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Efficiency of Remobilisation of Chromium Precipitates in an Aquifer Permeable Reactive Barrier

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Chromium exists largely in two oxidation states, namely Cr(VI) which is carcinogenic and mutagenic to living organisms including humans, and Cr(III) which is about 1,000 times less toxic than Cr(VI). It is therefore desirable in most cases to reduce Cr(VI) to Cr(III) as the first step towards complete treatment of Cr(VI). Various studies have been conducted on the Cr(VI) reduction process either in situ or ex situ. However, in situ bioremediation using permeable reactive barrier systems offers an attractive option compared to other in situ technologies. This study was conducted to evaluate the reduction of Cr(VI) to Cr(III) in the short term and regeneration of the biological reactive barrier to achieve continuous long-term operation. It was observed from the study that the chromium hydroxide $Cr(OH)_3(s)$ precipitated and thus affected the porosity and hydraulic conductivity of the barrier system. The precipitate could be washed using a dilute acid solution. However, lowering the pH in the reactor introduced harsh conditions which necessitated the evaluation of a possible culture shift during the regeneration phase. Microbial culture composition during bioremediation and after soil washing with dilute acid was evaluated using the 16S rRNA genotype fingerprinting. The microbial barrier was initially inoculated with indigenous bacterial species from dried sludge. The results showed the presence of well-known Cr(VI) reducers such as Bacillus mycoides, Lysinibacillus fusiformis and Micrococcus lylae in the microbial community of the barrier. The microbial barrier system successfully achieved near complete removal of Cr(VI), whereby approximately 75 % Cr(VI) removal was achieved within 63 days of operation. The formation of $Cr(OH)_3(s)$ was observed in the second week of operation. After 4 weeks of operating the microcosm under soil washing with 0.1 % HCl and electrokinetics remediation with a DC voltage of 50-150 V, an increase in total chromium (73 %) was observed suggesting that the trapped chromium species in the microcosm was effectively remobilized with the assumption that Cr(III) had attached to the cathode forming a white-yellow precipitate layer around the cathode. Additionally, more than 95 % Cr(VI) was transformed during electrokinetic and soil washing remediation. However, one of the limitations of electrokinetic remediation is the near anode focusing effect whereby a layer of precipitate is formed around the anode that leads to the reduction in mobility of the species through the aquifer medium.

1. Introduction

The element chromium was first isolated by the French chemist Nicolas-Louis Vauquelin in 1797 from a sample of a very beautiful orange-red material (Jacobs and Testa, 2005). Chromium in the environment exists mainly in two forms: trivalent chromium (Cr(III)) which readily forms the insoluble and less mobile species, $Cr(OH)_3(s)$ in water (Zayed and Terry, 2003), and hexavalent chromium (Cr(VI)), which exists as the soluble and mobile oxyanions, chromate and dichromate (CrO_4^{2-} or $Cr_2O_7^{2-}$). Hexavalent chromium is very toxic and carcinogenic such that it is listed as a Class A carcinogen by the U.S EPA (Federal Register, 2004). In biological systems, hexavalent chromium acts as a carcinogen, mutagen and teratogen. Panda and Sarkar (2012) showed that seed germination in grassy plants is inhibited by Cr(VI) at concentrations as low as 0.5 mg/L in water and 5 mg/L in soil medium. Trivalent chromium, on the other hand, produces no toxic effects in living organisms at concentrations as high as 600 mg/L (Vincent and Love, 2012). Trivalent chromium is needed in mammals for carbohydrate and lipid metabolism (Vincent,

