Capacity of Cr(VI) reduction in an aqueous solution using different sources of zerovalent irons

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Abstract–Zerovalent iron (ZVI) has drawn intense interest as an effective and inexpensive tool to enhance degradation of various environmental contaminants. Reduction of Cr(VI) to Cr(III) by ZVI merits environmental concern as a hazardous species is transformed into a non-hazardous one. Objectives of this research were to assess kinetics and capacity of Cr(VI) reduction by different sources of ZVIs, of which chemical parameters can base *in situ* application of ZVI to treat Cr(VI) contaminated water. Reduction kinetics were first-order and rapid showing that 50% of the initial Cr(VI) was reduced within 7.0 to 347 min depending on Cr(VI) concentration, temperature and ZVI source. The reduction rates were increased with decreasing the initial Cr(VI) concentrations and increasing the reaction temperatures. The J ZVI (Shinyo Pure Chemical Co., Japan) was more effective in Cr(VI) reduction than PU (Peerless Metal Powders, USA). The maximum reduction capacities of J and PU ZVIs at 25 °C were 0.045 and 0.042 mmol g^{-1} Fe^0, respectively. A relatively higher value of the net reaction energy (E_a) indicated that Cr(VI) reduction by ZVI was temperature dependent and controlled by surface properties of ZVI. Chemical parameters involved in the Cr(VI) reduction by ZVI such as temperature quotient, kinetic rates, and stoichiometry indicated that the ZVI might be effective for *in situ* treatment of the Cr(VI) containing wastewater.

Key words: Cr(VI) Reduction, Zerovalent Iron, First-order Kinetics, Reduction Capacity

INTRODUCTION

Environmental contamination by toxic metals is well recognized to be detrimental to living organisms. Among the toxic metals in the environment, Cr was ranked as the second in the occurrence frequencies at Department of Energy (DOE) sites in the USA and thus classified as a primary pollutant [Sparks, 1995; Lee et al., 2003]. Chromium has been widely used in various industrial processes in Korea, ultimately making its way into soils and waters through spills or waste landfill [Fendorf and Li, 1998; Yang et al., 2000]. It exists mainly as Cr(III) or Cr(VI) depending on oxidation-reduction states, and the Cr(VI) is generally more soluble, mobile and toxic than Cr(III) in environment [Lee et al., 2003]. Thus, it is crucial to assess the oxidation state of Cr in the environment and the mechanism of Cr reduction so as to develop a strategy for the remediation of the Cr-contaminated areas [Lee et al., 2000, 2002].

Precipitation, ion exchange and sorption are the most widely accepted techniques to remediate the Cr containing wastewater, but these methods have some limitations in economic and environmental aspects. For example, the precipitation method generally requires expensive equipment or reagents and generates significant amounts of the metal-containing sludge after completion of the process, which needs a further treatment. The use of the activated carbon in the wastewater treatment is relatively expensive despite its high sorption capacity of Cr [Babel and Kurniawan, 2003; Ok et al., 2003]. It is thus necessary to develop a technique that is economically viable and environmentally beneficial to treat the Cr(VI) containing wastewater.

Zerovalent iron (ZVI, Fe^0) has been used to treat soil and water contaminated with various organic and inorganic contaminants [Hernandez et al., 2004; Song et al., 2005; Ponders et al., 2000; Yang et al., 2006]. Iron exists as three oxidation states in the environment: 0, +2, and +3. The oxidation process of iron from Fe^0 to Fe^{2+} is thermodynamically stable ($Fe^{2+}+2e^- \rightarrow Fe^0$, Eh=−0.44 V). The negative sign of the oxidation-reduction potential (Eh) means the oxidation reaction is favorable. The ZVI is, thus, easy to oxidize to Fe^{2+} and Fe^{3+}, and contaminants having higher Eh values than −0.44 V in water under aerobic condition can be effectively reduced upon contacting with the ZVI [Losi et al., 1994; Blowes et al., 1997; EPA, 1998].

Reduction of Cr(VI) to Cr(III) is environmentally beneficial as the latter species is not toxic to most living organisms and also has a low mobility and bioavailability [Fendorf and Li, 1996]. Despite the importance of this redox reaction, few equilibrium parameters, which can determine the kinetic rate of Cr(VI) reduction and the optimum reaction condition, are available for the practical use of ZVI. Biogeochemistry of Cr(VI) in the aqueous solution is highly dependent on kinetics such as aqueous phase mass transfer [Choi and Kim, 2005] and chemical factors such as pH [Prakorn et al., 2004]. For example, Song et al. [2005] stated that natural decay of Cr(VI) was fitted to the zero-ordered reaction, but Cr(VI) adsorption on sand and reduction by ZVI were followed by first-order kinetics.

