Simulation of Biological Cr(VI) Removal in Aquifer Microcosm Columns

Phalazane J. Mtimunye, and Evans M.N. Chirwa[*]

Water Utilisation Division, Department of Chemical Engineering, University of Pretoria, Pretoria 0002, South Africa.
mtimunyepj@gmail.com

In the present work the effect of *in situ* bioremediation technology in containing the spread of Cr(VI) in groundwater aquifer systems was studied. Experiments in microcosm reactor columns were carried out under an oxygen stressed conditions which were maintained in each column after long hours of operation at various Cr(VI) feed concentrations: 20, 30, 40 and 50 mg/L respectively. The effect of carbon source was also evaluated in this study and it has been observed that the addition organic carbon source is essential for effective biological Cr(VI) removal in the deep aquifer zones. Experimental data collected along the five intermediate sampling ports of the column and also at the effluent port showed insignificant change in the Cr(VI) effluent concentration after three to four days of operation. The insignificant Cr(VI) reduction over long period of incubation, maybe associated with the toxic and the mutagenic effects of Cr(VI) towards the cells. The model developed in the study at a steady-state predicted effluent Cr(VI) concentration satisfactorily in both carbon source and non carbon source reactor with R-squared value above 95%. In an inoculated column reactor amended with sawdust, k (reaction rate coefficient) $=5.2\times10^{-8}$ was achieved at the second order reaction while in an inoculated column reactor without sawdust the kinetic reaction rate coefficient was adjusted to , k= 9.9×10^{-9} at the first order reaction.

1. Introduction

Effluents from textile, leather tanning, electroplating, metallurgical and paint industries contains considerable amounts of toxic metal ions (Shi *et al.*, 2009). Cr(VI) is one of the toxic heavy metals associated with environmental pollution and human health hazards. It is a so-called carcinogen and potential soil, surface water and groundwater contaminant (Cervantes *et al.*, 2001). Cr(VI) reduced form, Cr(III) on the other hand is relatively insoluble, less toxic and also it is required in trace amount for human nutrition (Viamajala *et al.*, 2004). Considering the toxicity and the mobility of Cr(VI) in the environment, its removal or transformation to less toxic Cr(III) is essential.
Some of the existing methods for treatment of Cr(VI) contaminated soil and groundwater include excavation or pumping out of the contaminated material that requires follow up chemical addition followed by precipitation and then adsorption. These methods are relatively expensive as they are either energy intensive or require large quantities of chemical reagents. Additionally, chemical addition generate large

quantities of toxic sludge that is difficult to dispose (Blowes, 2002; Gonzalez *et al.*, 2003).

Recently, bioremediation of Cr(VI) has gained considerable attention. This method can be applied either as an *in situ* or *ex situ* technology. *In situ* bioremediation technology appears as a novel remediation alternative to the *ex situ* remediation technique as it minimizes the risk associated waste transportation; additionally it also minimizes the cost associated with pumping and excavation of the contaminated material in the contaminated site.

Many bacterial strains are capable of utilizing Cr(VI) as a terminal electron acceptor in the respiratory process and transform Cr(VI) to Cr(III) (Ahmad *et al.*, 2010; Zahoor and Rehman, 2009; Congeevaram *et al.*, 2007; Molokwane *et al.*, 2008). Despite the large number of studies on microbial Cr(VI) removal from the environment, not much of research was done on biological treatment of spillage waste on the ground. The main aim of the current study is to evaluate the prospect of pollution control in groundwater aquifers using potential Cr(VI) reducing bacterial species from the local environment. Also to develop a numerical model that will simulate the biological Cr(VI) removal in the aquifer environment.

2. Materials and Methods

2.1. Soil sample
Aquifer cores were extracted from the actual contaminated site (Brits, North West Province, South Africa). The Cr(VI) concentration background in the aquifer media sample was in the order of 50 µg/kg.

2.2 Culture start-up
For inoculation, bacterial isolates from the local environment were nutritionally cultivated as a reconstituted consortium culture in the LB broth medium amended with 75 mg/L of Cr(VI) concentration for 24 hours at $30\pm2°C$ under shaking. The culture was then harvested by centrifuging at 6000 rpm for 10 minutes and thoroughly mixed with a MSM.

