CHEMICAL ENGINEERING TRANSACTIONS
VOL. 94, 2022
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš, Sandro Nižetić

ISBN 978-88-95608-93-8; **ISSN** 2283-9216
DOI: 10.3303/CET2294234

Biotreatment of Hexavalent Chromium in a Rectangular Column using Municipal Wastewater Sludge as a Bioreactive Barrier

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Contamination of the environment with hexavalent chromium [Cr(VI)] containing waste discharged from the production of alloys and stainless steel, dye industries, leather tanning, metal plating amongst others, it is a well-known global problem. Cr(VI) is highly mobile, soluble and bioavailable in the environment, it is the most toxic among chromium species, and is a known carcinogen. In contrast, trivalent chromium, [Cr(III)], is immobile, less stable in water and is an essential dietary element. As a results Cr(VI) has been placed under strict control measures by most national and international lists of high toxic materials. Bioremediation of Cr(VI) contaminated effluents appears to be more economical and environmentally friendly treatment method. This study investigates Cr(VI) removal in a bench-scale bioreactor using municipal dried sludge as permeable bioreactive barrier. Two series of experiments were conducted using two parallel bench-scale bioreactors under a hydraulic loading of 200 mL/h. During the first experiment, one system was used as a control, while the other received Cr(VI) concentrations equal to 40 mg/L. Experimental showed that the 20 cm thick permeable bioreactive barrier with a 30% sludge and 70% sand was able to achieve complete Cr(VI) removal during 30 operational days. The bioremediation technology proposed in this study significantly demonstrated the effectiveness of the permeable bioreactive barrier system in treating Cr(VI) containing process effluent streams. Fundamental knowledge and understanding of kinetic processes taking place within the bench-scale permeable bioreactive barrier system will be valuable in designing a proper pilot scale system.

1. Introduction

Water and soil are natural resources and form essential components of the ecological environment. Chromium (Cr) has been extensively used in various industrial applications and it is a persistent pollutant in many cases of water and soil contamination (Xue et al., 2017). Contamination of the environment with hexavalent chromium [Cr(VI)] containing waste discharged from the production of alloys and stainless steel, dye industries, leather tanning, metal plating amongst others, it is a well-known global problem (Kholisa & Chirwa, 2021). Amongst the Cr various valence states, Cr(VI) is the most toxic form. Due to its strong oxidizing properties, Cr(VI) exhibits biologically toxic, mutagenic, carcinogenic, and teratogenic properties (Kalola & Desai, 2020). Hence, Cr(VI) has been placed under strict control measures by most national and international lists of high toxic materials. Remediation of Cr(VI) requires the reduction of the mobile state [Cr(VI)] which exists in the natural environment as the oxyanionic species ($H_wCr_xO_y^{z-}$), where x = 1 or 2, y = 4 or 7, and w and z = 0 to 2 depending on the pH of the solution, to the less mobile trivalent state [Cr(III)] which readily forms the hydroxide precipitate [$Cr(OH)_3$(s)] under natural redox and pH conditions (Kaimbi & Chirwa, 2015). The tendency of Cr(III) to precipitate makes it less mobile in the environment and therefore much easier to manage its ecological impacts than Cr(VI) (Ren et al., 2018).

Biological remediation has been an effective technique to reduce Cr(VI) from polluted environments in recent years (Bharagava & Mishra, 2018). Transformation of Cr(VI) to Cr(III) by chromium resistant bacteria (CRB) is considered as a valuable, promising, and cost-effective approach for Cr(VI) remediation. The bacterial transformation of Cr(VI) to Cr(III) was reported for the first time in the 1970s by Romanenko and Koren'Kov

Paper Received: 12 December 2021; Revised: 10 March 2022; Accepted: 9 May 2022
Please cite this article as: Kholisa B., Matsena M.T., Chirwa E.M.N., 2022, Biotreatment of Hexavalent Chromium in a Rectangular Column Using Municipal Wastewater Sludge as a Bioreactive Barrier, Chemical Engineering Transactions, 94, 1405-1410 DOI:10.3303/CET2294234