The mechanism of contaminant reduction by the ZVI is proposed as three probable ways: direct reduction at the surface of Fe^0, a further reduction by ferrous iron (Fe^{2+}) and reduction by H_2 orig-

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Table 1. Properties of zerovalent irons (ZVIs) used in the experiment

ZVI	Effective particle size μm	Bulk density g cm^{-3}	Particle density g cm^{-3}	Surface area m^2 g^{-1}	Sources
J	196.46	2.15	7.07	0.065	Shinyo Pure Chemical Co., Japan
PU	195.37	2.43	7.15	0.055	Peerless Metal Powders Co., Detroit, MI, USA

inating from Fe^0 oxidation in water [EPA, 1998]. Although ZVI is an inexpensive and widely available material to promote the degradation of contaminants, its efficiency varies with chemical and morphological properties of the ZVI [Comfort et al., 2003; Park et al., 2004]. However, many reaction parameters related to Cr(VI) reduction using ZVI, such as type of iron, stoichiometry (reduction mass capacity) and rates, are not yet clearly quantified. These characteristics can be useful for *in situ* application of the ZVI technology to the treatment of the redox-sensitive metal in wastewater.

Objectives of this research were to assess the kinetics of Cr(VI) reduction by the different sources of the ZVI, the maximum capacity of the ZVI in the Cr(VI) reduction and the optimum conditions for the reaction.

MATERIALS AND METHODS

1. Materials

Two types of the commercially available ZVIs were used in this experiment: J ZVI by the Shinyo Pure Chemical Co., Japan and PU ZVI by the Peerless Metal Powders Co., USA (Table 1). The particle sizes of the experimental ZVIs were measured by using the Mastersizer 2000 (Malvern Instrument Co.) and the particle density of ZVI was determined on a helium gas pycnometer (Micromeritics Instrument Co.). Core method was used to measure the bulk density of ZVI. The specific surface area of ZVI was determined by the LASER granulometric method using the Coulter LS-230 instrument. All the measurements were at least performed in triplicate. In a previous study, Yang et al. [2005] showed that J and PU among the commercial ZVIs screened were effective in reducing Cr(VI) to Cr(III) in an aqueous solution. Table 1 shows the properties of the ZVIs used in this experiment.

2. Kinetics of Cr(VI) Reduction: Concentration and Temperature Effects

Kinetics of Cr(VI) reduction by ZVI were determined by batch experiments. Initial Cr(VI) concentrations were 1, 3, and 5 mM Cr(VI) as Na_2CrO_4 and ratios of ZVI were adjusted to 5% (w/v). The mixed solution was shaken at 150 rpm in the reciprocal shaker at 15, 25, and 35 °C. All of the reagents used were the ACS grade. A constant ionic strength was maintained by using 0.1 M NaCl electrolyte during the experiment [Fendorf and Li, 1996]. The initial solution pH was adjusted to pH 3 and pH change was measured with a pH meter (Corning, USA). At each time interval, samples were taken by a needle-less syringe, filtered through a 0.2 μm syringe filter and measured for Cr(VI) concentration by the diphenylcarbazide colorimetric method [Bartlett and James, 1996]. Kinetic models were employed to determine the kinetic parameters such as the kinetic order, rate constant, and rate curve [Sparks, 1995].

3. Reduction Capacity of Cr(VI)

Rate of Cr(VI) reduction by ZVI was measured by adding 5% (w/v) ZVI to the aqueous solutions having the initial Cr(VI) con-

centrations from 1 to 7 mM. Reaction temperatures were maintained at 15, 25, and 35 °C. Reduction capacity of Cr(VI) reduction by ZVI was calculated by using an equation proposed by Holan et al. [1993], and the maximum reduction quantity (q_{max}) was obtained from the b value as shown in the following Eq. (1) [Lee et al., 2000].

$$q=kC_e b/(1+kC_e) \tag{1}$$

q　: mass of reduced Cr(VI) per unit weight of ZVI [mmol g^{-1}]
C_e　: equilibrium concentration of Cr(VI) [mmol L^{-1}]
b　: maximum reducible concentration of Cr(VI) [q_{max}: mmol g^{-1}]
k　: constant related to binding strength

