Environ. Eng. Res. Vol. 10, No. 1, pp. 1~6, 2005
Korean Society of Environmental Engineers

WASTE LEAVES AS REACTIVE MEDIA IN PERMEABLE REACTIVE BARRIERS FOR Cr(VI) REMOVAL

Taeyoon Lee* **and Jae-Woo Park†**

*Construction Environment Research Department, 2311 Daehwa-Dong, ilsan-Gu, Goyang-Si, 411-712, Korea

Department of Civil Engineering, Hanyang University, 17 Haengdang-dong, Sungdong-gu, Seoul 133-791, Korea

(received June 2004, accepted January 2005)

Abstract : Hexavalent chromium in aqueous solutions was successfully removed via sorption and reduction in the presence of waste leaves. Cr(VI) removal followed a first-order reaction, and removal rates were proportional to the amount of waste leaves used in the tests. Most of Cr(VI) were removed via sorption in early stages of the tests, but the reduction reaction played a significant role in Cr(VI) removal later. Solution pHs were continuously decreased due to the microbial activity, which was induced from the microorganisms attached on waste leaves. The decreased solution pHs further enhanced the sorption and reduction of Cr(VI). To characterize the microorganisms found in the tests, a denaturing gradient gel electrophoresis (DGGE) method was used. The majority of microorganisms were composed of *Bacillus* sp. which can reduce Cr(VI). Thus, waste leaves can be effective reactive media for the treatment of Cr(VI) in the subsurface.

Key Words : Waste Leaves, Permeable Reactive Barriers, Hexavalent Chromium, Denaturing gradient del electrophoresis method, *Bacillus* sp.

INTRODUCTION

Permeable reactive barriers (PRBs) are a relatively new groundwater treatment technology. As a contaminant plume flows through a PRB, contaminants react with the media contained in the PRB, and are converted into less toxic or innocuous by-products. Effluent exiting a PRB is intended to meet groundwater quality requirements. The type of reactive medium used in a PRB depends on the contaminants in the plume. Zero-valent iron (Fe^0) has been used to treat chlorinated ethene compounds,[1~3] toxic heavy metals,[4~7] and chlorinated herbicides.[8,9]

Cr(VI) removal using zero-valent iron in PRBs has been known to be effective as the reaction rate is quite fast compared to other reactive media. However, long term effectiveness of PRBs is unclear due to the passivation of iron surfaces caused by reductive precipitation of Cr(VI) as shown in Eqs. (1) and (2).

$$CrO_4^{2-} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O \quad (1)$$

$$(1-x)Fe^{3+} + (x)Cr^{3+} + 2H_2O \rightarrow Fe_{(1-x)}Cr_xOOH_{(S)} + 3H^+ \quad (2)$$

† Corresponding author
E-mail: jaewoopark@hanyang.ac.kr
Tel: +82-32-860-7561, Fax: +82-32-865-1425

Considering the high cost of zero-valent iron and lack of longevity for Cr(VI) removal, a new reactive medium, which can replace zero-valent iron, is required to promote the use of PRBs for the Cr(VI) treatment. As a result, there has been a growing interest in using low-cost industrial byproducts, such as tire chips and fly ash, as the reactive media.[10,11] Therefore, the objective of this study was to assess the feasibility of using waste leaves as a low-cost reactive medium for PRBs used to treat groundwater contaminated with Cr(VI). Waste leaves generated at urban areas are normally collected and disposed as wastes in Korea, so use of waste leaves as a reactive medium is attractive in terms of sustainable development, and also allows the environment industry to accrue savings through reduced treatment costs.

MATERIALS AND METHODS

Materials

Potassium chromate (99% purity) was obtained from Aldrich Chemical Co. and used as received. Waste leaves were collected at Ewha Womans University campus, Korea. The samples were put in a glass jar without any pre-treatments, and then the sample was delivered to the laboratory. The waste leaves were cut into small pieces with diameters of between 1 mm to 3 mm. The water content of the sample was 20% by weight. The composition of the waste leaves is summarized in Table 1. Major components of the waste leaves were carbon, oxygen, and hydrogen.

