# Modelling Cr(VI) Removal in a Biological Permeable Reactive Barrier: Microcosm Simulation

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An indigenous Cr(VI) reducing mixed-culture of bacteria was shown to reduce high levels of Cr(VI) in laboratory samples. The effect of Cr(VI) toxicity on the removal efficiency was evaluated earlier in batch studies with initial concentrations up to 400 mg/L. The reaction rate in batch reactors followed non-competitive kinetics with a Cr(VI) inhibition threshold concentration of approximately 99 mg/L. Following the detailed evaluation of fundamental processes for biological Cr(VI) reduction, a predictive model for Cr(VI) breakthrough through aquifer microcosm reactors was developed. This study evaluates a model for Cr(VI) removal in continuous flow process with groundwater aquifer material as the immobile phase and kinetic parameters from the batch studies. The model developed from *advection-reaction* rate kinetics in a porous media fitted best the effluent Cr(VI) concentration. The model was also used to elucidate the logistic nature of biomass growth in the reactor systems.

## 1. Introduction

Chromium from the anthropogenic sources is discharged into the environment mainly as hexavalent chromium [Cr(VI)]. Most of the Cr(VI) is discharged in the toxic oxygen combined forms – chromate ($CrO_4^{2-}$) and dichromate ($Cr_2O_7^{2-}$). Cr(VI), unlike Cr(III), is a severe contaminant with high solubility and mobility in aquatic systems. Cr(VI) is a known carcinogen classified by the U.S.EPA as a Group A human carcinogen based on its chronic and subchronic effects (Federal Register, 2004). Cr(VI) is toxic, carcinogenic and mutagenic to animals as well as humans and is associated with decreased plant growth and changes in plant morphology (U.S.EPA, 1978, Rosko et al., 1977, Silverberg, et al., 1977). It is for this reason that most remediation efforts target the removal of Cr(VI) primarily.

Almost all chromium inputs to the natural systems originate from human activities and South Africa is no exception. Only 0.001% is attributed to natural geologic processes (Merian, 1984). Several chrome processing facilities in South Africa release Cr(VI) into groundwater resources. Currently, pump-and-treat remediation processes are implemented at some of the sites but have not been successful in reducing contamination levels. The current study is aimed at developing an environmentally friendly, cost effective and self-sustained biological method to curb the spread of chromium at the contaminated sites.

## 2. Experimental Methods

### 2.1 Source of Microorganisms

The mixed-culture of bacteria was obtained from dried sludge collected from sand drying beds at the Brits Wastewater Treatment Works (Brits, North West Province, SA). The treatment plant receives periodic flows from a nearby abandoned sodium dichromate processing facility reported to discharge high levels of Cr(VI) in the sewerage works. The chrome processing facility was commissioned as early as 1996, thus the bacteria at the treatment plant is expected to be acclimated to Cr(VI) toxicity.

### 2.2 Chromium Determination

Cr(VI) was measured using a UV/Vis Spectrophotometer (WPA, Light Wave II, Labotech, South Africa). The measurement was carried out at a wavelength of 540 nm (10 mm light path) after acidification of 0.2mL samples with 1N $H_2SO_4$ and 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 Series Atomic Adsorption Spectrophotometer (AAS) (Varian, Palo Alto, CA (USA)) equipped with a 3 mA chromium hollow cathode lamp. Cr(III) was determined as the difference between total Cr and Cr(VI) concentration.