RESULTS AND DISCUSSION

1. Rate of Cr(VI) Reduction by ZVI

Fig. 1 shows the rate of Cr(VI) reduction by two ZVIs as influenced by the initial Cr(VI) concentration and time under batch ex-
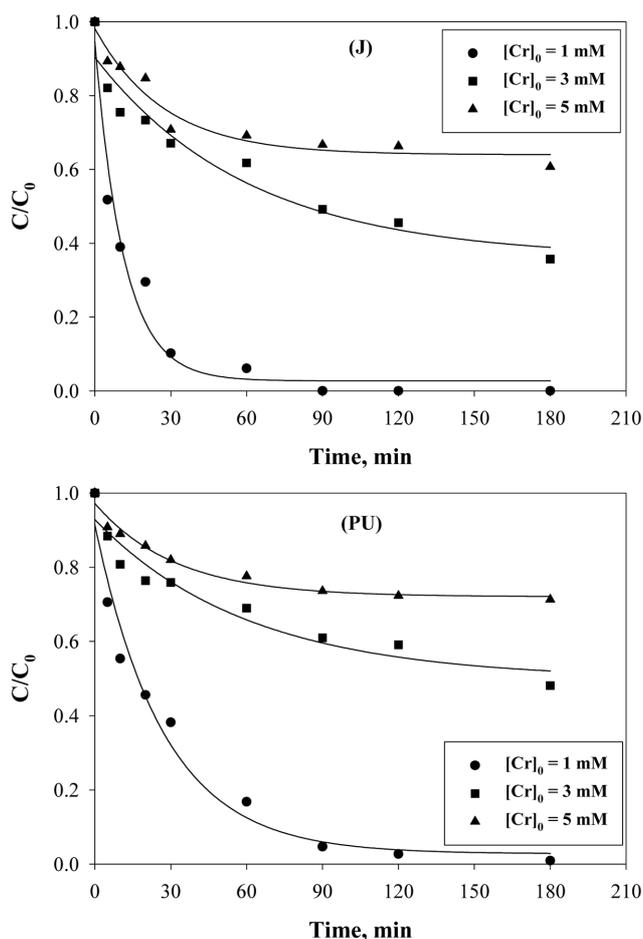

Fig. 1. Effect of the initial Cr(VI) concentrations and the reaction time on the Cr(VI) reduction by J and PU ZVIs.

Table 2. The rate curves of the first order kinetic models for the Cr(VI) reduction by the ZVI at different initial Cr(VI) concentrations

ZVIs	Cr(VI) concentration mM	Rate curve equations[a]	r^2	$t_{1/2}$[b] min
J	1	$\ln(C/C_0) = -45.0 \ast 10^{-03} t - 0.38$	0.90***	7.0
	3	$\ln(C/C_0) = -5.1 \ast 10^{-03} t - 0.18$	0.94***	101.5
	5	$\ln(C/C_0) = -2.4 \ast 10^{-03} t - 0.13$	0.76**	233.7
PU	1	$\ln(C/C_0) = -26.6 \ast 10^{-03} t - 0.24$	0.98***	17.0
	3	$\ln(C/C_0) = -3.5 \ast 10^{-03} t - 0.13$	0.92***	159.6
	5	$\ln(C/C_0) = -1.7 \ast 10^{-03} t - 0.10$	0.79**	347.3

[a]t: time (minute)
[b]$t_{1/2}$: time required to reduce a half of Cr(VI)
** and ***: significant at P<0.01 and P<0.001, respectively

perimental condition. The relative rates of Cr(VI) reduction by the J ZVI were faster than those by the PU ZVI at the same Cr(VI) concentration. When the initial Cr(VI) concentration was 1 mM, all of the Cr(VI) was reduced to Cr(III) within 3 hours. At the initial Cr(VI) concentration of 3 mM, half of the Cr(VI) reduced within 101 to 160 minutes depending on the ZVI source (Table 2). However, the Cr(VI) reduction efficiency was reduced as the initial Cr(VI) concentration increased up to 5 mM. Similarly, Lee et al. [2003] reported that the Cr(VI) removal rate by the iron waste was dependent upon the initial Cr(VI) concentration in an aqueous solution.

