

BIOLOGICAL TREATMENT OF GROUNDWATER WITH HIGH NITRATES CONTENT FOR HEXAVALENT CHROMIUM REMOVAL

PANOUSI E., MAMAIS D., NOUTSOPOULOS C., BERTOLI K. and KOUTOULA K.

Sanitary Engineering Laboratory, Department of Water Resources and Environmental Engineering,
School of Civil Engineering, National Technical University of Athens, Iroon Polytechniou 5,
Zografou 157 80, Athens, Greece
E-mail: mamais@central.ntua.gr

ABSTRACT

Several methods have been developed in order to tackle the problem of high hexavalent chromium concentrations in groundwater. Among these, physicochemical methods such as chemical oxidation, ion exchange, adsorption through activated carbon, membrane separation, are very often adopted. However all these methods present several disadvantages such as high capital and operational cost, need for management of the chemical sludge, etc. Because of the need to develop cost – effective and more environmentally friendly techniques, biological removal of Cr(VI) have aroused great interest the last few years. Biological systems, such as bio–reduction, bio–accumulation or bio–sorption using living cells have been examined for their chromium removal abilities. The objective of the present study is to evaluate the effectiveness of anoxic-anaerobic biological treatment systems to provide for appreciable hexavalent chromium reduction from groundwater. According to the results of the batch experiments, Cr(VI) removal can be achieved in a fully anoxic-anaerobic system dosed with an external organic carbon source at an influent COD concentration of 200 mg/L. Furthermore the effect of the hydraulic residence time on process performance was assessed through the operation of a series of anoxic-anaerobic sequential batch reactors at different hydraulic residence times. According to the results of the experimental systems, Cr(VI) removal can be achieved in a fully anoxic-anaerobic system dosed with an external organic carbon source at an influent COD concentration of 200 mg/L and operated at a hydraulic residence time of 1.7 d. Under these conditions almost complete Cr(VI) removal can be achieved for initial Cr(VI) groundwater concentration as high as 3000 µg/L. For lower concentrations of external carbon source hexavalent chromium removal is lower and does not exceed 90%. Complete Cr(VI) removal can also be achieved at lower hydraulic residence times as low as 0.6 d, for initial Cr(VI) concentrations equal to 200 µg/L and mixed liquor temperatures greater than 20°C.

Keywords: biological groundwater treatment, hexavalent chromium removal, hydraulic residence time; sequential batch reactors; anoxic-anaerobic systems

1. Introduction

High concentrations of hexavalent chromium, which have been detected in both surface water and groundwater, have caused concern as chromium poses serious risks to human health. In order to manage the problem of high Cr(VI) concentrations in groundwater, several treatment technologies have been developed. The most often used methods are physicochemical techniques such as: a) chemical reduction (Fruchter *et al.*, 2000; Jacobs *et al.*, 2001), b) ion exchange (Ren *et al.*, 2012), c) adsorption through activated carbon (Guertin *et al.*, 2005), d) membrane filtration (Hafiane *et al.*, 2000) and e) electrodialysis (Guertin *et al.*, 2005). Furthermore additional physicochemical methods have also been developed for chromium removal from water such as electrocoagulation (Parga *et al.*, 2005). All these methods present several disadvantages such as high capital and operational

