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In Situ Bioremediation of Chromium (VI) In a Simulated Ferrochrome Slag

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Stability of chromium in the tailing dumps and stockpiles of chromium concentrate at chrome mining fields is affected by pH, redox potential, and the presence of other metallic species in the waste rocks. It is desirable to keep chromium in the dump site in the trivalent state since the hexavalent state, Cr(VI), is highly mobile and carcinogenicity to aquatic life forms and humans, whereas the trivalent state, Cr(III), precipitates easily and is less toxic than Cr(VI). In this study, microbial remediation with indigenous bacteria was used to reduce Cr(VI) to Cr(III) in presence of Fe(II)/Fe(III) redox couple in simulated ferrochrome slag.
The consortium of bacterial culture strains were isolated from sand drying beds and dried sludge from the belt filter press at the Wastewater Treatment Works. Culture achieved 100 % Cr(VI) removal under aerobic condition for 100 mg/L Cr(VI) in 24 h and 100 % Cr(VI) removal under anaerobic condition for 20 mg/L Cr(VI) in 48 h. Increased Cr(VI) reduction occurred in the presence of Fe(II) which confirmed that Fe(II) served as an alternative electron donor for Cr(VI) reduction. Complete reduction of 50 mg/L Cr(VI) was achieved within 12 h using 50 - 100 mg/L Fe(II). Kinetic evaluation in the presence of Fe(III) found that Cr(VI) reduction was non-competitively inhibited by the presence of Fe(III).

1. Introduction

Chromium is an essential nutrient for plant and animal metabolism. When it accumulated at high levels it can cause serious health problems (Richard and Bourg, 1991). Chromium is very toxic (Mosca Angelucci et al., 2017) and is considered as a Class A carcinogen by the USEPA. The World Health Organization drinking water standard for total chromium is 50 µg/L (Tchounwou et al., 2012). Anthropogenic sources of chromium containing waste typically originate from the effluent discharge of industries such as leather manufacture (Zhang et al., 2017), chromium ore refining (Liao et al., 2017), production of steel and alloys (Kim et al., 2016), metal plating (Sukumar et al., 2014), wood preservation and pigmentation (Igboamalu and Chirwa, 2016).
Chromium ore exists in complex mineral composite together with other precious and earth metals in natural mineral rich ores. Tailing dumps and process water stockpile at chrome mining and ferrochrome processing sites contain significant levels of chromium (van Staden et al., 2014). Chromium in the tailing dumps can exists either as Cr(III) or Cr(VI) depending on the environmental conditions within the dump (Förstner and Wittmann, 2012). Interaction with other metals at the different oxidation states can influence the stability of the oxidation states of the chromium species inside the waste dump and its stability to leach into the surrounding bodies (Dhal et al., 2013). In areas where leachate water enters agriculture supply water, there is a high risk of contamination of the food products and bioaccumulation into higher order organism (Chirasha and Shoko, 2010).
Chromium, in its trivalent state, readily precipitates as chromium hydroxide $Cr(OH)_3(s)$ at near neutral to alkaline pH conditions (pH > 6.0). The tendency of Cr(III) to precipitate makes Cr(III) less mobile in the environment and much easier to manage its ecological impacts than Cr(VI) (Madhavi et al., 2013). The hexavalent form of chromium Cr(VI), exists mainly as the oxyanions of the form ($H_wCr_xO_y^{z-}$), where x = 1 or 2, y = 4 or 7, and w and z = 0 to 2 (where z = 2 - w) depending on the pH of the solution. Cr (VI), in its oxyanionic state, is highly mobile in water and is known to be carcinogenic in mammalian cells (Federal Register, 2004).
At disposal site, Cr is naturally deposited in the trivalent state Cr(III) mainly because chromium is mined as Cr^{3}- oxide complexes. Leachate from tailing dumps and storage pile is conventionally treated by converting

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Cr(VI) to Cr (III) using chemical agents such as sulphur dioxide gas, sodium bisulphite (Barrera-Díaz et al., 2012), and iron salts followed by precipitation to $Cr(OH)_3(s)$ (Hawley et al., 2004). This strategy is counterintuitive because the chemical agents produce toxic by-products that are released as toxic sludge, which is detrimental to the environmental (Stasinakis et al., 2003). A biological process could serve as a preventive measure since it could be implemented in situ within the interior of the dump heap.

