

A Simple Mathematical Analysis on the Effect of Sand in Cr(VI) Reduction using Zero Valent Iron

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(Received 28 June 2004 • accepted 23 November 2004)

Abstract—A simple mathematical model was proposed to analyze the enhancement of Cr(VI) reduction when sand materials are added to the zero valent iron (ZVI). Natural decay of Cr(VI) in a control experiment was analyzed by using a zero-order decay reaction. Adsorption kinetics of Cr(VI) to sand was modeled as a first-order reversible process, and the reduction rate by ZVI was treated as a first-order reaction. Natural decay of Cr(VI) was also included in other experiments, i.e., the adsorption to sand, the reduction by ZVI, and both adsorption and reduction when sand and ZVI are present together. The model parameters were estimated by fitting the solution of each model to the corresponding experimental data. To observe the effect of sand addition to ZVI, both adsorption and reduction rate models were considered simultaneously including the natural decay. The solution of the combined model was fitted to the experimental data to determine the first-order adsorption and reduction rate constants when sand as well as ZVI is present. The first-order reduction rate constant in the presence of sand was about 35 times higher than that with ZVI only.

Key words: Zero Valent Iron (ZVI), Cr(VI) Reduction, Adsorption Rate, Reduction Rate, Effect of Sand

INTRODUCTION

Recently, permeable reactive barrier (PRB) technologies have been studied as a means of remediating contaminated groundwater. Media for the PRBs are mainly zero valent iron (ZVI), organo-clays, natural zeolites etc. PRB technology is a promising environmental remediation technology with the merits of relatively low operating costs, long-term usage, treatment of chlorinated toxic compounds and various heavy metals, etc., and is currently being used in the United States [Mcnab and Ruiz, 2000; Vogan et al., 1999; Ludwig et al., 2002]. Among the barrier media, ZVI is being used most widely. Many works have been reported on the reductive dechlorination of the chlorinated organic solvent, but studies on the treatment of heavy metals and inorganic compounds are very rare [Matheson and Tratnyek, 1994; Helland et al., 1995; Johnson et al., 1996; Morales et al., 2002; Gu et al., 1998; Blowes et al., 2000; Cantrell et al., 1995]. Heavy metals like Cr, Pb, U, etc. were separated and removed from the groundwater through reduction and precipitation (i.e., reactive immobilization), instead of degrading them completely. Usually, the coating of byproducts reduced from the metals to the surface of ZVI results in lowering of its surface activity. Therefore, the prevention of surface deactivation of ZVI is a prerequisite for a widespread application of reactive barrier technologies. Various techniques on regeneration of surface activity were reported, such as acid washing and supersonic vibration [Hung and Hoffmann, 1998]. Kim et al. [2002] investigated the simultaneous removal of Cr(VI) and CCl_4 , and reported an interesting result on the effect of sand on the removal of Cr(VI). According to their results, the removal efficiency after 48 hours greatly increased from about 50% to 85% when sand was used together with the ZVI in

reducing highly toxic Cr(VI) to less toxic Cr(III). They maintained that reduction product Cr(III) adsorbs to the sand which shows higher sorption affinity than the ZVI, thus leaving a large portion of active sites of the ZVI unblocked.

In this work, we propose simple mathematical models for each experiment done by Kim et al. [2002], such as the control, adsorption to sand, reduction by ZVI, and both adsorption and reduction by both ZVI and sand, and interpret the enhancement of Cr(VI) removal efficiency by the ZVI when sand is present.

MATERIALS AND METHOD

The information required for the analysis is taken from Kim et al. [2002]: the batch-type reactor has a volume of 250 mL and its headspace volume was kept less than 1 mL. K_2CrO_4 solution (39.8 mg/L) was used as a source of the Cr(VI) ion. Samples collected at the predetermined time intervals were filtered through the nitrocellulose membrane (pore size of 0.45 μm) and the pH of the filtrate was maintained below 2 by using HNO_3 . Diphenyl carbazide solution was employed to form a complex with Cr(VI) and its concentration was analyzed at 542 nm with a UV spectrophotometer (8452A, Hewlett Packard, USA). They carried out four-types of experiment, measuring the solution concentration of Cr(VI) with time: (i) a control experiment without the ZVI and sand, (ii) an adsorption kinetic experiment with 40 g of sand (i.e., no separate adsorption equilibrium experiment was done), (iii) a reduction experiment with 20 g of ZVI, and (iv) a reduction and adsorption experiment with 20 g of ZVI and 20 g of sand.