(1977), where isolated Pseudomonas strain was studied. Since then, there has been a wide variety of bacteria strains, such as Bacillus, Pseudomonas, Ochrobactrum Microbacterium, Desulfovibrio, Achromobacter, Enterobacter, Halomonas, Cellulomonas, Micrococcus, Staphylococcus, and Escherichia amongst others (Kholisa et al., 2021). These microorganisms are isolated from numerous environmental sites such as waste disposal sites, tannery effluents, and industrial landfills. Although, the application of using a bacteria for biological reduction Cr(VI) has been widely studied. These studies have been mainly focused on batch systems which limits their applicability to lab scale. However, continuous-flow systems such as biological permeable bioreactive barrier (BPRB) on the other hand have the potential of continuously treating large volumes of Cr(VI) contaminated water. This study investigates Cr(VI) reduction performance of a mixed-culture of bacteria as a permeable reactive barrier in a bench-scale bioreactor system.

2. Materials and Methods

2.1 Sample collection

Dried sludge samples were collected from Brits Wastewater Treatment Works sand drying beds (North West Province, South Africa). The treatment works periodically receives high Cr(VI) levels from an abandoned sodium dichromate processing facility. Therefore, the bacteria in the sludge was thus expected to be acclimatized to high Cr(VI) exposure conditions. The samples were stored in sterile containers at 4 °C for further use.

2.2 Bioreactor set-up

Two horizontal flow tanks with the dimensions 820 mm x 170 mm x 200 mm (L x B x H) were constructed using 5 mm thick transparent Perspex sheets (Evonik Rohm GmbH, Essen, Germany) as shown in Figure 1. The reactor consists of five compartments: The influent and effluent reservoirs (100 mm × 170 mm × 200 mm), the sand (230 mm × 170 mm × 200 mm), and the biobarrier (150 mm × 170 mm × 200 mm). Sand compartments were filled with thoroughly washed pure river sand with granular size ranging 0.6 mm to 1.5 mm. To simulate the biobarrier conditions, the middle compartment was filled with a mixture of dried sludge and sand with a mass ratio of 30% to 70%. The compartment dividers were perforated to ensure evenly distrusted flow. The reactor was operated as plug-flow systems with four sampling ports along the length.