cost, production of chemical sludge, sludge disposal problems, etc. Chemical reduction of hexavalent chromium to trivalent form and subsequent precipitation is a common method employed for chromate decontamination but only a limited removal can be achieved by the conventional methods (Patterson, 1985). This problem has stimulated interest in microorganisms and biological methods are now being explored for metal decontamination as alternatives to conventional methods due to their eco-friendly nature. Several microorganisms have been reported to be capable of reducing Cr(VI) including *Bacillus*, *Pseudomonas*, *Escherichia*, *Arthrobacter*, *Ochrobactrum*, *Brevibacterium*, *Shewanella*, *Rhodococcus*, *Shigella*, *Acinetobacter*, *Enterobacter*, *Brevibacterium*, *Pannonibacter*, *Sphaerotilus* (Caravelli *et al.*, 2008; Contreras *et al.*, 2011; Wang *et al.*, 1997; Camargo *et al.*, 2005). Studies performed have shown that microbial chromium (VI) removal from solutions typically includes the following stages (Singh *et al.*, 2010): i) binding of chromium to cell surface, ii) translocation of chromium into the cell, and iii) reduction of chromium (VI) to chromium(III) in the sludge flocs. Recently Mamais *et al.*, (2013) demonstrated that effective biological treatment of highly polluted groundwater for hexavalent chromium reduction can be achieved under anaerobic conditions. The authors report that treatment of groundwater in an anaerobic sequential batch reactor (SBR) operating at a sludge age of 10 d and a hydraulic residence time around 1.7 d can provide for a complete hexavalent chromium reduction to trivalent chromium for groundwater with hexavalent chromium concentrations as high as 200 µg/L.

This particular study evaluates the ability of anoxic-anaerobic SBR systems to perform appreciable hexavalent chromium reduction under high nitrate concentration and different hydraulic residence times and initial hexavalent chromium concentrations.

2. Materials and methods

In order to evaluate the effectiveness of biological groundwater treatment for hexavalent chromium removal under anoxic-anaerobic conditions three bench scale units were employed. All experimental units were operated as SBR systems. All systems were operated as anoxic-anaerobic systems and were fed with groundwater water which was supplemented with a mixture of milk and sugar (80% sugar, 20% milk on a COD basis) as the external substrate and a mixture of nutrients to support microbial growth, which included a nitrate concentration (NO₃-N) equal to 15 mg/L. The concentration of Cr(VI) in the influent water was achieved through hexavalent chromium addition in the form of K₂Cr₂O₇ solution. System A1 was fed with influent water once a day. The water was supplemented with a mixture of milk and sugar as the external substrate at a total COD concentration of 150 mg/L. System A1 received groundwater supplemented with Cr(VI) to reach a concentration of 200 µg/L. System A2 was fed with influent water once a day supplemented with a mixture of milk and sugar as the external substrate at a total COD concentration of 200 mg/L. System A2 received groundwater supplemented with various amounts of Cr(VI) depending on the desired influent Cr(VI) concentration. During the various operating phases of System A2, Cr(VI) concentration in the influent groundwater, was equal to: a) 200 µg/L, b) 800 µg/L, c) 1200 µg/L and d) 3000 µg/L. System A3 was fed with influent water three times a day. Feeding water was supplemented with a mixture of milk and sugar as the external substrate at a total COD concentration of 200 mg/L. System A3 received groundwater supplemented with Cr(VI) to reach a concentration of 200 µg/L. The nominal hydraulic residence time of systems A1, A2 and A3 was equal to 1.7 d, 1.7 d and 0.6 d, respectively. All systems operated on a constant sludge age of 10 d. Average operating temperature for all systems was in the 20-22°C, range.

The performance of the bench scale units was assessed by routine measurements of temperature, total and soluble COD, TSS, VSS, NH₄-N, NO₃-N, redox, pH, DO, total and hexavalent chromium throughout the experimental period. All analyses were done in accordance with Standard Methods (APHA, 2005).

3. Results and discussion

A series of bench scale anoxic-anaerobic SBRs were operated in order to evaluate the ability of the systems to perform appreciable hexavalent chromium reduction during the presence of high nitrate concentration. The results from the operation of the three units are shown in Figure 1 and summarized in Table 1. Based on the results it seems that all systems exhibited significant hexavalent chromium removal along with an appreciable COD removal. Average Cr(VI) effluent concentration ranged from 1 – 22 µg/L. Lower Cr(VI) removal was obtained in System A1 that received lower amount of substrate in the feed (COD in the feed water was 150 mg/L vs 200 mg/L in systems A2 and A3). On the other hand influent Cr(VI) groundwater concentration did not appear to limit hexavalent Cr removal in the 200 – 3000 µg/L range studied, since all systems receiving groundwater with a substrate concentration of 200 mg/L achieved complete Cr(VI) removal.