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2004). Notably, chromium (as chromium picolinate) is used as a nutritional supplement (weight loss agent) by athletes. Among the main exporters of chromite ore in the world are South Africa, Kazakhstan and Zimbabwe. Exports from these countries account for 97 % of the world wide chromite ore production.
Cr(VI) is discharged into the environment from industrial processes such as paint and pigment production, leather tanning, wood preservation, rubber and steel production thereby causing serious pollution. In South Africa, large scale pollution of groundwater and surface water bodies have been attributed to illegal discharge from abandoned mines and chrome refineries (DWAF, 2005).
As mentioned above, Cr(VI) is highly toxic and its discharge is discouraged or disallowed in most countries. The allowable concentration for exposure to natural ecosystems is 0.05 mg /L (Federal Register, 2004). The common remediation strategies for Cr(VI) involves its reduction to the trivalent state (Cr(III)) followed by immobilization by precipitation and/or absorption to substrates (Silgado et al., 2014). Trivalent chromium mobility can be decreased by adsorption to clays and oxide minerals below pH 5. At pH values above 5, formation of $Cr(OH)_3(s)$ occurs.
Chinthamreddy and Reddy (1998) indicated three strategies for possible remediation of chromium. In other studies, metal contaminated soils were treated using techniques such as soil washing, excavation, solidification and stabilization. Recent developments in the remediation of chromium contaminated soil include the evaluation of Cr(VI) immobilization using biological permeable reactive barriers. Biological remediation barriers have been used more successfully in treating toxic organic compounds in water. Gibert et al. (2007) successfully removed Polycyclic Aromatic Hydrocarbons (PAHs) and BTEX compounds with a biological sequential reactive barrier.
Other in situ barrier studies showed that some chromium reducing bacteria such as Bacillus cereus are capable of reducing Cr(VI) to facilitate the formation of chromium hydroxide. $Cr(OH)_3(s)$ clogs the pores spaces of the barrier and reduces flow through the barrier (Molokwane, 2009). This leads to the decrease in the effectiveness of the barrier in which case the barrier material may be excavated and replaced.
Soil washing has been developed and tested in the remediation of chromium using extracting agents such as acids, neutral salts and chelating agents. Isoyama and Wada (2006) previously used hydrochloric acid to effectively remove chromium and lead from contaminated soils. This study describes the use of soil washing with a mineral acid to remobilize $Cr(OH)_3$ at the same time regenerating the barrier and subsequently collecting the mobile Cr(III) at the cathode under the influence of an electrokinetics potential. Soil washing is found to be economically feasible and easy to carry out according to Mann (1999). Studies on the combination of bioremediation and acidification through soil washing studies are fairly new. However, by combining these two technologies, some of the limitations experienced with each technology can be mediated and thus increase the efficiency of the system as a whole.

2. Materials and methods

2.1 Microbial culture and growth medium

Cr(VI) reducing bacteria were sourced from Brits Wastewater Treatment Works (North West Province, South Africa). Bacteria sourced from the above environment was exposed to periodic loadings of Cr(VI) from a nearby chrome ore refining plant. The bacteria from the wastewater treatment plant was thus expected to be resistant to Cr(VI) toxicity. Organisms were cultured by adding 0.2 g of sludge to 400 mL sterile Luria-Bertani broth (LB) prepared by dissolving 25 g powder of Luria-Bertani (LB) broth followed by autoclaving at 121 ℃ for 15 min. The broth was cooled to room temperature before introducing the bacteria. The broth was spiked with 50 to 75 mg/L Cr(VI) to select for Cr(VI) reducing organisms followed by incubation under continuous shaking for 24 h 1 mL samples from the inoculums culture were plated on agar plates and the colonies which formed were sub-cultured and tested for Cr(VI) reducing capability individually. Cr(VI) reducing colonies were characterised using the 16S rRNA genotype fingerprinting method as described earlier by Molokwane et al. (2010).

2.2 Batch analysis

Cr(VI) reduction was evaluated in cultures comprised of cells from competent Cr(VI) reducing single colonies. A kinetic analysis was conducted for the derived mixed culture to determine the Cr(VI) reduction rate coefficient and Cr(VI) reducing capacity of the culture. The mixed culture was preserved by successive transfers, once every two weeks, and was used later to inoculate the barrier in the horizontal flow aquifer microcosm reactor.

2.3 Microcosm system setup

Operation of an aquifer barrier simulation was conducted in a horizontal flow reactor with the dimensions, 123 × 52 × 50 cm (L × B × H), constructed from Plexiglass ® (Evonik Rohm GmbH, Essen, Germany) and

reinforced by steel bars (Figure 1). Aquifer medium from the previously contaminated site at Brits (North West Province, South Africa) was compacted into the reactor to a compaction consistent with the ground conditions. During the packing process nine sampling ports of 30 cm in length and 11 mm diameter glass tubing were inserted in the aquifer medium. Sample ports were strategically placed to capture the longitudinal concentration across the continuous flow reactor.