### 2.3 Microcosm System Setup

Soil columns extracted from the aquifer (below the water table) were installed in a continuous dose experiment as shown in Figure 1. Eight microcosm columns were installed with the first acting as the control, Reactor HR2 evaluates the sludge bacteria acting alone, and Reactors HR3 and HR4 evaluate the native soil bacteria acting alone
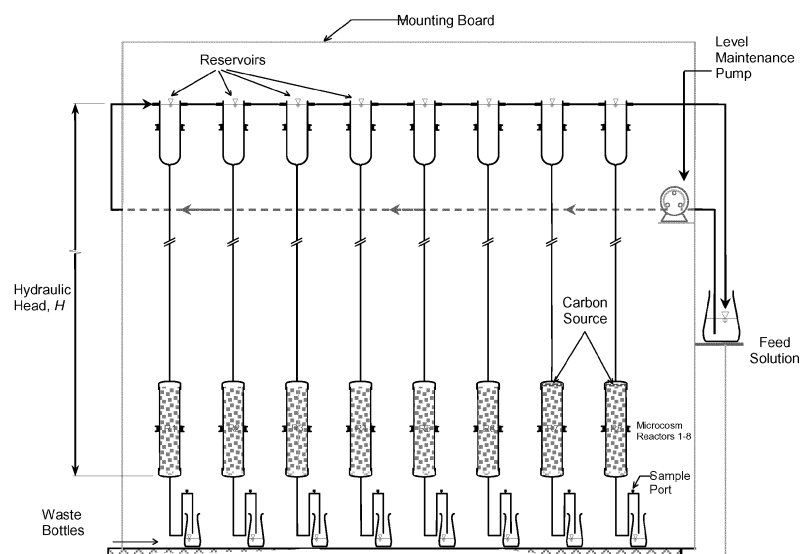


*Figure 1: Aquifer microcosm columns (HR1-HR8) to simulate the performance of microbial barrier systems in aquifer media.*

*Table 1: Conditions for the aquifer microcosm range of experiments.*

| Reactor(s) | Experiment |
|---|---|
| Reactor HR1 | Killed native bacteria + no inoculation |
| Reactor HR2 | Killed native bacteria + inoculated (sludge bacteria) |
| Reactors HR3 and HR4 | Live native soil bacteria + no inoculation |
| Reactors HR5 and HR6 | Live native soil bacteria + inoculated (sludge bacteria) |
| Reactors HR7 and HR8 | Live native soil bacteria +inoculated + carbon source |

(in duplicate). The main experiments comprised (in duplicate) HR5 and HR6 with both sludge bacteria and native soil bacteria but operated without carbon source, and HR7 and HR8 with soil bacteria and sludge bacteria operated with added carbon source. The carbon source in HR7 and HR8 consisted of a natural matrix of organics leached from saw dust. This was intended to simulate humic organics leaching from stems of dead plants in the veldt.

# 3. Results and Discussion

### 3.1 Microcosm Performance
93% of the 50mg/L Cr(VI) removal was achieved in HR7 with carbon source after operation for 45 days. Reactor HR5 without carbon source achieved approximately 66%. Table 2 summarises the performance of the bacteria in microcosm reactors.

*Table 2: Capability of mixed cultures in reducing Cr(VI) in aquifer microcosms at day 45.*

| Reactor No. | Flow rate (Q) $cm^3/h$ | Measured Cr(VI) (Effluent) mg/L | Total Removal % (at day 45) | Removal Rate g Cr(VI)/$m^3$/d |
|---|---|---|---|---|
| HR1 | 0.660 | 47.2 | 0 | 0 |
| HR2 | 0.259 | 45.8 | 4.5 | 0.07 |
| HR3 | 0.714 | 48.7 | 0 | 0.37 |
| HR4 | 0.290 | 48.8 | 0 | 0.56 |
| HR5 | 0.228 | 16.9 | 66.3 | 3.08 |
| HR6 | 0.430 | 13.5 | 73.0 | -- |
| HR7 | 0.304 | 3.1 | 93.0 | 5.69 |
| HR8 | 0.433 | 10.9 | 78.2 | 4.54 |

## 3.2 Simulation of Cr(VI) Reduction in Microcosm Systems

The microcosm reactors were modelled as plug flow reactors with the Cr(VI) removal influenced by the following internal processes: (1) advection influenced by the interparticle velocity $u$ $(LT^{-1})$, (2) mass transport into media particles governed by mass transport rate coefficient $k_L$ $(LT^{-1})$, (3) adsorption rate governed by mass transport and surface reaction, (4) Cr(VI) reduction kinetics and (5) cell replacement rate with the cells acting as the catalyst in the Cr(VI) reduction process as adopted from AQUASIM 2.0 (Reichert, 1998). The above fundamental processes in the reactor during transient state operation can be represented by the Equation 1.

