

Effective bioreduction of hexavalent chromium-contaminated water in fixed-film bioreactors

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ABSTRACT

Hexavalent chromium (Cr⁶⁺) contamination from a dolomite stone mine in Limpopo Province, South Africa, has resulted in extensive groundwater contamination. In order to circumvent any further negative environmental impact at this site, an effective and sustainable treatment strategy for the removal of up to 6.49 mg/l Cr⁶⁺ from the groundwater was developed. Laboratory-scale, continuous up-flow bioreactors were constructed to evaluate reduction of Cr⁶⁺, with a residence time of 24 h, an efficiency porosity of 44% and a flow rate of 1.5 ml/min. Stoichiometrically balancing terminal electron acceptors in the feed water with a selected electron donor, directed reactor balance for complete Cr⁶⁺ reduction. The microbial community shifted in relative dominance during operation to establish an optimal metal-reducing community, including *Enterobacter cloacae*, *Flavobacterium* sp. and *Ralstonia* sp., which achieved 100% reduction. Evaluation after reactor termination with SEM-EDX and XRD confirmed the establishment of biofilm on the reactor matrix, as well as trivalent chromium (Cr³⁺) precipitation within the reactor. Due to gravitational force, high concentrations of Cr³⁺ were found in the bottom third of the reactor. Based on the results from the laboratory investigation, a 24 000 l fixed-film pilot bioreactor was designed and constructed at this site. Influent flow rates, electron donor injection and automated sampling were remotely controlled by a programmable logic controller (PLC). Similar to the laboratory column study, steady state conditions could be achieved and successful Cr⁶⁺ reduction was evident. This is the first up-scaled, effective demonstration of a biological chromium(VI) bioremediation system in South Africa.

Keywords: Bioreduction, fixed-film reactor, hexavalent chromium, microbial diversity

INTRODUCTION

The study source site is located in the Limpopo Province of South Africa at a facility that actively mines and processes marble and dolomite stone as a graded aggregate for landscaping and construction purposes. Unrelated historic land-use activities resulted in ground and surface water contamination with hexavalent chromium (Cr⁶⁺). Despite efforts to prevent migration of site wastes to the surrounding environment, leaching of Cr⁶⁺ into the groundwater has occurred over the 80-year history of the site. Over a 5-year sampling period, measured Cr⁶⁺ concentrations in site groundwater ranged between 2.30 and 6.49 mg/l.

Hexavalent chromium is classified as a SABS 0228 danger group 8(II) compound leading to birth defects and reproductive impairment (Arlauskas et al. 1985; DWAF, 1998; Kanojia et al., 1998). It can cross the cellular membrane via sulphate transporters and, once inside the cell, can generate reactive oxygen species (ROS), implicated as mutagens and carcinogens, from the cyclic single electron transfer between Cr⁶⁺, molecular oxygen and Cr⁵⁺ (Ackerley et al., 2004). Trivalent chromium, on the other hand, is considered to be relatively innocuous and usually occurs as insoluble organic and inorganic complexes due to its strong Lewis acid nature (Barceloux, 1999).

The preferred technology for treatment of Cr⁶⁺ in South Africa is chemical reduction with ferrous sulphate or sodium

sulphite, followed by co-disposal and landfilling of residues (DWAF, 1998). However, chemical treatment of Cr⁶⁺ requires high concentrations of reagents, generates environmentally hazardous by-products and is generally more effective at higher concentrations (Szpyrkowicz et al., 2001). The potential for application of bioreduction of Cr⁶⁺ as an alternative remediation strategy has been highlighted in several publications; however, this is the first attempt at a systematic study aimed at an industrial-scale bioreactor with larger volumes (Thacker et al., 2006; Amoosegar et al., 2007).

Biological reduction of Cr⁶⁺ with indigenous bacteria in semi-passive systems can be an environmentally sound alternative or complementary technology to active chemical treatment technologies, but at comparatively lower lifecycle costs with less specialised labour requirements. Bacterial reduction of Cr⁶⁺ to its less toxic form is a complex phenomenon and can proceed under both aerobic and anaerobic conditions utilising membrane or cytoplasmic proteins that may or may not require the presence of co-factors (Opperman and Van Heerden, 2007). Dissimilatory chromate-reducing bacteria utilise Cr⁶⁺ as terminal electron acceptor, ultimately precipitating it as insoluble chromium hydroxides, demonstrating the potential for remediation (Desai et al., 2008).

A fixed-film bioreactor is a treatment process which employs a porous media with an attached biofilm through which contaminated water is passed and treated. The main functions of the media are to provide attachment sites for the biofilm, a hydraulic network for conveying flow through the system as well as minerals for biofilm development. The biofilm helps to create a physical environment within the bioreactor

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