CHEMICAL ENGINEERING TRANSACTIONS
VOL. 45, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

ISBN 978-88-95608-36-5; **ISSN** 2283-9216
DOI: 10.3303/CET1545163

Kinetics of Cr(VI) Reduction and Remobilisation in an Aquifer Permeable Reactive Barrier: Microcosm Simulation

Lapaka A. Kaimbi, Evans M. N. Chirwa*

Water Utilisation and Environmental Engineering Division, Department of Chemical Engineering, University of Pretoria, Pretoria 0002
evans.chirwa@up.ac.za

Chromium is found in the environment mainly as hexavalent chromium, Cr(VI), and the trivalent form, Cr(III). Cr(VI) is carcinogenic and mutagenic to living organisms including humans whereas trivalent chromium is 1,000 times less toxic than Cr(VI). Most of the anthropogenic Cr discharged to the environment is in the hexavalent state since most human activities oxidise chromium ore (Cr(III)) to chromates and dichromates (Cr(VI)). The detoxification of Cr therefore involves reduction of Cr(VI) to Cr(III). Unfortunately, for in situ bioremediation systems, this causes accumulation of the Cr(III) precipitate, $Cr(OH)_3(s)$. The accumulated precipitate, if the water is underground, reduces the porosity and permeability of aquifer medium. In this study, a cleanup method for an *in situ* underground remediation barrier system is evaluated. The process involved the remobilisation of the $Cr(OH)_3$ precipitate in a horizontal flow aquifer microcosm reactor using a dilute acid (0.1 % HCl) followed by recover of Cr(III) species on the negatively charged electrode (anode) of an electrokinetic field located downstream of the remediation zone. The reactor was operated for 28 d 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 barrier was effectively remobilized. A gradient of yellow and green precipitate was observed around the anode confirming the migration of Cr(III) species toward the anode. A non-competitive inhibition model for Cr(VI) reduction successfully predicted effluent conditions at different loading conditions and during barrier regeneration by acid washing and electrokinetic remobilization. Optimum parameters that resulted in the best fit to experimental data comprised of maximum Cr(VI) reduction rate coefficient k_m = 0.221 h^{-1}, half velocity concentration K_c = 11.6 $mg.L^{-1}$, non-competitive inhibition coefficient K = 145 $mg.L^{-1}$, and the cells' Cr(VI) reduction capacity R_c = 0.964 $g.g^{-1}$. The results demonstrated for the first time, the potential for sustainable long-term operation of biological permeable reactive barriers for treatment of Cr(VI).

1. Introduction

Cr(VI) is known to be carcinogenic, mutagenic and teratogenic in biological systems (De Flora, 2000). In plants, concentrations as low as 0.5 ppm in the pore water and 5 ppm in soils results in the inhibition of seed germination in cereal plants (Panda and Sarkar, 2012). Cr(III) on the other hand, exists in cationic or complexed hydroxyl forms $Cr(OH)^{2+}$, $Cr(OH)_3$, $Cr(OH)^{4-}$and $Cr(OH)_5^{2-}$ depending on the pH of the solution. Notably, Cr(III) is not toxic to living organisms as it is necessary in animal nutrition (Saha et al., 2011). Cr(III) is an essential nutrient for mammals as it is used in dietary supplements to maintain normal glucose, (Hu and Deming, 2005) and fatty acid metabolism (Rossouw, 2009). In humans, exposure to Cr(VI) as high as 10 ppm causes kidney and liver failure, and can negatively affect the immune system (Costa, 1997).

Unlike other metals, Cr(VI) easily combines with oxygen to form water soluble, negatively charged oxyanions such as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) which adsorb to positively charged species in contrast to cationic metal species (Scialdone et al., 2014). Therefore, hexavalent chromium species are not strongly adsorbed in many soils under alkaline to slightly acidic conditions. For this reason, Cr(VI) species tend to be very mobile in subsurface environment moving at the same rate as groundwater.

Please cite this article as: Kaimbi L.A., Chirwa E.M.N., 2015, Kinetics of cr(vi) reduction and remobilisation in an aquifer permeable reactive barrier: microcosm simulation, Chemical Engineering Transactions, 45, 973-978 DOI:10.3303/CET1545163

Cr(VI) is conventionally treated by reduction of the hexavalent form to the trivalent species using chemical reagents followed by precipitation of the Cr^{3+} as chromium hydroxide, $Cr(OH)_3$, at a pH above 8 (Owlad et al., 2009). In moving waters in the underground environment, this can be achieved by using permeable reactive barriers containing reactive materials such as zero-valent iron (Fe^0) or ferrous iron (Fe^{2+}) (US EPA, 1999).