$$\frac{dX}{dt} = Y\left(\frac{k_{ms}S}{K_s - S}\right) - k_d X \tag{1}$$

where: $Y$ = cell yield coefficient $(M \cdot M^{-1})$, $k_{ms}$ = specific substrate utilisation rate coefficient $(T^{-1})$ and $k_d$ = cell death rate coefficient $(T^{-1})$, $X$ = viable cell concentration $(ML^{-3})$ at any time $t$.

The predominant processes in the reactor are thus limited to advection, reduction, mass transport and cell growth. These processes were used in the mass balance for Cr(VI) removal across the bulk liquid phase in the microcosm reactor:

$$\frac{d(C \cdot V)}{dt} = A\sum_{l=0}^{l=L_i} u(C_{in} - C) + j_c.a_i + (q_c + r_c) \cdot \Delta V \tag{2}$$

where $\Delta V$ $(L^3)$ = change in reactor volume associated with any unit change in length $\Delta L$ $(L)$, $a_i$ = surface area in the segment $(L^2)$, and $r_c$ = Cr(VI) reduction rate $(ML^{-3}T^{-1})$. The interstitial velocity, $u$ $(LT^{-1})$, is assumed to be constant throughout the entire reactor at any given time, whereas the adsorption rate, $q_c$ $(ML^{-3}T^{-1})$, approached zero in the order of 6 to 10 hours.

The activity of viable biomass in the reactors is predicted based on the activity of known values from batch studies. In this study, the simulated performance of the microcosm reactors is plotted together with the simulated biomass activity as shown in Figures 2 and 3. Figure 2 shows the observed Cr(VI) removal and simulated biomass under control conditions — with only native soil bacteria and no Cr(VI) reducing isolates. Figure 3 shows the performance of the native microflora supplemented with Cr(VI) reducing isolates from the activated sludge samples. In Figure 2, the shows sensitivity to Cr(VI) toxicity but the effect is delayed as Cr(VI) spread through the reactor. But after 6.5 days, the toxicity in the reactor was probably too high for the native culture.