The viability of in situ biotransformation of Cr(VI) to Cr(III) has been demonstrated in both laboratory scale (Dhal et al., 2013) and pilot scale system for effective removal for Cr(VI) from water (Dimitroula et al., 2015). The long-term stability of chromium in their dump sites is not guaranteed mainly due to possibility of intrusion of the oxidative species and the occurrence of biologically mediated reactions that could oxidise Cr(III) in the dump to Cr(VI). Fe(II) can be oxidised to Fe(III) upon exposure to oxygen in the presence of iron oxidising microorganism (Mesa et al., 2002) such as bacteria species Acidithiobacillus ferroxidans (Liu et al., 2015). The Fe(III) produced could serve as an electron acceptor in the biological oxidation of Cr(III) to Cr(VI) (Fendorf and Li, 1996), resulting in the remobilisation of Cr species (Brookshaw et al., 2014).

In this study, the reduction of toxic Cr(VI) by natural occurring bacteria in the absence and presence of Fe(II)/Fe(III), a common co-pollutant that exists in most chrome refinery waste and residue from ore extraction, is evaluated. It is hypothesised in this report that the Fe(II)/Fe(III), redox couple may work either as a catalyst for Cr(IV) reduction to the trivalent state, or as a stabiliser of Cr in the trivalent state, Cr(III). A Cr(VI) reducing culture isolated from Cr(VI) contaminated sludge was used as the biocatalyst to achieve the stabilisation of chromium as Cr(III) in a ferrochrome slag.

2. Material and method

2.1 Chemicals

All reagents used in this study were of analytical grade with the highest purity level from Sigma Aldrich (South Africa) and used without any further purification.

2.2 Culture media

Basal mineral medium (BMM) was prepared as a 10 % v/v dilution of the stock solution comprised of (in 1 L deionised water): 0.535 g NH_4Cl, 4.259 g Na_2HPO_4, 2.722 g KH_2PO_4, 0.114 g Na_2SO_4, 0.0136 g $ZnCl_2$, 0.0341 g $CuCl_2$, 0.0103 g NaBr, 0.0121 g Na_2MoO_4, 0.0198 g $MnCl_2$, 0.0166 g KI, 0.0124 g H_3BO_3, 0.0238 $CoCl_2$ and 0.0128 g $NiCl_2$, (Roslev et al., 1998). The medium was sterilised by autoclaving at 121 °C. (2.5 bar) for 15 min and cooled to room temperature before use.

2.3 Preparation of chromium (VI) solution

Stock solution of K_2CrO_4 was prepared by dissolving K_2CrO_4 in distilled water. Other desired concentration was prepared daily by diluting the stock solution.

3. Experimental

3.1 Microbial culture isolation

Cr(VI) tolerant bacteria were obtained from dried sludge from sand drying beds collected from a Wastewater Treatment Plant at Brits (North West province, South Africa). The treatment plant had received effluent from a nearby abandoned sodium dichromate processing facility reported to discharge high level of Cr(VI) in sewerage works from 1996 to 2005 (SA-IDC, 2014). Samples were collected in sterile containers and stored under refrigeration at 4 °C.

3.2 Microbial culture characterisation

Phylogenetic characterisation of cells was performed on individual colonies of bacteria cultured from 7^{th} to 10^{th} tube in serial dilution preparation. Genomic DNA was extracted from colonies using a DNeasy tissue kit (QIAGEN Ltd, Wrest Sussex, UK). The 16S rRNA gene of isolates were amplified by reserve transcriptase-polymerase chain reaction (RT-PCR) using primers pA and pH1 (Primer pA correspond s to position 8 - 27: Primer pH to position 1,541 – 1,522 of the 16S gene). The resulting 16S rRNA gene sequences was checked with the 16sRNA gene sequences of other organisms that had already been submitted to GenBank database using basic BLAST search of the Bethesda's National Centre for Biotechnology Information. The microbial composition of the original culture from Brits Wastewater Treatment Works in Brits used as the inoculum was published earlier (Molokwane, 2010).