Permeable reactive subsurface barriers are defined as an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms and attain remediation concentration goals down gradient of the barrier (Puls and Powell, 1997). The reactive material can be chemical reagents such as iron as indicated above or specially isolated microbial communities with the capability of converting toxic compounds to environmentally compatible forms.

In the case of treatment of metallic pollutants such as chromium, the reduced species precipitate can accumulate in the barrier system thereby affecting porosity and hydraulic conductivity during long-term operation (Molokwane and Chirwa, 2013).

In this study, a process for remobilising the precipitate is proposed using a dilute acid wash. The metallic species were thereafter migrated to a negatively charged electrode of an electrokinetic system and pumped out of the system to avoid pollution of the aquifer downstream of the barrier. A kinetic model was developed which was used to simulate Cr(VI) breakthrough during operation of the barrier after the cleanup process.

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 °C 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. (2008).

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 tank.

2.3 Microcosm system setup

Operation of an aquifer simulation barrier was conducted in horizontal flow tank 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) concentration (50 mg/L) which was slightly higher than the concentration in contaminated groundwater at the target site in Brits. The tank 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 to be 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, a 150 V (0000 Amps) DC current was passed between the electrode resulting in the accumulation of chromium species at the anode (downstream). Excess cations were pumped from inside the perforated PVC tubes surrounding the electrode as shown in Figure 1.

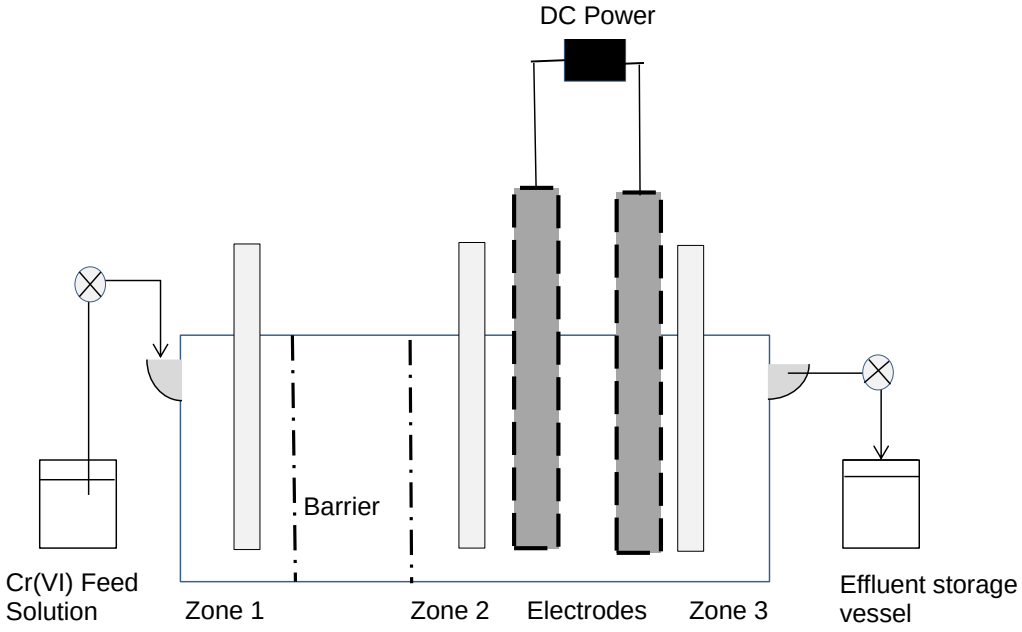

Figure 1: The horizontal flow microcosm reactor showing the pumping scheme and layout of electrodes and sample ports. Each sample port shown in the figure represents three sample ports across the width and the second electrode represents two electrodes placed 25 cm apart.

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 color (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., 2008). 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., 2008).

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 systems 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) were 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 Figure 2 and the summary of parameters obtained is shown in Table 1.