Table 1. Operating parameters and average performance results from the three experimental units

Parameter	System A1		System A2			System A3
		a	B	c	d	
HRT (d)	1.7	1.7	1.7	1.7	1.7	0.6
Sludge age (d)	10	10	10	10	10	10
Cr(VI) _{in} (mg/L)	200	200	800	1200	3000	200
NO ₃ -N _{in} (mg/L)	15	15	15	15	15	15
COD _{in} (mg/L)	150	200	200	200	200	200
MLSS (mg/L)	518	593	347	426	708	737
MLVSS/MLSS	0.83	0.7	0.7	0.74	0.65	0.90
TSS _{eff} (mg/L)	20	11	40	22	21	27
Cr(VI) _{eff} (µg/L)	22	5	3	< LOD*	< LOD*	< LOD*
Cr(VI) _{rem} (%)	89	98	>99	>99	>99	>99
COD ^{sol} _{eff} (mg/L)	10	8	23	7	7	35
COD ^{sol} _{rem} (%)	95	96	89	97	97	82
Tot-Cr _{eff} (µg/L)	38	25	239	60	99	62

*: LOD = 2,5 µg/L

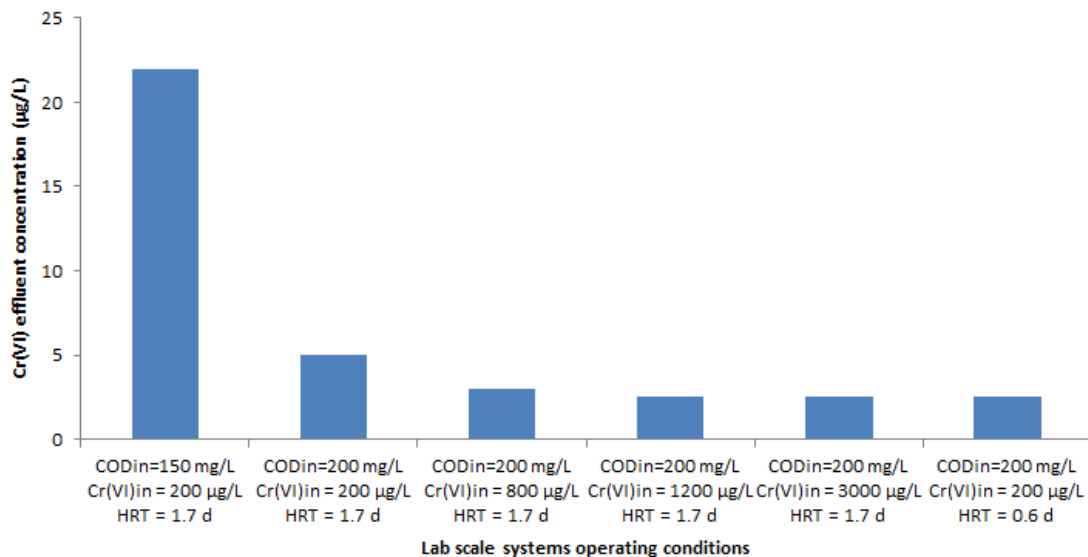


Figure 1: Average hexavalent chromium concentration in treated groundwater in the three anoxic – anaerobic experimental systems

Finally, as can be seen from Table 1, effluent total chromium concentrations in the order of 25-239 µg/L were recorded for all experimental systems. Based on the fact that in all bench scale units almost complete hexavalent chromium removal was achieved, effluent chromium is trivalent chromium mostly in a colloidal and particulate form which can be easily removed from treated water in a post-treatment stage (e.g. sand filter) as reported by Mamais *et al.*, (2013).