2.3 Cr(VI) removal system set-up
A schematic of the fixed-media microcosm reactor system employed for the reduction of Cr(VI) to Cr(III) by reconstituted consortium culture is represented in Figure1. The experimental columns used were constructed from the Plexiglas (60cm long, 5cm internal diameter). Five sampling ports were drilled along each column reactor. The columns were then tightly packed with aquifer media and then capped on both ends with drilled PVC caps. Prior capping the columns on both ends the sterile control column was sterilized by autoclaving at 121°C for 20 minutes and the other two columns were amended with sawdust to simulate the carbon source leached from overlying vegetation above the ground.
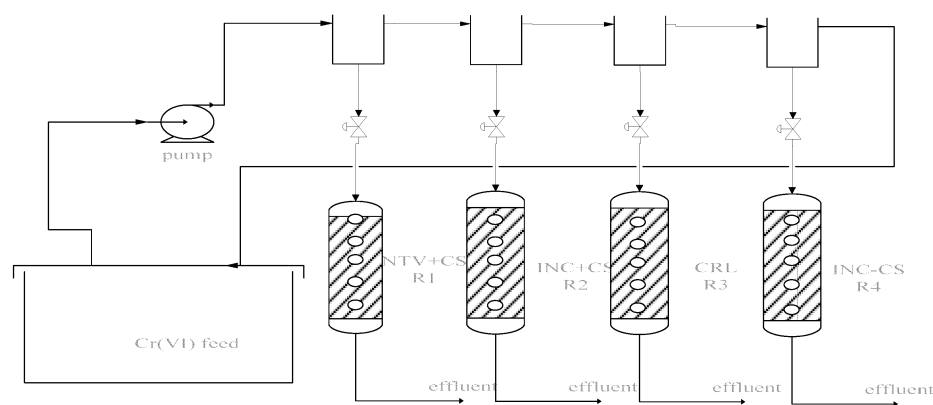
Figure 1: Laboratory microcosm reactor set-up

2.4 Column Start-up

Primarily experimental runs, distilled water were fed in each of the packed columns to saturate the soil particles. Flow rates were measured and adjusted to establish the hydraulic retention time of 24 hours in each column. The cultivated cells were then introduced into two reactors (R2 and R4) for a period of 24-48 hours enough time to allow uniform distribution of cells in the reactors before contaminant loading.

2.5 Experimental Run

Cr(VI) loading in the reactor columns was simulated by gravity feeding as in the case of open aquifers at the site. Microcosm reactors were operated as packed beds at different Cr(VI) concentrations of 20, 30, 40 and 50 mg/L respectively. Samples withdrawn from the five equally spaced intermediate ports and from the effluent port were centrifuged at 6000 rpm for 10 minutes to remove soil particles and then followed by analysis of Cr(VI).

2.6 Analytical Methods

Cr(VI) was measured using a UV/vis spectrophotometer (WPA, Light Wave II, Labotech, South Africa) at a wavelength of 540 nm (10 mm light path) after acidification and reaction with 1,5-diphenyl carbazide to produce a purple-pink 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.

2.7 Cr(VI) Reduction at Various Lengths

The slope of Cr(VI) concentration profiles along the reactor columns at a steady state was defined by an ordinary differential equation representing Cr(VI) reduction rate (r_c) derived as follows:

$$\frac{-dF_c}{dW} = r_c \tag{1}$$

$$\text{where: } r_c = kC\left(1 - \frac{C}{C_r}\right)^n \tag{2}$$

F_c (molar flow rate of Cr(VI)) and W (mass of aquifer media) can be represented as:

$$F_c\left(\frac{mole}{s}\right) = QC \tag{3}$$

$$W(g) = \rho_c A_c L \tag{4}$$

Therefore using equation 2, 3 and 4 above, equation 1 can be represented as:

$$-\frac{dC}{dL} = kC\left(\frac{\rho_c A_f}{Q_{in}}\right)\left(1 - \frac{C}{C_r}\right)^n \tag{5}$$