2.4 Barrier operation

The aquifer microcosm system was loaded with Cr(VI) at a concentration of 50 mg/L which was slightly higher than the concentration in contaminated groundwater at the target site in Brits. The reactor was loaded by peristaltic pumps at a retention time of 30 min across a 45 mm biological barrier. After operating the reactor for 45 d, the regeneration procedure was operated involving acid washing with a dilute HCl solution (0.1 % HCl).

2.5 Barrier acid washing and regeneration

The remobilization technique used in this experiment was soil washing by using a single agent- 0.1 M HCl. Soil washing involves the separation of contaminants that are adsorbed onto fine soil particles with liquid. 0.1 M HCl was made up in a 10 L bucket and this was fed into the reactor from the influent tray. The acid was allowed to flow through the system for three weeks, during this time the reading of Cr(VI) and total chromium was still being carried out. Soil properties were investigated before soil washing was carried out as these properties influence the efficiency of soil washing. The soil analyses were conducted by the Department of Plant Production and Soil Science, University of Pretoria. While acid washing the barrier, a 150 V potential was across a section of the downstream zone which caused the mobilisation of reduced Cr species towards anode. Excess cations were pumped from inside the perforated PVC tubes surrounding the electrode as shown in Figure 1.

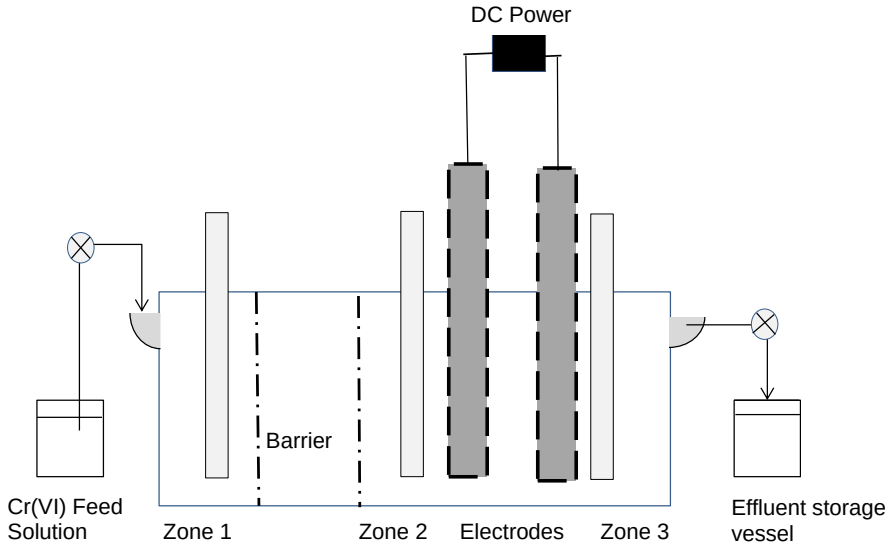

Figure 1: The horizontal flow microcosm reactor showing the pumping scheme and layout of electrodes and sample ports. Each sample port shown in the figure represents three sample ports across the width and the second electrode represents two electrodes placed 25 cm apart.

2.6 Analytical methods

Cr(VI) was measured in water samples by a 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 samples with 2 mL of 1M H_2SO_4 and dilution with distilled water to 10 mL, followed by reaction with 1,5-diphenyl carbazide to produce a purple colour (APHA, 2005). Total Cr was measured at a wavelength of 359.9 nm using a Varian AA-1275 Atomic Adsorption Spectrophotometer (AAS) (Varian, Palo Alto, California, USA) equipped with a 3 mA chromium hollow cathode lamp. Cr was leached from soil samples using a dilute HCl solution (1 N HCl) (Molokwane et al., 2010). Cr(III) was determined as the difference between total Cr and Cr(VI) concentration.