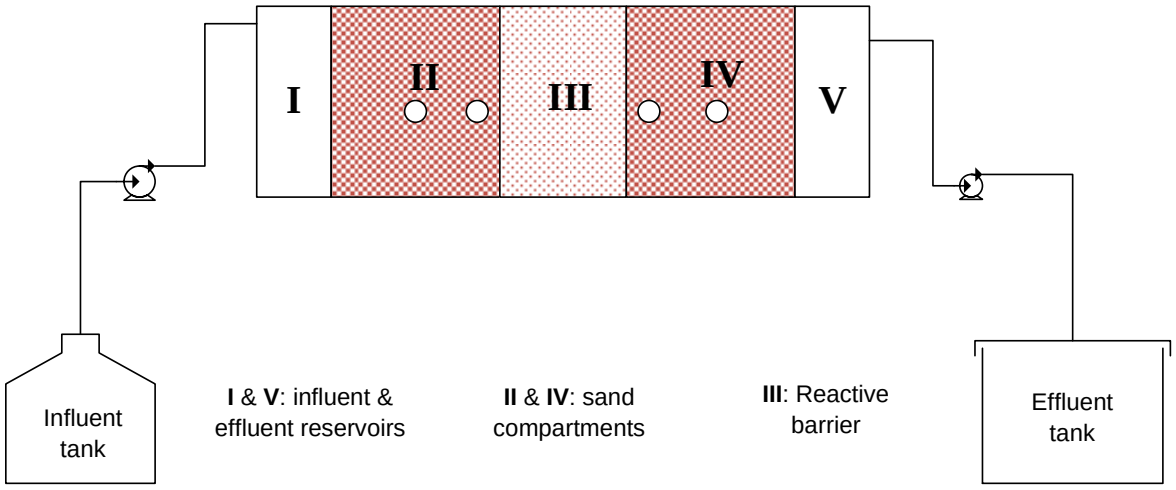

Figure 1: Bench scale set-up of a permeable reactive barrier system

2.3 Reactor startup

Two reactors were operated under constant flow rate of 200 mL/h. Before the starting up of experiments, the two reactors were saturated with distilled water for 14 days. The other reactor was filled with sand quartz only, to serve as a control. The influent solution of 40 mg/L Cr(VI) (initial pH = 6.8) was pumped into the reactors using a peristaltic pump and a liquid detention time of about 8 h in the biobarrier for a 30 days. Samples of the Influent and effluent were collected periodically for Cr(VI) and pH analysis. The operation of the reactors was without any supplementary organic carbon sources and minerals except from those already found in the sludge.

2.4 Determination of Cr(VI) and total chromium

Measurement of Cr(VI) was carried out by sampling 2 mL of sample across each reactor at regular time intervals using a disposable syringe. The sample was then centrifuged for 10 minutes at 6000 rpm (2820 *g*) using a Minispin® Microcentrifuge (Eppendorf, Hamburg, Germany) to remove the suspended solids. The sample was then analysed in UV/vis spectrophotometer (WPA, Light Wave II, and Labotech, South Africa) at the wavelength of 540 nm using DPC method as described by Kholisa and Chirwa (2021). Total chromium in each sample was measured using a Varian AA – 1275 Series Flame Atomic Adsorption Spectrophotometer (AAS) (Varian, Palo Alto, CA (USA)) at a wavelength of 359.9 nm

3. Results and Discussion

3.1 Reactor Performance

Cr(VI) removal and performance by biotic and abiotic permeable reactive barrier (PRB) were carried out using a bench scale horizontal flow reactors and the results are presented in Figure 2. Both reactors operated at hydraulic loading of 200 mL/h and were fed with distilled water for 14 days to saturate the reactors, to remove air space between the pores and to acclimatize the bacteria. The control reactor compartments were packed with sand quartz only to study the abiotic effect on the Cr(VI) removal and was fed with Cr(VI) concentration of 40 mg/L. It can be seen that effluent Cr(VI) concentration in the control reactor gradually increased until day 6. After day 6, the reactor reached a steady state as the influent Cr(VI) concentration was the same as effluent. Tang et al. (2021) pointed out that quartz sand is easily saturated and have low adsorption capacity.
In the PRB reactor, compartments 2 and 4 were backed with quartz sand while the compartment 3 was packed with 70 wt% and 30 wt% sand-sludge mixture. After the saturation phase which lasted 14 days, the PRB reactor was fed with distilled water containing Cr(VI) concentration of 40 mg/L and the results. The 20 cm barrier had a hydraulic retention time (HRT) of 8 h. After feeding the reactor with Cr(VI) for 30 days, no Cr(VI) was detected in the effluent for this period. This indicated that the Cr(VI) removal was 100% in the PRB. This demonstrates the potential of PRB system using indigenous bacteria species as the reactive barrier which was operated without continuous addition of external organic carbon source. Total Cr measurements in the PRB reactor effluent were similar to that Cr(VI) indicating that Cr(III) was trapped within pore spaces in the reactor as $Cr(OH)_3(s)$. This further characterised by the presence of dark-green colour after PRB, showing accumulation of Cr(III).

