in pH agrees well with reaction equation (1). The increase of conductivity, probably due to the release of ferrous ions (i.e., reaction (3)) became the dominant process when the chromium concentration was lower. The chromium reduction-adsorption and iron-oxidation processes are influenced by multiple factors, such as the initial chromium concentration, the presence of other heavy metals in the solution, the redox potential of each ion, the pH, the mixing conditions, the available fresh iron surface, and the dissolved oxygen in the solution.

(6)   In the biological reduction study, we tested the effects of mixed bacteria culture or the *Bacillus cereus* strain and found that

   (a)   the presence of low concentrations of chromium (between 0.6 and 3.1 mg/liter) in the samples did not inhibit bacterial growth,

   (b)   the initial chromium-reduction rates over 24 hours for the mixed cultures and *Bacillus cereus* were comparable (0.05 ± 0.03 mg/liter/hr), and

   (c)   the reduction process using bacteria is considerably slower than that using iron powder.

(7)   When the sample containing 8.9 mg/liter of chromium was treated using the mixed bacteria culture enriched by methanol, the total chromium concentration was reduced to 5.5 mg/liter within one day. However, during the first 5 days, no bacteria growth was observed in the sample. This suggests that the bacterial growth might be inhibited, but not completely suppressed, by chromium when its initial concentration is relatively high.

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