MODEL DEVELOPMENT

1. Natural Decay of Cr(VI) in Control Experiment

Cr(VI) ion disappeared from the solution without the presence

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of either ZVI (i.e., reductant) or sand (i.e., adsorbent). The disappearance rate was assumed to be zero-order as follows:

$$-\frac{dc}{dt} = k_0; \quad c = c_0 \text{ at } t = 0 \quad (1)$$

where k_0 denotes zero-order rate constant ($\text{mg L}^{-1} \text{hr}^{-1}$), c_0 , initial concentration ($=39.8 \text{ mg/L}$), and c , concentration of Cr(VI) ion at time t . The solution of the above differential equation is

$$c(t) = c_0 - k_0 t \quad (2)$$

where k_0 was estimated by curve fitting to the data of control experiment.

2. Adsorption of Cr(VI) to Sand

Adsorption rate of Cr(VI) to sand was assumed to be first order and reversible [Song, 1996]. Zero-order natural decay of Cr(VI) was also assumed to occur simultaneously with the adsorption process. The disappearance rate of Cr(VI) from the solution was obtained under the assumption that the two processes were occurring independently.

$$-\frac{dc}{dt} = k_s^0(c - c_e) + k_0; \quad c = c_0 \text{ at } t = 0 \quad (3)$$

where k_s^0 and c_e are the first-order adsorption rate constant (hr^{-1}) and equilibrium solution concentration (mg/L) of Cr(VI), respectively. The solution to Eq. (3) is

$$c(t) = c_0 e^{-k_s^0 t} - \frac{k_0 - k_s^0 c_e}{k_s^0} (1 - e^{-k_s^0 t}) \quad (4)$$

where c_e and k_s^0 were determined by fitting Eq. (4) to the experimental data.

3. Reduction of Cr(VI) by ZVI

Reduction rate of Cr(VI) was assumed to be first-order and irreversible, and natural decay of Cr(VI) was also assumed to occur simultaneously with the reduction. The disappearance rate of Cr(VI) from the solution was obtained by combining both reduction and natural decay rates as was done in the adsorption to sand.

$$-\frac{dc}{dt} = k_{fe}^0 c + k_0; \quad c = c_0 \text{ at } t = 0 \quad (5)$$

where k_{fe}^0 represents first-order reduction rate constant (hr^{-1}) and can be estimated by fitting Eq. (6) (the solution to Eq. (5)) to the experimental data.

$$c(t) = c_0 e^{-k_{fe}^0 t} - \frac{k_0}{k_{fe}^0} (1 - e^{-k_{fe}^0 t}) \quad (6)$$

4. Reduction of Cr(VI) by ZVI with the Presence of Sand

The adsorption rate constant was assumed to change from k_s^0 to k_s when sand was present with the ZVI. Furthermore, the reduction rate constant of Cr(VI) was considered to change from k_{fe}^0 to k_{fe} when the ZVI was present with the sand. In other words, we assumed there are interactions between the reduction and the adsorption rates of Cr(VI) when both ZVI and sand are present together. These interactions were assumed to affect both the reduction and adsorption rate constants. Natural decay of Cr(VI) was considered to occur independently. Therefore, the disappearance rate of Cr(VI) will be as follows:

$$-\frac{dc}{dt} = k_s(c - c_e) + k_{fe}c + k_0; \quad c = c_0 \text{ at } t = 0 \quad (7)$$

where the first, second, and third terms on the right hand side represent the first-order reversible adsorption rate, first-order reduction rate, and zero-order natural decay rate constant, respectively. The solution to Eq. (7) reads

$$c(t) = c_0 e^{-(k_s + k_{fe})t} - \frac{k_0 - k_s c_e}{k_s + k_{fe}} (1 - e^{-(k_s + k_{fe})t}) \quad (8)$$

where k_s and k_{fe} can be estimated by fitting Eq. (8) to the experimental data.