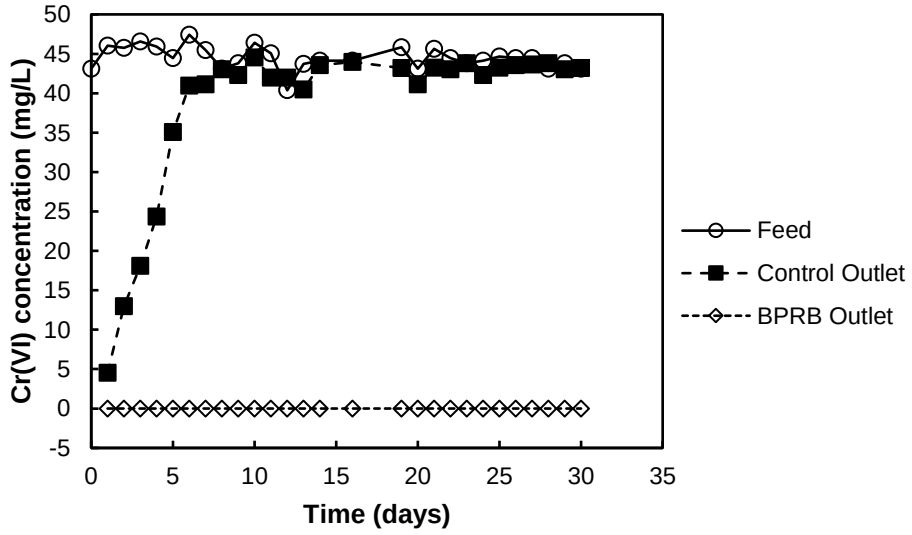

Figure 2: Cr(VI) removal of biotic and abiotic in the permeable reactive barrier system

3.2 Spatial Cr(VI) Profile

Spatial and temporal variation of Cr(VI) in the BRBP system with mixed-culture of bacteria from the dried sludge was evaluated under noncarbon source conditions. It can been seen that in the control experiment there was a sharp increase in the Cr(VI) concentration in the first five days in all the sampling ports. Thereafter the Cr(VI)

concentration normalized to approximately 40 mg/L in the first two ports, while the last two ports reached the 40 mg/L Cr(VI) concentration a day later (Figure 3). Therefore, control system reached the steady state after 6 days, as there was no significant variation in Cr(VI) concentration throughout the enter reactor. Thereafter, sampling in the sampling ports was stopped and only feed and effluent were monitored for control reactor. During the operation of the BPRB system, in Figure 4 it can be seen that Cr(VI) concentration increased sharply in the first two sampling ports similarly to that of the control reactor. This was because both reactors had the second compartment filled with sand only. In port 3, no Cr(VI) concentration detected in the first 6 days. After day 6, increase in Cr(VI) concentration was observed, and continued to increase up to 15 mg/L in day 10. Thereafter, Cr(VI) concentration decreased reached complete reduction in day 12. This was because microorganisms were still acclimatizing to long Cr(VI) stressed conditions. Complete Cr(VI) reduction was achieved in the barrier compartment, as it can be seen that Cr(VI) concentration in port 2 is approximately 40 mg/L while port 3 and port 4 are nearly 0 mg/L.