where: C = Cr(VI) concentration at anytime, (ML^{-3}), L= length of the reactor,(L), k= reaction rate coefficient, $(L.mol^{-1}.s^{-1})$, ρ_c = density of aquifer soil particles (ML^{-3}), A_f= biofilm surface area (L^2), Qin = inflow rate $(L^3 T^{-1})$, C_r= Cr(VI) toxicity threshold coefficient (ML^{-3}), and n = reaction order, (MM^{-1}). N.B: The dimension of k (reaction rate coefficient) is independent on the order of the reaction thus implies that k varies with varying n.

3. Results and Discussion

3.1 Cr(VI) removal kinetics along the reactor column

Cr(VI) effluent concentration along the reactor column was simulated using Equation 5. Cr(VI) toxicity threshold, C_r, in the model was assumed to be 50 mg/L based on the results obtained at the microcosm experimental run of 50 mg/L. The experimental result at 50 mg/L showed no significant Cr(VI) reduction along the reactor column with the removal efficiency of only 9% in an inoculated carbon source reactor after two weeks of operation. The effluent Cr(VI) concentration did not stabilize until a steady state, which occurred after three to four days of operation was achieved. At this state no significant reduction of Cr(VI) was observed over time in both the inoculated column amended with sawdust and the inoculated column without sawdust. This result may be associated to Cr(VI) toxicity within the cell over time. The developed model for biological Cr(VI) reduction along the inoculated columns at the steady state fits the experimental data well Figure 2 (A-C). It is observed in Figure 2 (A-B) that the model best fitted the experimental data in a carbon source reactor at n=2 which indicates that the rate of
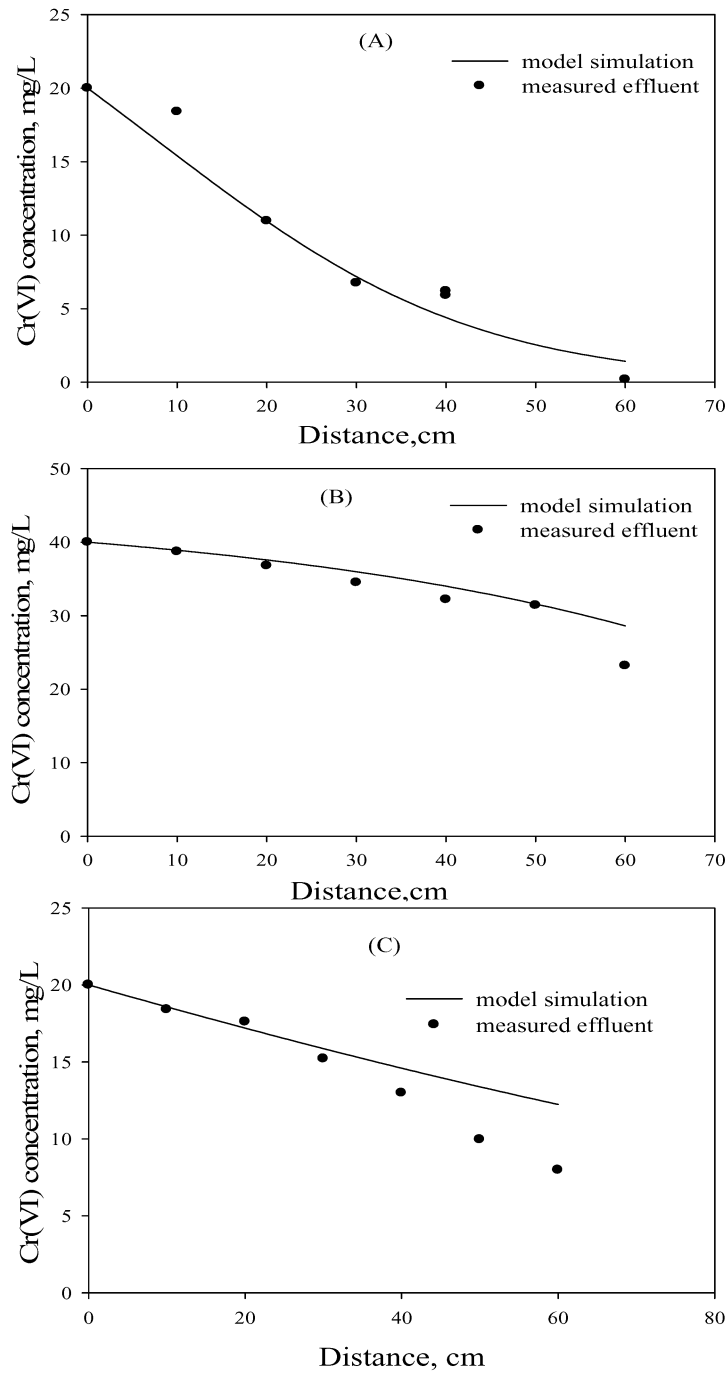
Figure 2: Simulation of Cr(VI) effluent across the reactors at (A) 20 mg/L and (B) 40 mg/L in (+C-Source) and (C) 20mg/L in a (-C-Source) reactor.