The embedded model fittings of the curves in Fig. 1 indicate that
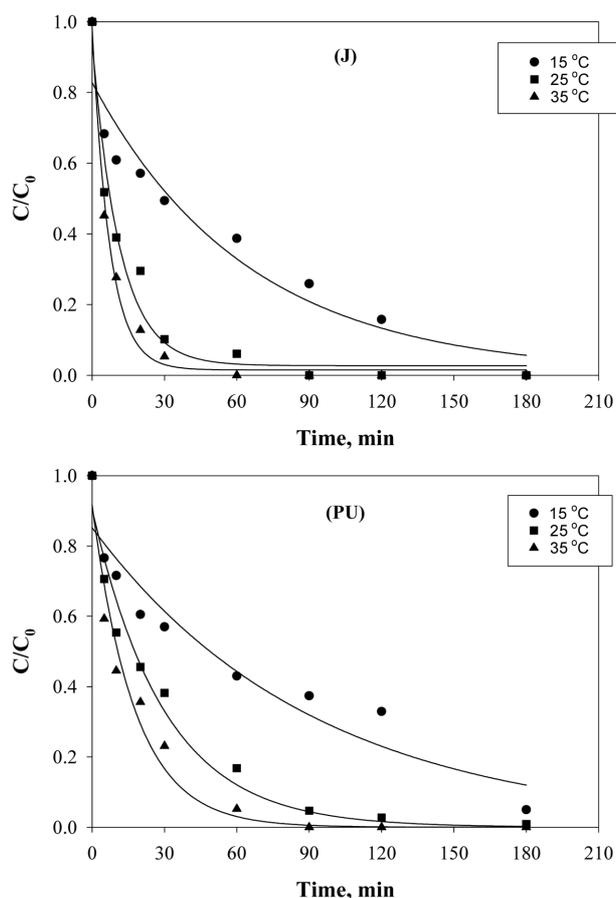
Fig. 2. Effect of temperature on the Cr(VI) reduction by J and PU ZVIs.

the Cr(VI) reduction by ZVI followed a first-order kinetic model. Among the kinetic models, the first-order kinetic model was the best fit based on the highest coefficient of determination (r^2) and lowest standard error [Yang and Skogley, 1992]. The first-order rate constants for all the tests are listed in Table 2. Reductions of the Cr(VI) by the J and PU ZVIs were temperature-dependent showing a higher reduction rate at higher temperature (Fig. 2). The proportional increase of Cr(VI) reduction with temperate demonstrated that Cr(VI) reduction was thermodynamically favorable [Yang and Skogley, 1992; Sparks, 1995].

2. Net Reaction Energy and Capacity of Cr(VI) Reduction

Changes in rate constants with 10 °C rise in temperature (temperature quotient: Q_{10}) are shown in Table 3. The Q_{10} values of the J ZVI were greater than those of the PU ZVI, but all the values were greater than 1. Salisbury and Ross [1992] indicated that most chemical reactions had Q_{10} values between 2 and 3, while physical processes such as diffusion have Q_{10} slightly greater than 1. Comparison between Q_{10}-I and Q_{10}-II values can provide the relative temperature effects on the reaction rates. The Q_{10}-I value was greater than Q_{10}-II for all cases indicating that the reduction of Cr(VI) by ZVI might not be necessary to increase the temperature higher than 25 °C.

The net reaction energy, E_a, measuring the force to be overcome during the reaction, was 73 and 45 kJ mol^{-1} for J and PU, respectively. The magnitude of E_a, besides providing the temperature dependency of the reaction rate, offers a clue regarding the reaction mechanism [Yang and Skogley, 1992]. Surface-controlled reactions have higher E_a values than do diffusion-controlled reactions [Lasaga, 1983]. The relatively high values of E_a indicated that Cr(VI) reduction was mainly surface-controlled reaction. Salisbury and Ross [1992] reported that reactions having greater Q_{10} values have a higher activation energy.

The water quality standard of wastewater for Cr^{6+} is 0.50 mg L^{-1} in Korea [Yang et al., 2000]. Provided that an industrial wastewater contains 50 mg L^{-1} of Cr(VI) and is subject to the kinetic equilib-

Table 3. Effect of temperature on the net reaction energy (E_a) and Q_{10} values for the Cr(VI) reduction by the J and PU ZVIs

ZVIs	E_a (kJ mol^{-1})	Q_{10}-I ($=k_{25}/k_{15}$)[a]	Q_{10}-II ($=k_{35}/k_{25}$)
J	72.90	3.46	2.07
PU	45.44	1.97	1.74