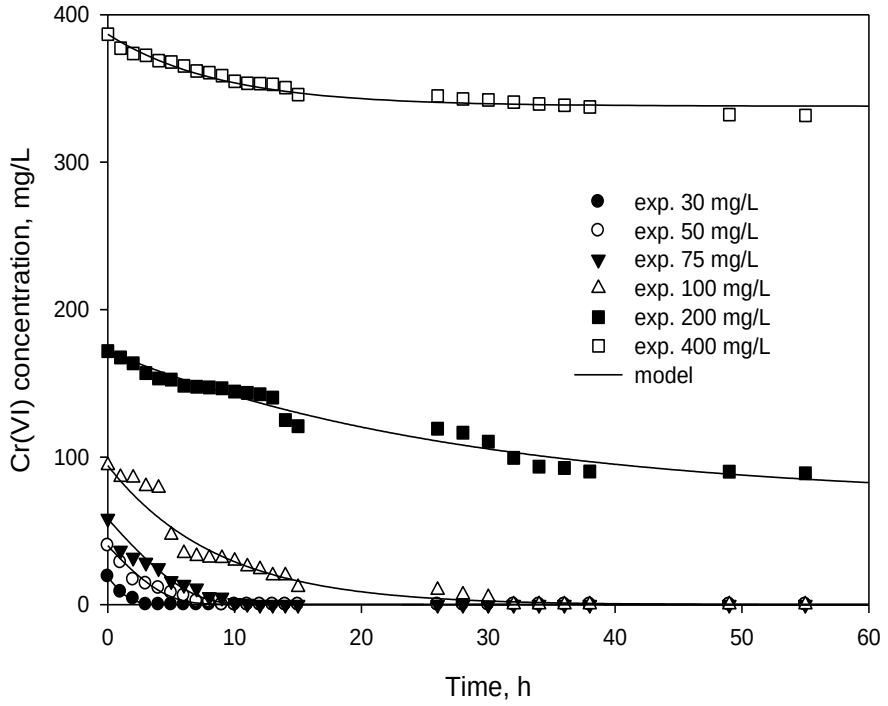

Figure 2: Anaerobic batch culture model validation at (30 - 400mg/L).

Table 1: Optimum kinetic parameter in anaerobic batch cultures

Prepared Feed Conc'n ($mg.L^{-1}$)	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

The operation of the inoculated microbial barrier system under a continuous Cr(VI) loading of 50 $mg.L^{-1}$ and at a hydraulic loading rate of 13.3 $L.h^{-1}$ resulted in equilibrium state reached in 35 d. 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 was measured. The high values of total Cr measured in ports downstream of the barrier confirmed that the acid wash regiment

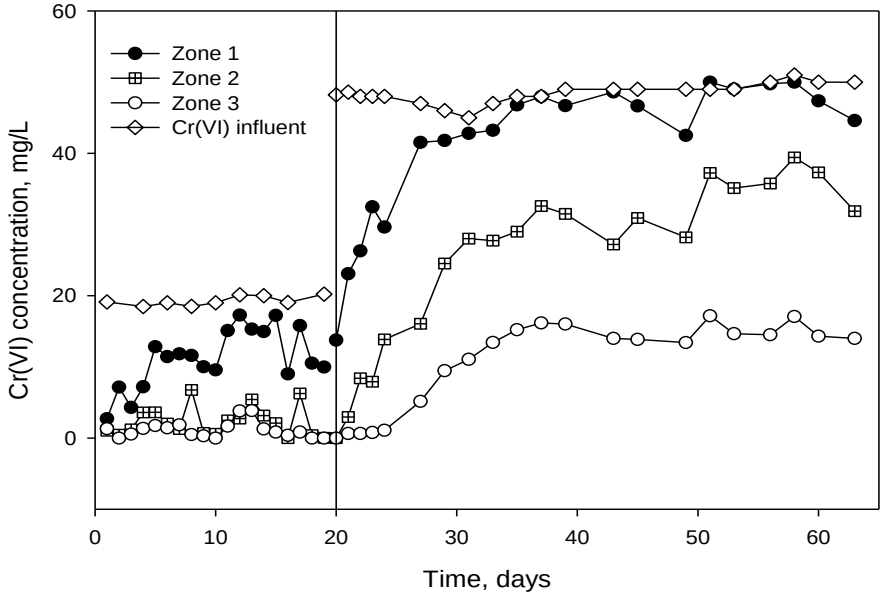

Figure 3: Concentration profiles before the barrier (black circle), after the barrier (crossed square) and exit zone (white circle).