Table 1. Elemental analysis of waste leaves

Elements	% by Weight
N	1.73±0.02
C	42.83±0.20
H	5.70±0.07
S	0.06±0.08
O	48.59±0.38

Methods

Batch Kinetic Tests

Batch kinetic tests were performed to evaluate the removal rate of Cr(VI) in the presence of different mass of waste leaves under a fixed initial Cr(VI) concentration of 40 mg/L and a temperature of 24°C. A designated amount of waste leaves was placed in each 30 mL centrifuge bottle containing Cr(VI) solution. Then, the bottle was tumbled at 50 rpm and centrifuged. Subsequently, the supernatant was collected and analyzed for Cr(VI) following U. S. EPA Method 7196.

Cr(VI) solutions with no waste leaves were used as controls to estimate losses. Final concentrations of these controls were used as the initial concentration of the mixtures to account for losses during the tests. One test was performed using autoclaved waste leaves to determine the effects of indigenous microorganisms on the Cr(VI) removal. All samples and controls were tumbled at 50 rpm and centrifuged to maintain procedural similarities.

Aqueous phase Cr(VI) was measured with the standard colorimetric 1,5-diphenylcarbazide method. The sample was filtered with 0.45μm syringe filter after centrifugation. Standards for calibration with the UV absorbance were prepared volumetrically from Cr(VI) stock solution. All calibration curves were based on three standards prepared over the range of expected concentrations. The removed mass of Cr(VI) was calculated from the differences in concentrations between aqueous solutions and controls.

An alkaline digestion procedure in U. S. EPA Method 3060A was used to extract the sorbed Cr(VI) on 2 g of waste leaves, in order to characterize the sorption of Cr(VI) on waste leaves. After extraction, the concentration was measured according to U. S. EPA Method 7196.

Microbial activity was evaluated by measuring ATP using the bioluminometer (New Horizons Diagnostics, Model 3550ib). The activity of all samples was measured after suspended particles had been allowed to settle for 5 min. The remaining solution was centrifuged at 8,000 rpm for 10 min., and then supernatant was used to measure the pH.

Characterization of Indigenous Microorganisms

To cultivate the indigenous microorganisms attached on waste leaves, one gram of waste leaves was placed in a 500 mL serum bottle containing 40 mg/L of Cr(VI) solution and the bottle was agitated at 50 rpm for 3 days at a temperature of 30°C. The cultured solution was diluted with autoclaved DI water to the factor of 10^{-10} and inoculated into Luria Bertani (LB) agar plates. Then, the plates were placed into a constant temperature bath fixed at 30°C for 24 hrs. The microorganisms cultured on LB agar plates were isolated based on their shape and color. The isolated microorganisms were transferred for 5 or 6 times to obtain purified microorganisms, which were then identified by analyzing 16S-rDNA sequencing.

RESULTS AND DISCUSSIONS

Batch Kinetic Tests

Removal Rate

Waste leaves effectively removed Cr(VI) as shown in Figure 1, except the one autoclaved before the test. A first-order decay model was used to determine apparent first-order removal rate for Cr(VI). The model is:

$$C_{aq}(t) = C_o \text{ Exp } (k \cdot t) \qquad (1)$$

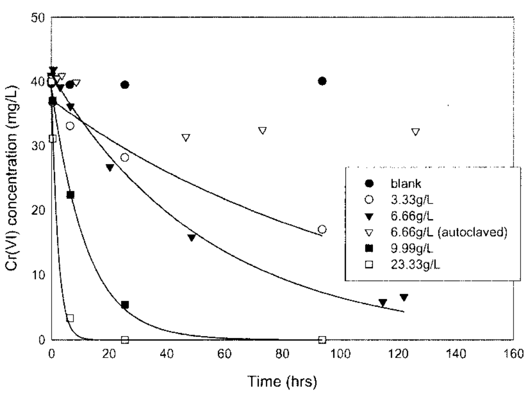

Figure 1. Removal of Cr(VI) in the presence of different mass of waste leaves. (Solid lines represent apparent first-order model fits.).

where C_{aq} is the concentration of Cr(VI) in a batch reactor at time t, C_o is the initial Cr(VI) concentration, k is a bulk first-order removal rate constant.