3.3 Measurement of Cr(VI) and total Cr

Cr (VI) was measured in water samples by UV-Vis spectrophotometer (WPA, Light Wave II, Labotech, South Africa) operated at a wavelength of 540 nm (10 mm light path) after acidification of 0.2 mL sample with 1 mL of 1 N H_2SO_4 and dilution with distilled water to 10 mL followed by reaction with 1,5-diphenyl carbazide to produce

a purple colour (Eaton et al., 2005). Total Cr was measured at wavelength of 359.9 nm using a Varian AA-1275 Atomic Adsorption Spectrophotometer (AAS) (Varian, Palo California, USA) equipped with a 3 mA chromium hollow cathode lamp. Cr was leached from soil samples using a dilute HCl solution (1N HCl) (Molokwane et al., 2008). Cr(III) was determined as the difference between total Cr and Cr(VI) concentration.

3.4 Experimental batches

Experimental batches for Cr(VI) reduction were prepared in the range 20-400, mg/L in 100 mL BMM supplemented with a carbon source (0.1 g/L D-glucose) based on level of organic residues in tailings. The following estimation of TOC contribution from glucose was used Eq (1):

$$TOC = Y_{toc} \times Glucose \quad (1)$$

TOC yield factor Y_{toc} = 0.40 g TOC/g glucose based on expected efficiency of conversion in a biological system (Stander and Theodore, 2007). Aerobic experiments were conducted in 250 mL Erlenmeyer flasks covered with cotton plugs, whereas anaerobic cultures were grown in 100 mL (capacity) serum bottles sealed with silicone rubber stoppers after purging with 99 % pure nitrogen gas for 10 min. Analytical samples were withdrawn from the aerobic batch reactors at predetermined intervals using a sterilised pipette. From the anaerobic batches, syringe was used to draw samples. Cr(VI) was added from stock solution of K_2CrO_4, iron species were added as $FeCl_3.6H_2O$ for Fe(III) and Mohr's salt for Fe(II). All experiments were conducted in duplicate sets. "Cell free" and "heat killed culture" batches were used as abiotic batch controls to evaluate the extent of Cr(VI) reduction by elements in the medium and the Fe species. Heat killed cultures were prepared by autoclaving cells harvested from enrichment vessels and re-suspending in fresh medium after washing three times in sterile 0.85 % NaCl solution.

3.5 Cr(VI) reduction rate kinetics

The reaction rate was developed earlier based on the assumption that each Cr(VI) reducing living cell in the reactor produces a certain amount of enzyme (E') and that deactivating the cell deprives the system of that particular amount of enzyme (Shen and Wang, 1994). Assuming that the remaining active enzyme E_a is proportional to the amount of living cells in the system ($E_a \propto X_a$), then the reaction rate catalysed by the enzymes could be considered as being directly proportional to the reaction rate catalysed by cells.

Molokwane (Molokwane, 2010) suggested Cr(VI) reduction in aerobic conditions, can be best represented by Eq (2). This equation shows a higher concentration of C_0 (higher than a certain inhibition threshold, C_r) the reaction rate law became competitive with Cr(VI).

$$-\frac{dC}{dt} = \left(\frac{k_{mc}}{1 + C_0/K_i}\right)\left(\frac{C}{K_c + C}\right)\left(X_0 - \frac{C_0 - C}{R_c}\right) \quad (2)$$

Where C = Cr(VI) concentration (ML^{-3}) at any time (t), k_{mc} = maximum specific Cr(VI) reduction rate coefficient (T^{-1}), K_c = half velocity constant (ML^{-3}), K_i = coefficient of inhibition (competitive) (ML^{-3}) , X_0 = initial viable cell concentration and the term (C_0-C)/R_c represents cells killed due to exposure to Cr(VI) such that the term brackets is the concentration of active cells available at time t.