3. Results and Discussion

3.1 Microbial culture composition

The presence of a range of Cr(VI) reducing species of bacteria in sludge samples and microcosm barrier media was confirmed by the genetic characterisation. Among Gram(−ve) species, known Cr (VI reducers such as *Pseudomonas mosselii*, *Pseudomonas plecoglossicida* and *Pseudomonas oryzihabitans* were identified (Kiambi and Chirwa, 2013). The predominant Gram(+ve) Cr(VI) reducing species were *Bacillus thirungiensis*, *Bacillus cereus*, and *Bacillus sphaerococcus* (Molokwane et al., 2009).

3.2 Cr(VI) reduction kinetics

Based on earlier studies in batch and columns (Mtimunye and Chirwa, 2014), it was determined that Cr(VI) in the microcosm system could be competitively inhibited by Cr(VI) since Cr(VI) served as an electron acceptor under oxygen stressed conditions. Therefore, only the results from the batch analysis performed under anaerobic conditions are presented in this article. The reaction term derived from enzyme kinetics (Molokwane, 2010) was then used. The reaction term was modified for non-competitive inhibition to arrive at the equation:

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

where k_m = maximum specific rate of Cr(VI) reduction (T^{-1}), K_c = half-velocity concentration (ML^{-3}), X_o = initial biomass concentration (ML^{-3}), C = Cr(VI) concentration (ML^{-3}) at time, t, C_o= initial Cr(VI) concentration (ML^{-3}), K = limiting constant (ML^{-3}) and R_c = Cr(VI) reduction capacity of cells (MM^{-1}). The parameters were estimated using the Simplex method in the Software for Simulation of Aquatic Systems (AQUASIM 2.3, EAWAG, Switzerland). The results of fitting the model to experimental data are shown in Table 1.

Table 1: Optimum kinetic parameter in anaerobic batch cultures

Prepared Feed Concentration ($mg.L^{-1}$)	Estimated Initial Value, C_0 ($mg.L^{-1}$)	K_c ($mg.L^{-1}$)	k_m (h^{-1})	K ($mg.L^{-1}$)	R_c ($mg.mg^{-1}$)	X_o ($mg.L^{-1}$)	χ^2 $(mg.L^{-1})^2$
30	19	11.6	0.221	--[a]	0.964	752	1.5
50	48	11.6	0.221	--	0.964	532	66
75	64	11.6	0.221	148	0.964	523	226
100	90	2.36	0.118	145	0.105	888	1077
200	193	2.36	0.058	145	0.164	748	652
400	397	2.36	0.118	151	0.105	571	419

[a] -- parameter not sensitive enough in this range.

The validity of the model in the given data range was tested by performing a sensitive analysis on all obtained parameters by measuring the effect of an incremental change in the parameter on the value of the simulated concentration. The results showed that the model was least sensitive to the Cr(VI) reduction rate capacity of the cells K_c. However, removing the saturation rate coefficient resulted in larger estimation errors in the estimated parameters.

3.3 Bioremediation and barrier regeneration

Cr(VI) reducing performance in an un-inoculated (control zone) Zone 1 in the microcosm reactor system was evaluated at the target initial feed concentration of 20 mg/L (Figure 2). The results show that Cr(VI) reduction in Zone 1 was insignificant throughout the operation indicating abiotic processes are negligible. The effluent increased gradually to the influent levels following a first order accumulation consistent with accumulation in continuous flow reactor without reactions. Additionally, the tracer line showed a characteristic of exponential rise of Cr(VI) in the system also suggesting that the physical-chemical processes were insignificant over time.

3.4 Bioremediation and barrier regeneration

The operation of the inoculated microbial barrier system under a continuous Cr(VI) loading of 50 $mg \cdot L^{-1}$ and at a hydraulic loading rate of 13.3 $L \cdot h^{-1}$ resulted in equilibrium state reached in 35 days. The transient-

state Cr(VI) concentration response to the loading is shown in Figure 3. After steady-state operation, the microcosm was operated under acid washing for 40 d. Effluent Cr(VI) and total Cr were measured. The high values of total Cr measured in ports downstream of the barrier confirmed that the acid wash regiment