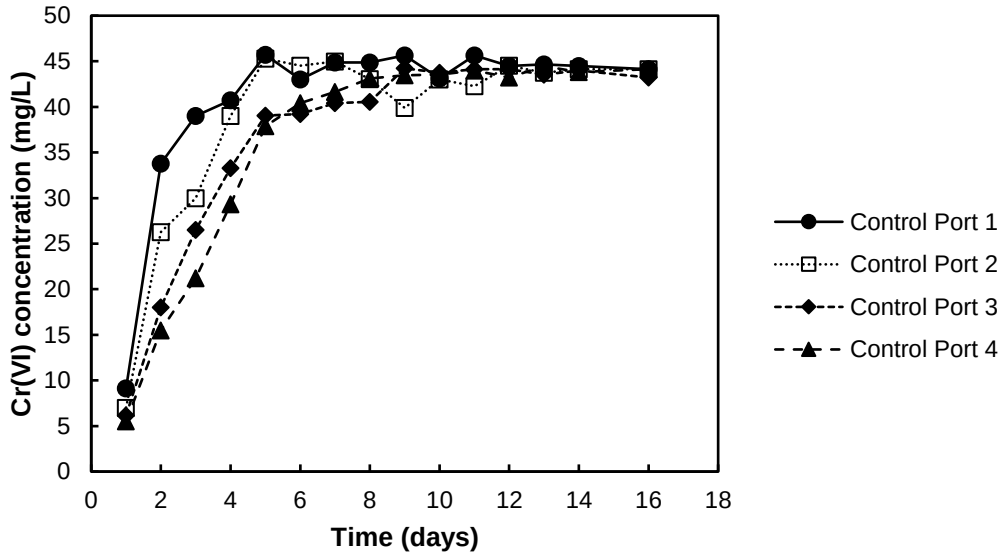

Figure 3: Spatial and temporal variation of Cr(VI) in the control system

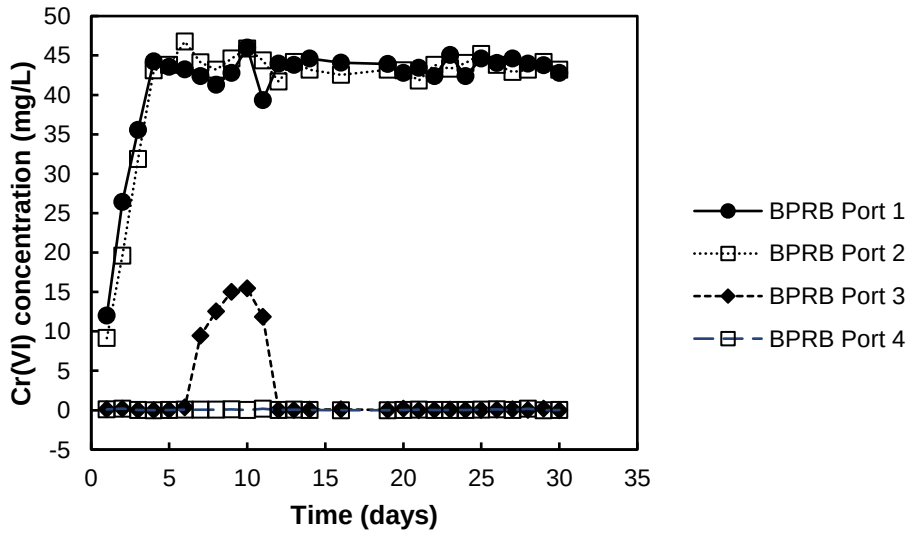

Figure 4: Spatial and temporal variation of Cr(VI) in the BRBP system

3.3 Environmental Parameters

There are many environmental parameters that can affect the performance of Cr(VI) reduction by microorganisms, amongst others include temperature and pH (Tan et al., 2020). For this reason, influent and effluent pH and temperatures were monitored throughout the entire duration of the study. The influent pH to reactors ranged between 6.8 and 7.5 while the effluent pH of the PRB reactor ranged 6.7 – 6.9 and control reactor ranged 6.5 – 6.91 as shown in Figure 5. The influent pH values were consistent with average input value of 6.96 throughout the whole experiment. Similarly, the effluent pH values for both the control and PRB reactors were stable for the first 30 days. Indicating no significant variation in the influent and effluents pH values. The time series plot for influent and effluent temperatures for both reactors are shown in Figure 6. The influent and effluent temperatures did not show significant variation during the course of this study. Influent temperature varied between 16.3 °C and 24.6 °C, while the effluent control varied between 21.4 °C and 27.4 °C for the 30 days of operation and PRB reactor effluent ranged between 21.3 °C to 29.7 °C.