Figure 3 shows growth of biomass from a low inoculation value of approximately 8.5 g/m$^3$ to a maximum value of approximately 45.5 g/m$^3$. The cell performance is reflected in the increased Cr(VI) reduction removal rate after day 6. The limitation of biomass at 45.5 g/m$^3$ under non-carbonaceous substrate conditions shows that a biological barrier
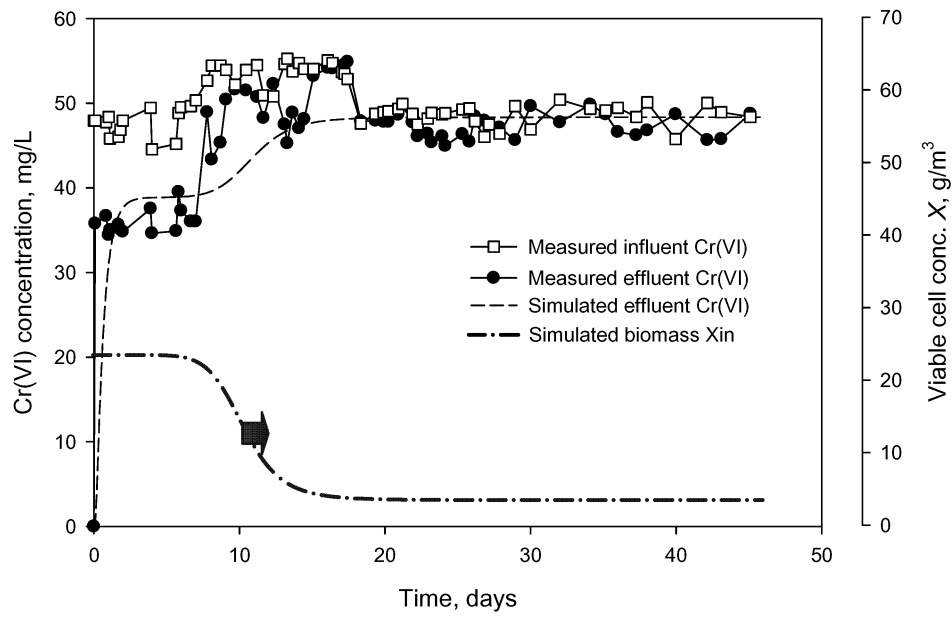
*Figure 2: Model simulation of the sterilized microcosm reactor inoculated with live cultures from sludge (Reactor HR4).*
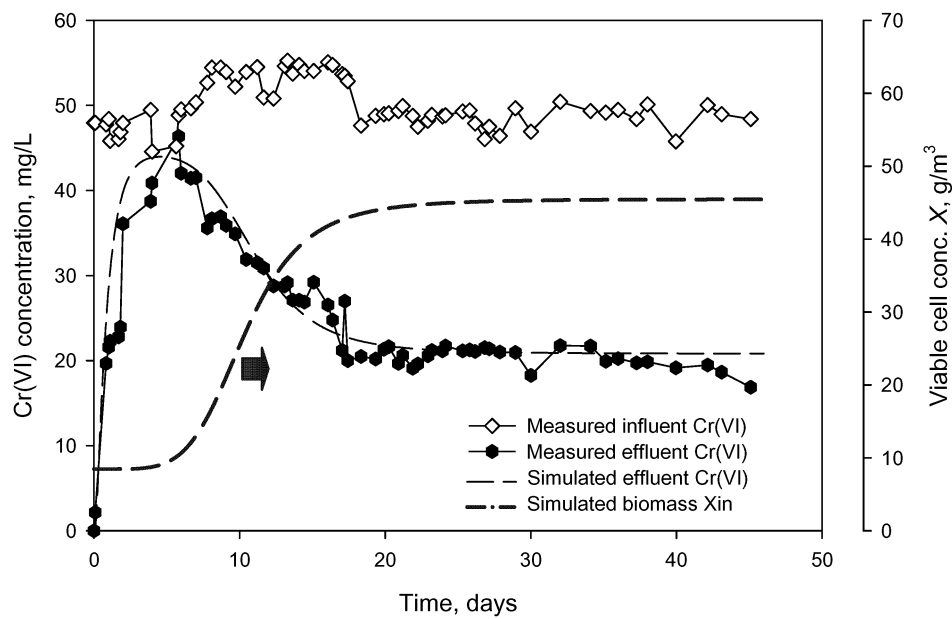


*Figure 3: Model simulation of the live soil culture microcosm inoculated with live cultures from sludge and operated without carbon source (Reactor HR5).*

formulated under these conditions may operate longer before experiencing blockages from excess biomass in the pores. The model simulation results helped validate the parameters previously determined in batch and made possible the evaluation of the viable biomass component which is difficult to measure directly in a heterogeneous media environment.

## 4. Conclusion

Model simulation confirms the effect of inhibition (inhibition threshold $C_r$ = 99 mg/L) and direct toxicity (cell inactivation coefficient $R_c$ ≈ 0.50 mg/mg) as the dual mechanisms limiting the extent of Cr(VI) reduction in the aquifer media. The accurate determination of these parameters together with the mass transport and biomass terms is critical in the future development of a pilot study for contaminated aquifer systems. The simulation of biomass under non-carbon source conditions shows that a biological barrier formulated under these conditions may operate longer before experiencing blockages from excess biomass in the pores. Overall, the model successfully captured the effluent trend and Cr(VI) reduction capacity of the columns. However, only an empirical evaluation of biomass growth was possible at this point. A more accurate model for the growth term is under investigation based on improved methods for determination of viable biomass in soil media.

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