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Innovative Approaches to Increase the Longevity of PRBs Containing Zero-Valent Iron

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요약문

The removal capacity of zero-valent iron for Cr(VI) was evaluated using batch kinetic tests. The rate constants for zero-valent iron dramatically increased as initial Cr(VI) concentration decreased. Generally, the reaction rates of Cr(VI) with zero-valent iron were faster than that of a biotic degradation of Cr(VI), and furthermore the reaction rates were inversely proportional to the initial Cr(VI) concentrations. After certain reaction time elapsed. no further decrease of Cr(VI) was observed, indicating a loss of iron reactivity. The loss of iron reactivity was primarily due to the passivation of iron surfaces with iron-Cr precipitates, but the reactivity of iron was recovered by adding iron-reducing bacteria. Even though the addition of bacteria itself removed Cr(VI), the combination of iron-reducing bactera and oxidized iron significantly enhanced the reaction rate for Cr(VI) removal. The results from column tests also confirmed that the innoculation of iron-reducing bacteria to the column containing completely oxidized iron partially enhanced the recovery of the iron reactivity.

Keywords: Cr(VI), passivation, iron-reducing bacteria, dry leaves, rate constant

1. Introduction

Among various remediation technologies, permeable reactive barriers (PRBs) technology become popular because of its simplicity for construction and wide applicability to various groundwater contaminants including chlorinated solvents and heavy metals (Blowes et al. 1995, Benner et al. 1997).

Among many toxic compounds possibly presented in groundwater, Cr(VI) was tested to determine its reaction characteristics with zerovalent iron, which has been used as a popular reactive medium in PRBs.

Cr(VI) removal using zero-valent iron has been widely known to be effective for the remediation of groundwater contaminated with Cr(VI) because the reaction rate is quite fast compared to other reactive media. In other words, zero-valent iron is easily oxidized when it contacts with groundwater containing Cr(VI). The oxidized iron surfaces lose thier reactivity due to the insulation of electron transfer between iron surfaces and Cr(VI) in solution. The general reaction for the Cr(VI) removal using zero-valent iron is explained by the following reaction:

$2Feo(s)+2H2CrO4+3H2O \rightarrow 3(Cr0.67Fe0.33)(OH)3(S)+FeOOH(S)$

Also, biotic methods using Cr(VI) reducing bacteria have been used in the wastewater treatment. However, this method require two separate procedures. For example, the Cr(VI) in solution is first reduced to Cr(III) by the biotic reaction and pH is increased by adding sodium hydroxide to form $Cr(OH)_3$ that is sparingly soluble. On the contrary, PRBs containing iron can reduce Cr(VI) to Cr(III) and subsequently make forms of Cr-Fe precipitates. However, long term effectiveness of PRBs is quite unclear due to the passivation of iron surfaces caused by a reductive precipitation of Cr(VI). A new approach to increase the reaction rate of iron and recover the reaction capacity of completely oxidized iron was initiated in this study.

2. Materials and Methods

(1) Materials

Zero-valent iron particles were obtained from Pohang Iron and Steel Co. The mean particle size was 0.6 mm and the specific surface area was 0.7 m^2/g. Potassium dichromate (99% purity) was obtained from Aldrich Chemical Co. Inc.

(2) Methods

Batch kinetic tests were performed to evaluate the rate constant of Cr(VI) in the presence of iron particles under different initial Cr(VI) concentrations. A 2g of iron was placed in each 30 mL centrifuge bottle containing Cr(VI) solution. Then, the bottles were tumbled at the speed of 50 rpm and sampled at the designated sampling time. After centrifuging the bottle, the supernatant was collected and analyzed using U.S.EPA Method 7196.

Another test was also conducted to determine the removal capacity of iron for Cr(VI). A 10g of iron was placed in a 1,000 mL volumetric flask containing 100 mg/L of Cr(VI). A stirring bar was used to mix the iron particles and soluion. The concentration was periodically measured, and the removal capacity was calculated based on the difference between the initial and final concentrations. After the capacity test, the oxidized iron was collected and dried in a dessicator filled with N_2 for 24 hrs. The dried iron particles were reused in the batch kinetic tests employing iron-reducing bacteria to determine whether the bacteria could recover the reactivity of iron, which was inactivated by Cr(VI).