4. Conclusions

The objective of this study was to evaluate the ability of anoxic-anaerobic SBR systems to perform biological hexavalent chromium removal. Based on the results it is shown that an anoxic-anaerobic SBR system treating groundwater with hexavalent chromium concentrations as high as 3000 µg/L, can provide for complete hexavalent chromium removal when operating at a nitrate concentration of 15 mg/L, HRT of 1.7 d, a sludge age of 10 d and for temperatures greater than 20°C.

ACKNOWLEDGMENTS

This work was supported by the LIFE+ CHARM project (LIFE10 ENV/GR/000601).

REFERENCES

1. American Public Health Association (2005), Standard Methods for Examination of Waters and Wastewaters, 21st Ed., Washington D.C.
2. Caravelli H.A., Giannuzzi L., Zaritzky E.N. (2008), Reduction of hexavalent chromium by *Sphaerotilus natans* a filamentous micro – organism present in activated sludges. *Journal of Hazardous Materials* 156 , 214 - 222.
3. Contreras E.M., Ferro Orozco A.M., Zaritzky N.E. (2011), Biological Cr(VI) removal coupled with biomass growth, biomass decay, and multiple substrate limitation, *Water Research*. **45**, 3034–3046.
4. Camargo F.A.O., Okeke B.C., Bento F. M., Frankenberger W.T. (2005), Diversity of chromium-resistant bacteria isolated from soils contaminated with dichromate. *Applied soil ecology*, 29, 193-202.
5. Fruchter, J.S., Cole, C.R., Williams, M.D., Vermeul, V.R., Amonette, J.E., Szecsody, J.E., Istok, J.D., and Humphrey, M.D. (2000), "Creation of a subsurface permeable treatment barrier using in situ redox manipulation", *Groundwater Monitoring and Remediation Review*
6. Guertin J., Jacobs J.A., Avakian C. P. (2005), "Chromium (VI) Handbook", Independent Environmental Technical Evaluation Group (IETEG), CRC Press.
7. Mamais D., Noutsopoulos C. Kavallari I., Nyktari E. Kaldis A. (2013), Biological groundwater treatment for total and hexavalent chromium removal. *Proceedings of the 13th Conference on Environmental Science and Technology*, Athens, Greece, September 2013.
8. Hafiane, A., Lemordant, D., and Dhahbi, M. (2000), "Removal of Cr(VI) by nanofiltration, Desalination", 130, 305–312
9. Jacobs, J., Hardison, R.L., and Rouse, J.V. (2001), "In-situ remediation of heavy metals using sulfur-based treatment technologies", *Hydrovisions*, 10, 2, 1–4
10. Parga J.R., Cocke D.L., Valverde V., Gomes J.A.G., Kesmez M., Moreno H., Weir M., Mencer D. (2005), Characterization of electrocoagulation for removal of chromium and arsenic., *Chem. Eng. Technol.* 28 (5), 605–612.
11. Patterson, J.W. (1985), *Industrial Wastewater Treatment Technology*. Butterworth Publishers, Stoneham, MA.
12. Ren J., Li N., Zhao L. (2012), Adsorptive removal of Cr(VI) from water by anion exchanger based nanosized ferric oxyhydroxide hybrid adsorbent. *Chemical and Biochemical Engineering Quarterly*, 26 (2), 111-118.
13. Singh R., Kumar A., Kirrolia A., Kumar R., Yadav N., Bishnoi N., LohchabR. (2011), "Removal of sulphate, COD and Cr(VI) in simulated and real wastewater by sulphate reducing bacteria enrichment in small bioreactor and FTIR study", *Bioresource Technology* 102 , 677–682.
14. Wang Y.T. and Shen H. (1997), Modelling Cr(VI) reduction by pure bacteria cultures, *Water Res.* 31, 727-732.