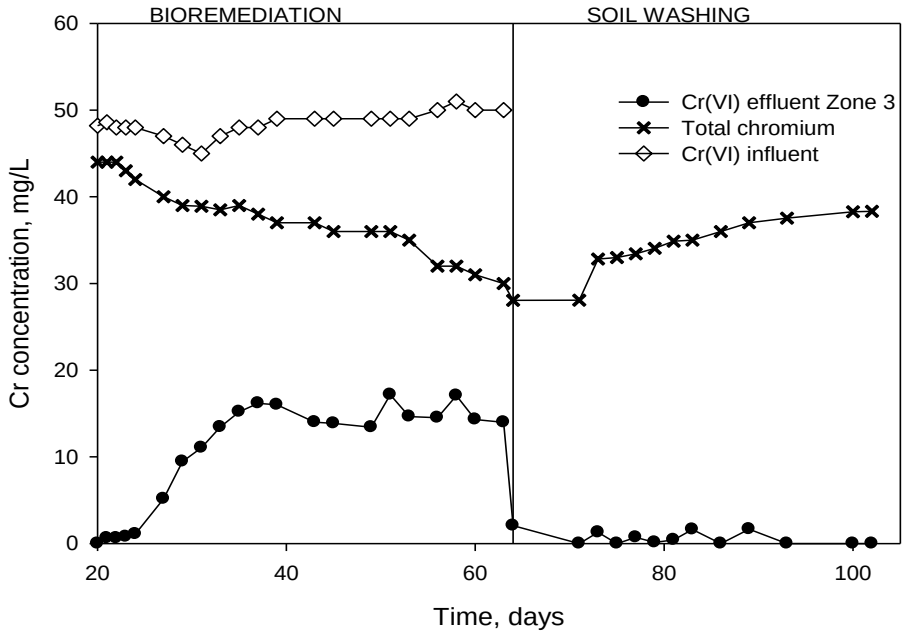

Figure 4: Cr(VI) and total Cr before and after the acid wash run showing an increase in total Cr in the effluent zone (Port 2) during the acid wash cycle.

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. $Cr(OH)_3$ 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 next step in this research will be to develop a method for inhibiting re-hydroxylation and precipitation of $Cr(OH)_3$ and divalent cationic salts around the negatively charged electrodes which decreased the efficiency of transport of reduced chromium to the brine extraction well around the electrode. The application of the acid wash and electrokinetic system will help extend the operational life of the barrier by cleaning the barrier intermittently thereby avoiding the cost and labour associated with excavation and replacement of the barrier materials to remove the precipitates.

References

APHA 2005. Standard Methods for the Examination of Water and Wastewater, 21st Edition, American Public Health Association, American Water Works Association, Water Environment Federation: Washington, DC, USA.

Costa M. 1997. Toxicity and carcinogenicity of Cr (VI) in animal models and humans, CRC Crit. Rev. Toxicol., 27, 431-442.

Hu G., Deming R.L., 2005, Speciation of bio-available chromium in soils by solid-phase extraction and graphite furnace atomic absorption spectrometry, Analyt. Chimica Act., 535, 237-242.

Kaimbi L.A., Chirwa E.M.N., 2013, Remobilization of trivalent chromium and the regeneration of in situ permeable reactive barriers during operation, Chem. Eng. Trans., 35, 835-840.

Molokwane P.E., Nkhalambayausi-Chirwa E.M., Meli K.C., 2008, Chromium (VI) reduction in activated sludge bacteria exposed to high chromium loading: Brits culture (South Africa), Water Res., 42, 4538-4548.

Molokwane P.E., 2010, Simulation of in situ bioremediation of Cr(VI) in groundwater, PhD Thesis, University of Pretoria, Pretoria, South Africa. <upetd.up.ac.za/thesis/available/etd-09252010-154146> accessed 10.06.2015

Molokwane P.E., Chirwa E.M.N., 2013, Modelling Biological Cr(VI) Reduction in Aquifer Microcosm Column Systems, Water Sci. Technol., 67, 2733-2738.

Mtimunye P.J., Chirwa E.M.N., 2014, Biochemical optimisation and control of uranium (VI) reduction in facultative uranium VI reducing cultures, Chemosphere, 113, 22-29

Owlad M., Aroua M.K., Daud W.A.W., Baroutian S., 2009, Removal of hexavalent chromium-contaminated water and wastewater: A review, Water Air Soil Pollut., 200, 59-77.

Panda J., Sarkar P., 2012, Bioremediation of chromium by novel strains *Enterobacter aerogenes* T2 and *Acinetobacter* sp. PD 12 S2, Environ. Sci. Poll. R., 19, 1809-1817.

Puls R.W., Powell R.W., 1997, Permeable reactive subsurface barriers for the interception and remediation of chlorinated hydrocarbon and chromium(VI) plumes in ground water, 4 pp. US EPA Remedial Technology Fact Sheet, EPA/600/F-97/008, US EPA, Washington DC, USA.

Rossouw P.S., 2009, Environmental extractability of chromium (III) and nickel from soils of South Africa's Eastern Highveld, M.Sc. Dissertation, University of Pretoria, Pretoria, South Africa, <www.repository.up.ac.za/handle/2263/28688> accessed 12.05.2012

Saha R., Nandi R., Saha B., 2011, Sources and toxicity of hexavalent chromium, J. Coord. Chem., 64, 1782-1806.

Scialdone O., D'Angelo A., De Lumè E., Alessandro Galia A., 2014, Utilization of reverse electrodialysis processes for the abatement of pollutants in water, Chem. Eng. Trans., 41, 139-144.

U.S.EPA, 1999, An In Situ Permeable Reactive Barrier for the Treatment of Hexavalent Chromium and Trichloroethylene in Ground Water: Volume 2 Performance Monitoring, United State Environmental Protection Agency, Report No. EPA/600/R-99/095b, September 1999, Washington, DC, USA.