Glass columns (60cm in length x 5cm in diameter) were used to simulate the removal of Cr(VI) in PRBs. Three lateral sampling ports were installed at 15, 30, and 45 cm from the inlet of the column. The reactive media (80% sand + 20% iron by weight) were tamped into a column in three layers to a dry density expected under field placement conditions.

3. Results and Discussion

The rate constants seem to depend on the initial Cr(VI) concentration (Fig. 1).
When the initial concentration is less than 20 mg/L, the rate constant dramatically increases. Thus, for the convenience of the tests, the following tests (i.e., bio-enhanced, capacity, and column tests) use 40 mg/L of Cr(VI) as the initial or influent concentration.

The removal capacity of the iron is 11,400 mg Cr(VI)/kg Iron (not shown).
Fig. 2 illustrates the dramatic effect of innoculation of iron-reducing bacteria. The rate of

Cr(VI) removal is apparently increased. For comparison, results of two other tests using only oxidized iron or iron-reducing bacteria are included in Fig. 2. The Cr(VI) concentrations with oxidized iron are slightly decreased over the testing period. the newly formed iron surfaces produced by friction between iron particles may enhance the Cr(VI) removal. Furthermore, the iron-reducing bacteria is found to be effective for the removal of Cr(VI) with the first-order rate constant of 0.027/hr, which is 9 and 19 times slower than that for pure zero-valent iron and for oxidized iron innoculated with iron-reducing bacteria.

Therefore, the addition of iron-reducing bacteria could recover the reactivity of iron, which may increase the longevity of PRBs installed in subsurface.

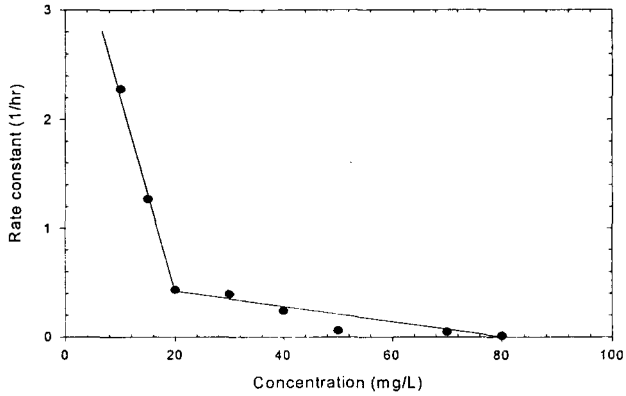

Fig. 1. Rate Constants of Cr(VI) Removal Using Zero-Valent Iron

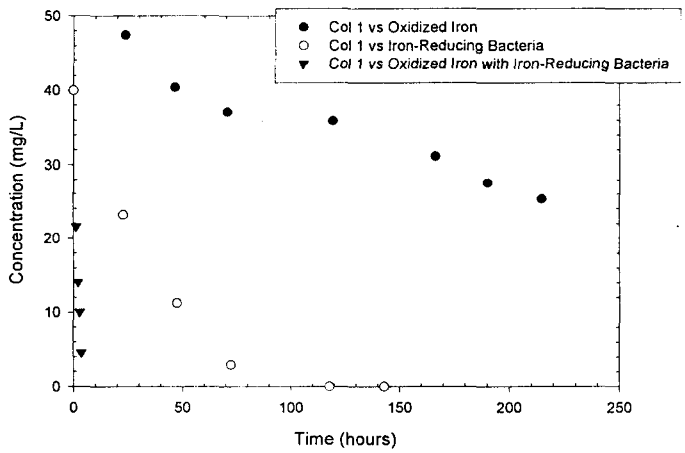

Fig. 2. Concentrations of Cr(VI) When Oxidized Iron, Iron-Reducing Bacteria, and Combination of Oxidized Iron and Iron-Reducing Bacteria were Used.

4. References

1) Blowes, D., Ptacek, C., Cherry, J., Gillham, R., and Robertson, W. (1995), "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.

2) Benner, S., Blowes, D., and Ptacek, C. (1997), "A Full-Scale Porous Reactive Wall for Prevention of Acid Mine Drainage," *Ground Water Monitoring and Remediation*, 17(3), 99-107.