Cr(VI) removal in this reactor is dependent on both the presence of sludge culture and organic carbon source. It is also observed in Figure 2 (C) that the model satisfactorily fitted the experimental data in a non-carbon source reactor at n=1and at an adjusted reaction rate coefficient compared to the later reactor, which indicates that the rate of Cr(VI) reduction in the non-carbon reactor is only dependent on the presence of the sludge culture in the reactor.

4. Conclusion

The microbes isolated from sand drying beds at the local environment were able to sustain Cr(VI) concentration of 40 mg/L, which is the current highest groundwater Cr(VI) concentration at the remediation wells at the study site.

Acknowledgement

References

Ahmad, W.A., Zakaria, Z.A., Khasim, A.R., Alias, M.A., Ismail SMHS, 2010, Pilot-scale removal of chromium from industrial wastewater using the ChromeBac[TM] system, Bioresource Technol, 101, 4371-4378.

APHA, 2005, Standard methods for the examination of water and wastewater. In: Eaton, A.D., Clesceri, L.S., Rice, E.W., Greenberg, A.E., Franson, M.A.H. (Eds.), 21st ed. American Public Health Association, American Water Works Association, Water Environment Federation, USA (centennial edition).

Blowes, D., 2002, Environmental chemistry. Tracking hexavalent chromium in groundwater, Science, 295, 2024-2025.

Cervantes, C., Campos-Garcia, J., Devars, S., Gutierrez-Corona, F., Loza-Tavera, H., Torres-Guzman, J.C., Moreno-Sanchez, R., 2001, Interactions of chromium with microorganisms and plants, FEMS Microbiology, 335-347.

Congeevaram, S., Dhanarani, S., Park, J., Dexilin, M., Thamaraiselvi, K., 2007, Biosorption of chromium and nickel by heavy metal resistant fungal and bacterial isolates, J Hazard Material, 146, 270-277.

Gonzalez, C.F, Ackerley, D.F., Park, C.H., Matin, A., 2003, A soluble flavoprotein contributes to chromate reduction and tolerance by Pseudomonas putida, Acta Biotechnologica, 23, 233-239.

Molokwane, P.E., Meli, C.K., Chirwa, E.M.N., 2008, Chromium (VI) reduction in activated sludge bacteria exposed to high chromium Loading, Water Science and Technology, 58(2), 399-405.

Shi, W.Y., Shao H.B., Li, H., Shao, M., Du, S., 2009, Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite,J Hazard Material,170,1-6.

Viamajala, S., Peyton, B.M., Sani, R.K., Apel, W.A., Petersen, J.N., 2004, Toxic effects of chromium (VI) on anaerobic and aerobic growth of Shewanella oneidensis MR-1, Biotechnology Progress, 20(1), 87-95.

Zahoor, A., Rehman, A., 2009, Isolation of Cr(VI) reduction bacteria from industrial effluents and their potential use in bioremediation of chromium containing wastewater. J Environ Sci, 21, 814-820.