For anaerobic reduction condition at higher value of Cr (higher than a certain inhibition threshold, C_r) Eq (3) fits best. Eq (3) shows reaction rate is non-competitively inhibited.

$$-\frac{dC}{dt} = \frac{k_{mc}.C}{K^{1-C_r/C_0}.(K_c + C)}\left(X_0 - \frac{C_0 - C}{R_c}\right) \quad (3)$$

3.6 Parameter optimisation

Computational solutions of kinetic equations were implemented in the Computer Program for the Identification and Simulation of Aquatic system AQUASIM 2.0 (Reichert et al., 1995). Model comparison with experimental data was conducted by minimising the sum of squares error between the measured data point and calculated data points using the simplex function in AQUASIM.

4. Result and discussion

4.1 Microbial culture identification

The results from the genotype characterisation of gram-negative aerobic species in the enrichment culture most probably belonged to the Pseudomonas and Serratia genus. The genotypic characterisation of the anaerobic culture showed the presence of Klebsiella genus. The specific strains of microorganisms were Pseudomonas aeruginosa, Serratia marescens and Klebsiella oxytoca.

4.2 Cr(VI) reduction under aerobic condition

To determine the optimal Cr(VI) concentration for Cr(VI) reduction under anaerobic conditions, batches were setup with varying Cr(VI) concentration in the range 20-400 mg/L. Figure 1 shows in the absence of Fe 100 % of removal efficiency was achieved at initial Cr(VI) concentration of 100 mg/L within 24 h of incubation. When the initial Cr(VI) was increased, the rate of Cr(VI) removal in the media decreased significantly showing the effect Cr(VI) toxicity on the cultures.

4.3 Cr(VI) reduction under anaerobic condition

Experiments conducted under anaerobic conditions without Fe(II) and Fe(III), showed a similar trend in terms of decreasing Cr(VI) reduction rate (20 - 100 mg/L). The results showed that the cultures growth without oxygen supply achieved almost 100 % removal efficiency at the initial Cr(VI) concentration of 20 mg/L in 48 h. This again showed the effect Cr(VI) toxicity on the cultures.

4.4 Cr(VI) reduction in presence of iron

The rate of reduction of Cr(VI) was also studied in presence of Fe(II) and Fe(III) under aerobic as well as anaerobic conditions. Experiments showed presence of Fe(II) with Cr(VI) make a positive impact in reduction rate in both aerobic and anaerobic conditions.

Complete Cr(VI) reduction occurred in all cultures containing Fe(II) concentrations varying from 5 mg/L to 100 mg/L within 24 h of incubation. Presence of Fe(III) with chromium have an inhibiting effect on Cr reduction rate under aerobic as well as anaerobic condition.