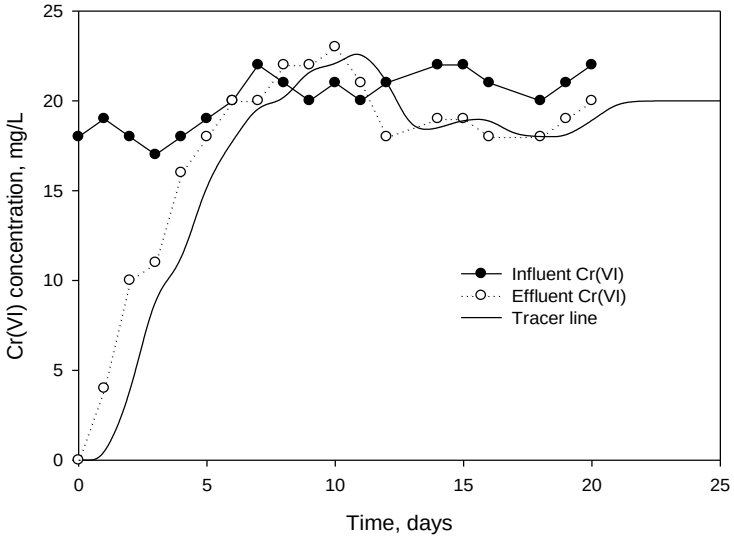

Figure 2. Performance on non-inoculated zone in the continuous flow reactor system which results in the exponential rise in the effluent Cr(VI).

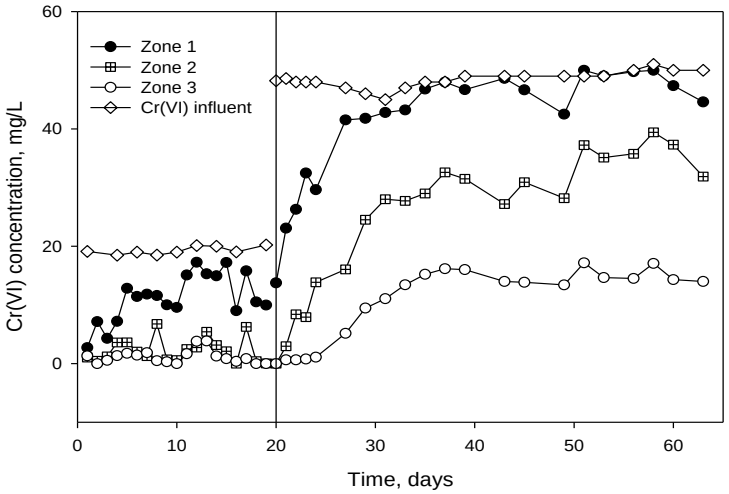

Figure 3: Concentration profiles before the barrier (black circle), after the barrier (crossed square) and exit zone (white circle).

succeeded in dislodging Cr(III) precipitates from the barrier (Figure 4). After applying the direct current voltage of 150 V across a distance of 25 cm, accumulation of Cr species around the node was observed as evidenced by accumulation of a yellow and green precipitate around the anode electrodes. The actual concentration profile towards the anode was not measured at this stage due to the size limitation of the experimental reactor.

4. Conclusions

In this study, a process to be used in unclogging a microbial barrier system by elution with 0.1 % HCl was investigated. $Cr(OH)_3(s)$ that accumulated after 14 - 65 d was remobilised by washing with 0.1 % HCl. Total Cr during acid wash was maintained at 73 % of the influent Cr(VI) value. The microbial culture remained viable after the barrier was subjected to the acid wash cycle which demonstrated that the barrier could be operated continuously without the need for excavation of the barrier material for maintenance.

The proposed system could, therefore, result in savings in the operation cost due to reduced labour. The accumulation of precipitates around the anode electrode resulted in the reduction of mass transport of cationic species towards the anode reduction in the potential to remove Cr(III) from the simulated barrier. Further experiments are being conducted to evaluate the potential of charge alternation to avoid the formation of the ion focusing band around the anode which results in the cation transport resistant. Overall, the project demonstrated that the cations including Cr^{3+} could be successfully remobilised during a regeneration phase thereby freeing the void space for continued Cr(VI) removal in biological barrier zone.

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