The removal rates were substantially increased as the amount of waste leaves increased. For example, Cr(VI) was completely removed within 20 hrs when 0.7 g of waste leaves was mixed with 30 mL of Cr(VI) solution at 40 mg/L whereas about 20 mg/L of Cr(VI) was still observed for 0.1 g of waste leaves until the end of the test.

Apparent first-order model fits were obtained from least-squares approximation and shown in Figure 1 as solid lines. The rate constants were proportional to the ratio of mass of waste leaves (g) and volume of Cr(VI) solution (L) as shown in Figure 2. The rate constants, however, increased 10 times greater when the ratio (Waste leaves/Cr(VI) solution) was more than 7 g/L than when it was less than 7 g/L.

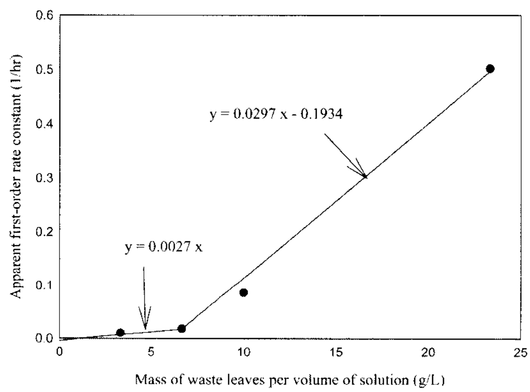

Figure 2. Apparent first-order rate constants for Cr(VI) as a function of mass of waste leaves used in the batch experiments.

Effect of Sorption on Cr(VI) Removal

The mass of Cr(VI) removed continually increased with time, but the sorbed mass of Cr(VI) remained constant (Figure 3(a)). While 58% of Cr(VI) was removed via sorption within 3 hrs (Figure 3(b)), the contribution of sorption to the overall removal of Cr(VI) after 20 hrs was less than 6%. Therefore, the sorption is not the major reaction of Cr(VI) removal by waste

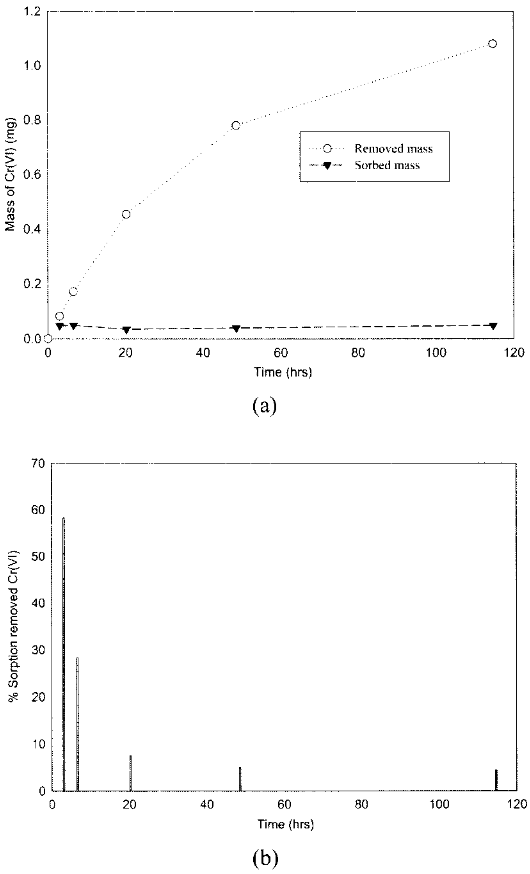

Figure 3. Change in Cr(VI) : (a) removal and sorbed mass ; (b) kinetics of removal fraction.