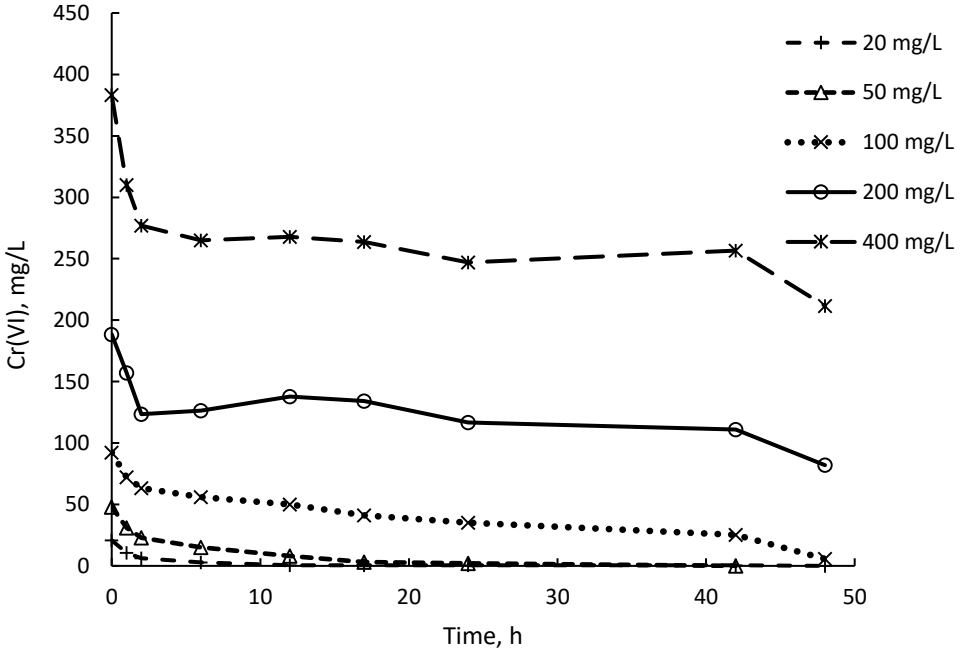

Figure 1: Aerobic Cr(VI) reduction under varying initial Cr(VI) concentration

4.5 Kinetics results

After fitting the model to the anaerobic and aerobic batch data, optimum kinetic parameters were obtained as shown in Tables 1 and 2. The results show the maximum specific reaction rate coefficient (k_{mc}) in the aerobic systems is higher than the values from the anaerobic batches, i.e. there is a faster initial drop in Cr(VI) concentration in the aerobic cultures than in the anaerobic cultures. The non-competitive inhibition model with Cr(VI) toxicity threshold concentration (C_r) of 100 mg/L best represented Cr(VI) reduction in anaerobic conditions (Molokwane, 2010).The aerobic kinetic model (Table 1) indicates inhibition at Cr(VI) concentrations of less than 10 mg/L. In contrast, the fitted anaerobic kinetics (Table 2) shows that the level at which Cr(VI) concentration under anaerobic conditions were inhibitive were outside of the range of the levels normally observed in chrome refinery waste.

Table 1: Optimum kinetic parameters using the non-competitive inhibition model under aerobic conditions

Initial [Cr(VI)] (mg/L)	k_{mc} (1/h)	K_c (mg/L)	R_c (mg/mg)	K_i (mg/L)	X_o (mg/L)
20	0.8	650	0.019	9	5,780
50	0.85	620	0.025	9.5	5,940
100	0.82	950	0.022	7.5	6,220
200	0.85	950	0.0225	7.5	5,720

Table 2: Optimum kinetic parameters using the cell inactivation model with threshold inhibition under anaerobic conditions

Initial [Cr(VI)] (mg/L)	k_{mc} (1/h)	K_c (mg/L)	R_c (mg/mg)	K (1)	X_o (mg/L)
20	0.12	180	0.01	10	2,240
50	0.12	180	0.01	10	2,280
100	0.12	180	0.0097	10	2,160

5. Conclusions

The study shows the potential of acclimated microorganisms to reduce hazardous form Cr(VI) to nontoxic form Cr(III). The detailed batch experiments confirmed that Cr(VI) is reduced for various concentrations (20 - 400 mg/L). Aerobic systems were found to be better performing for Cr(VI) reduction than the anaerobic systems. Anaerobic reduction of Cr(VI) followed a similar trend to aerobic reduction, which indicates that the presence of anaerobic and aerobic chromium reducing cultures can be effectively used for the in situ bioremediation of Cr(VI) in chrome refinery waste, even in cases where lack of oxygen transfer can limit aerobic pathways. High Cr(VI) concentrations resulted in the inhibition of the Cr(VI) removal processes. The Cr(VI) concentration at which inhibition under aerobic conditions were observed was significantly lower (less than 10 mg/L) than under anaerobic conditions. Anaerobic reduction is most relevant for the in situ bioremediation of chrome in ferrochrome slag. The presence of Fe(II) in the system acts as an electron donor which facilitates the reduction of Cr(VI) and can thus help to further stabilise chromium in chrome refinery waste, while the presence of Fe(III) appeared to inhibit the reduction process.

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