[a]k is the rate constant for Cr(VI) reduction at each temperature
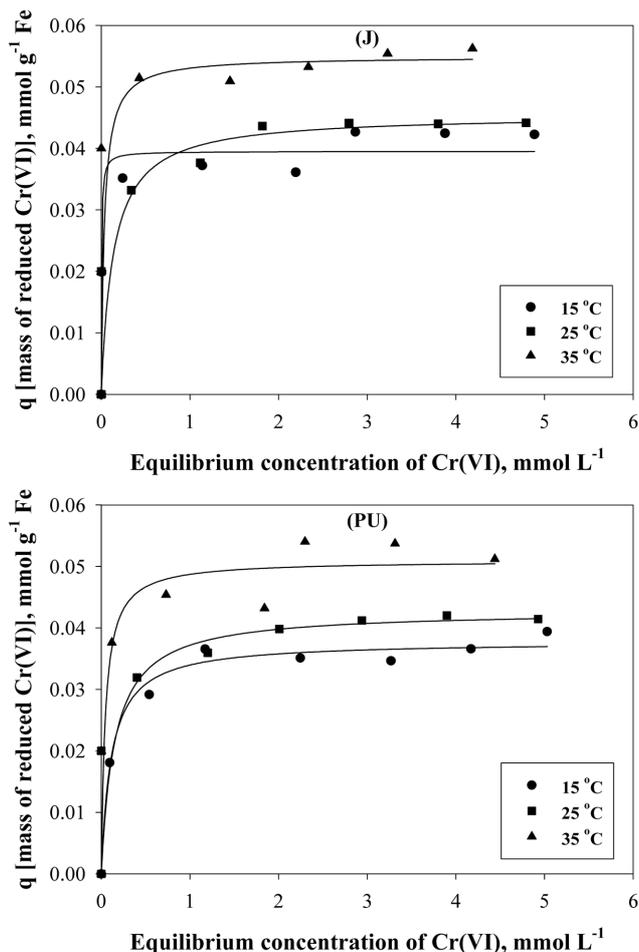
Fig. 3. The isotherm model for the Cr(VI) reduction by J and PU ZVIs at different temperatures.

Table 4. Langmuir equations of the Cr(VI) reduction by J and PU ZVIs at different temperatures

ZVI	Temperature (°C)	Regression equations[a]	q_{max}	r^2
J	15	$C_e/q = 23.51\, C_e + 1.88$	0.043	0.99***
	25	$C_e/q = 22.38\, C_e + 1.47$	0.045	0.99***
	35	$C_e/q = 17.93\, C_e + 0.60$	0.056	0.99***
PU	15	$C_e/q = 26.04\, C_e + 3.21$	0.038	0.99***
	25	$C_e/q = 23.73\, C_e + 1.81$	0.042	0.99***
	35	$C_e/q = 19.12\, C_e + 1.15$	0.052	0.99***

[a]Refer to Eq. (1) for the parameters
***: significant at $P < 0.001$

tures (Table 5). The overall results suggest ZVI might be a useful tool for remediation of wastewater containing Cr(VI) based on the kinetics, mechanisms and stoichiometric parameters.

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rium parameters obtained in this experiment, it will take only 2.5 hours to remove the Cr(VI) in the wastewater below the regulatory level with the operating conditions of 5% J ZVI at pH 3 in an ambient temperature.

The capacity of ZVIs for Cr(VI) reduction was temperature dependent (Fig. 3 and Table 4), and the patterns were fitted to the Langmuir-type model. Reduction capacities of J and PU ZVIs were increased as increasing the reaction temperature. The maximum reduction capacities of J and PU ZVIs at 35 °C were 0.056 and 0.052 mmol g^{-1} Fe^0, respectively. Removal capacities of the J ZVI were relatively higher than those of various adsorbents such as sawdust, diatomite, bentonite and iron(III) hydroxide reported in the litera-

Table 5. Removal capacities (mg g^{-1}) of the miscellaneous adsorbents for Cr^{6+}

Materials	Capacities mg g^{-1}	Source properties	References
Chabazite	3.60	Natural zeolite	Ouki and Kavannagh, 1997
ZVI	2.50	Untreated (air-dried)	This study
Sawdust	2.29	Pyrolysis	Hamadi et al., 2001
Diatomite	1.68	Treated with microemulsion	Dantas et al., 2001
Bentonite	0.57	Sieved through 250 mesh	Khan et al., 1995
Iron(III) hydroxide	0.47	Waste from fertilizer industry	Namasivayam and Ranganathan, 1993

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