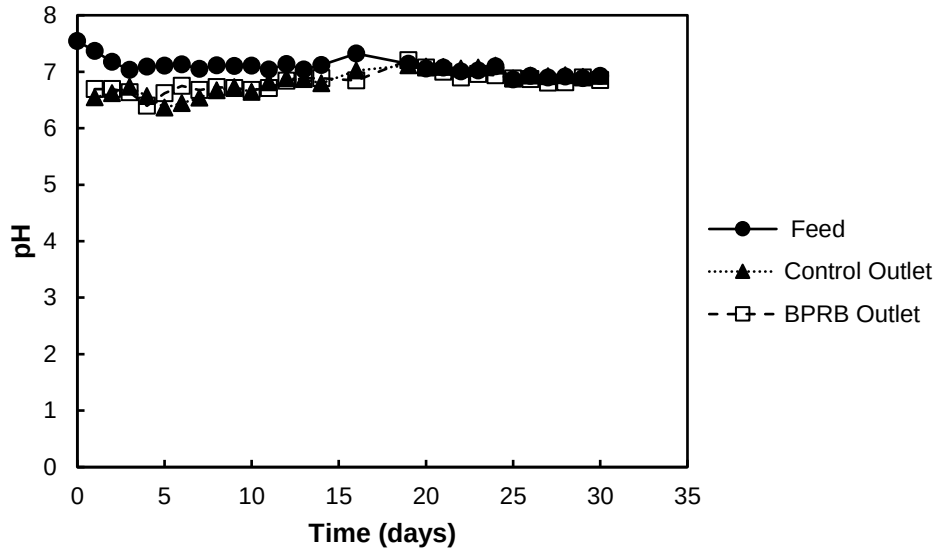

Figure 5: Time course of pH during Cr(VI) removal operation

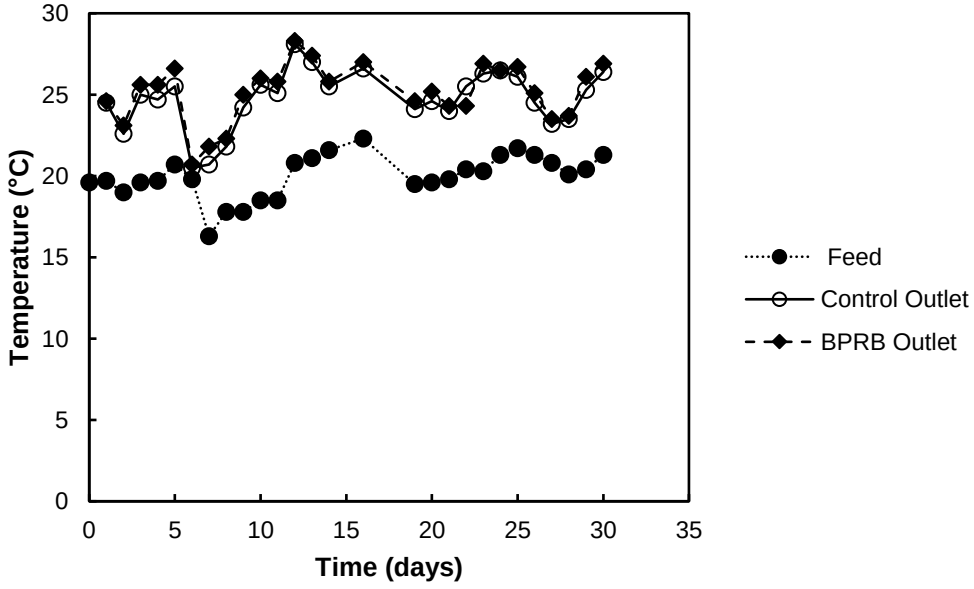

Figure 6: Time course of temperature variation during Cr(VI) removal operation

4. Conclusions

Continuous-flow bioreactor systems such as biological permeable reactive barrier have the potential of treating Cr(VI) concentrations at much higher volumes. Successful Cr(VI) reduction was achieved over the operational period of the BPRB system. Therefore, it can be concluded that the indigenous bacteria obtained in a wastewater treatment plant were able to effectively treat Cr(VI) over a period of 30 days without any biostimulation. Although, results presented in this study have strong implications of biological Cr(VI) reduction ex-situ through the use of the bioreactor system, these results could also be effective in optimizing and improving the operation and performance of in situ bioremediation of Cr(VI) at target site. Further studies are required to understand the interaction of bacteria with other heavy metals that co-exist with Cr(VI) in the environment and also to evaluate effect of operating the BPRB under various HRT's while occasionally backwashing or dislodging the accumulated precipitate from the system.

Acknowledgments

This research was funded by the research was funded through the National Research Foundation (NRF) Grant No. IFR200206501999, CSUR210111581519, EQP210111581520 awarded to Prof Evans MN Chirwa of the University of Pretoria. Buyisile Kholisa would like to acknowledge the National Research Foundation (NRF) for granting him the Doctoral Scholarship, Grant No. MND190613447392.

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