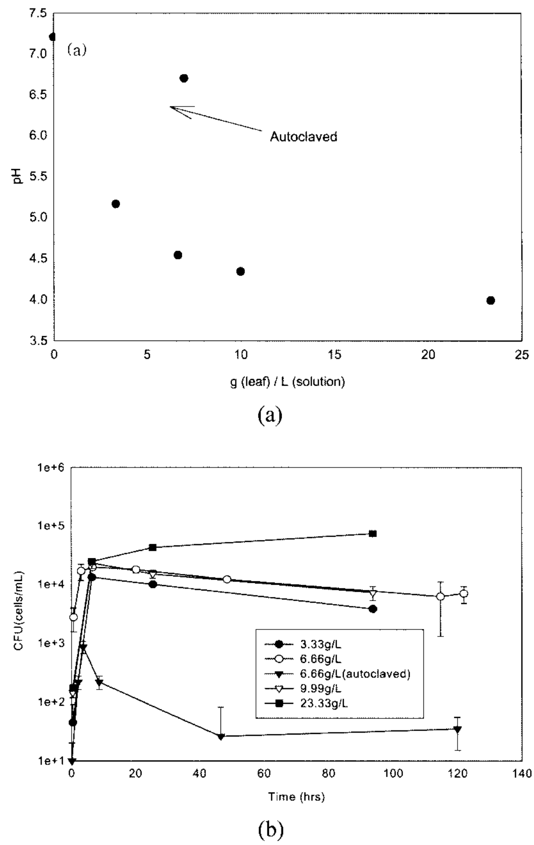

Figure 4. pH and CFU changes during the batch test. : (a) pH ; (b) CFU.

leaves. One possibility for the major removal mechanism can be the reduction induced by chemical or microbial activity. In these cases, waste leaves act as electron donor and Cr(VI) acts as electron acceptor as reported by Cimino et al. (2000).

Solution pH and Microbial Activity

Equilibrium pHs from the tests gradually decreased as more waste leaves were used (Figure 4(a)). On the contrary, the decrease in equilibrium pH for the test containing autoclaved waste leaves was relatively smaller than those for the others. The pHs for the control without the leaves remained constant during the entire period.

Microbial activities in colony forming unit (CFU) are shown in Figure 4(b). In general, the CFUs rapidly increased within 10 hrs, and then slightly decreased or increased. The test containing autoclaved waste leaves showed the lowest CFU due to the inhibition of microbial activity. In general, the CFUs were proportional to the mass of waste leaves used, and inversely proportional to the equilibrium solution pHs.

Solution pH played an important role for the reduction and sorption of Cr(VI) on a biosorbent (soya cake).[12] At pH less than 3, a reduction reaction play an important role for Cr(VI) removal. In the range of pH between 3.0 and 5.0, the overall removal efficiency for total Cr and Cr(VI) was decreased, and both sorption and reduction reactions were responsible for the removal reactions. For pH over 5.0, the removal of total Cr and Cr(VI) was negligible due to negligible reduction process of Cr(VI) and few active site protonation.[13] Thus, the Cr(VI) re-

Table 2. Microorganisms from two different colonies (Strain A and B) for the tests containing waste leaves using clone library method

Colony	Microorganism	Average sequence similarity (%)
Strain A	Exiguobacterium acetylicum	99
	B.acetylicum (NCIMB 9889)	99
	Glacial ice bacterium SB12K-2-2	99
	Exiguobacterium ssp.	98
	Exiguobacterium sp. LP15	98
Strain B	Uncultured soil bacterium clone 431-1	97
	Enterobacter aerogenes	97
	Enterobacter asburiae	97
	Uncultured gamma proteobacterium clone ccslm2118	97
	Enterobacterium EA61	97

moval in this research could be induced from both reduction and sorption because the equilibrium pHs were mostly in the range of pH 3 and 5.

Identifications of Microorganisms

Two kinds of microorganisms were isolated from the cultured sample. These microorganisms were named as strain A and B. The strain A and B were identified by analyzing partial 16S-rDNA using a clone library method. Microorganisms identified from the cultured solution are summarized in Table 2. The strain A and B contained Exiguobacterial acetylicum in Bacillaceae species and Enterobacter asburiae in Entrobacteriaceae species, respectively. The Bacillaceae sp. found in strain A were known Cr(VI) reducing bacteria.[14)]

CONCLUSIONS

Waste leaves were found to be effective media for the Cr(VI) removal via microbial reduction and sorption reactions where waste leaves acted as substrates for the growth of indigenous microorganisms and provided sorption sites for Cr(VI). In this study, microorganisms attached on waste leaves contained Bacillaceae sp., which are known Cr(VI) reducing bacteria, acted major role of Cr(VI) removal. On the contrary, sorption of Cr(VI) on waste leaves was not significant compared to the reduction of Cr(VI) by indigenous microorganisms. Therefore, using waste leaves instead of expensive reactive media such as zero-valent iron in PRBs could be beneficial because material cost could be significantly reduced and valuable landfill space for waste leaves could be saved.

Further research is required to clarify the exact mechanisms of Cr(VI) reduction that are induced from direct reduction of Cr(VI) by oxidation of waste leaves or microbial reduction of Cr(VI) by *Bacillus* sp. found in this research.

REFERENCES

1. Arnold, W. and Roberts, A., "Pathways of chlorinated ethene and chlorinated acetylene reaction with Zn(0)," *Environ. Sci. Technol.*, **32**(19), 3017-3025 (1998).
2. Blowes, D., Ptacek, C., Cherry, J., Gillham, R., and Robertson, W., "Passive remediation of groundwater using In situ treatment curtains," *Geoenvironment 2000: Characterization, Containment, Remediation, and Performance in Environmental Geotechnics (2)*, Daniel, D. and Acar, Y. (Eds.), ASCE, GSP 46, 1588-1607 (1995).
3. Roberts, A., Totten, L., Arnold, W., Burris, D., and Campbell, T., "Reductive elimination of chlorinated ethylenes by zero-valent metals," *Environ. Sci. Technol.*, **30**(8), 2654-2659 (1996).
4. Benner, S., Blowes, D., and Ptacek, C., "A full-scale porous reactive wall for prevention of acid mine drainage," *Ground Water*

Monitoring and Remediation, **17**(3), 99-107 (1997).
5. Francis, A. and Dodge, C., "Remediation of soils and wastes contaminated with uranium and toxic metals," *Environ. Sci. Technol.*, **32**(24), 3923-3998 (1998).
6. Shokes, T. and Möller, G., "Removal of dissolved heavy metals from acid rock drainage using iron metal," *Environ. Sci. Technol.*, **33**(2), 282-287 (1999).
7. Su, C. and Puls, R., "Arsenate and Arsenite removal by zero-valent iron: kinetics, redox transformation, and implications for in situ groundwater remediation," *Environ. Sci. Technol.*, **35**(7), 1487-1492 (2001).
8. Eykholt, G. and Davenport, D., "Dechlorination of the chloroacetanilide herbicides alachlor and metolachlor by iron metal," *Environ. Sci. Technol.*, **32**(10), 1482-1487 (1998).
9. Koppensteiner, B., "The degradation of the herbicides alachlor and metolachlor by iron metal in water and soil systems," *M.S. Thesis*, Dept. of Civil and Environmental Engineering, University of Wisconsin-Madison (1998).
10. Bailey, S., Olin, T., Bricka, M., and Adrian, D., "A review of potentially low-cost sorbents for heavy metals," *Water Res.*, **33**(11), 2469-2479 (1999).
11. Kim, J., "Retardation of volatile organic compound movement in landfills using scraptires," *Ph.D Dissertation*, Department of Civil and Environmental Engineering, University of Wisconsin-Madison (1996).
12. Daneshvar, N., Salari, D., and Aber, S., "Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake," *J. Hazard. Mater.*, B94, 49-61 (2002).
13. Wang, Y. and Xiao, C., "Factors affecting hexavalent chromium reduction in pure cultures of bacteria," *Water Res.*, **29**(11), 2467-2474 (1995).
14. Giuseppe, C., Amedeo, P., and Giovanni, T.," Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell," *Water Res.*, **34**(11), 2955-2962 (2000).