RESULTS AND DISCUSSION

Fig. 1 shows the four types of experimental data taken from Kim et al. [2002]. The zero-order natural decay rate constant, k_0 was estimated to be $0.0825 \text{ mg L}^{-1} \text{hr}^{-1}$ by fitting Eq. (2) to the experimental data, and the fitted curve is shown for comparison. Parameters estimated from fitting in each type of experiment are listed in Table 1.

Eq. (4) was fitted to the adsorption data obtained with 40 g of sand to estimate the following parameters involved in the model: $c_e = 30.3 \text{ mg/L}$, $k_s^0 = 0.292 \text{ hr}^{-1}$. Equilibrium solid-phase concentration, q_e was computed from the material balance [Cho et al., 2003] to be $q_e = 0.0590 \text{ mg/g}$ when 40 g of sand was used.

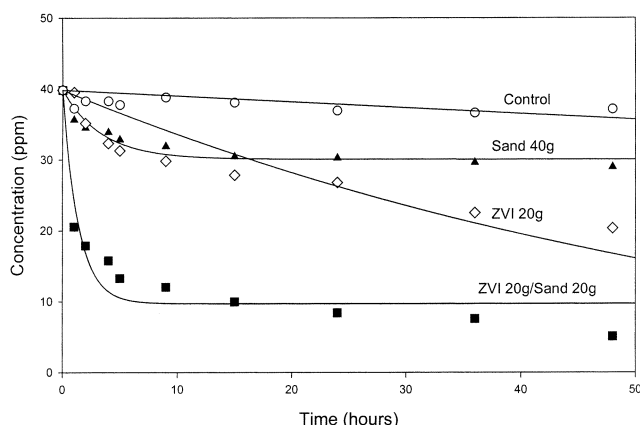


Fig. 1. Solution-phase concentration changes of Cr(VI) with time in control experiment, in the presence of sand, zero valent iron (ZVI), or both sand and ZVI. Solid lines represent fitted lines.

Table 1. Summary of model parameters obtained from curve fitting to the experimental data

Experiment	Fitted parameter(s) ± standard error	R ²	Equation used in fitting
Control	$k_0 = 0.0825 \pm 0.0195 \text{ mg L}^{-1} \text{hr}^{-1}$	0.6743	(2)
Sand (40 g)	$k_s^0 = 0.292 \pm 0.0532 \text{ hr}^{-1}$ $c_e = 30.3 \pm 0.448 \text{ mg L}^{-1}$	0.9244	(4)
ZVI (20 g)	$k_{fe}^0 = 0.0147 \pm 0.00230 \text{ hr}^{-1}$	0.7206	(6)
Sand (20 g) /ZVI (20 g)	$k_s = 0.203 \pm 0.0609 \text{ hr}^{-1}$ $k_{fe} = 0.509 \pm 0.102 \text{ hr}^{-1}$	0.9153	(8)

$$c_0V = q_e W + c_e V \quad (9)$$

where V and W denote the volume of solution (L) and the weight of sorbent used (g), respectively. We took V to be approximately the volume of the batch-type reactor (=0.25 L) since the headspace volume was always kept less than 1 mL. Considering that the concentration of Cr(VI) was low, we assumed a linear adsorption isotherm:

$$q_e = 0.00194c_e \quad (10)$$

When 20 g of ZVI was used, Eq. (6) was fitted to the reduction data and the computed curve was also drawn in Fig. 1 for comparison. The first-order reduction rate constant was estimated to be $k_{Fe}^0 = 0.0147 \text{ hr}^{-1}$.

When sand (20 g) and ZVI (20 g) were present together, two model parameters involved in Eq. (8), the first-order adsorption and reduction rate constants, were estimated by fitting to the experimental data: $k_s = 0.203 \text{ hr}^{-1}$ and $k_{Fe} = 0.509 \text{ hr}^{-1}$, respectively. In this fitting, the equilibrium solution-phase concentration (c_e) in Eq. (8) was recomputed since the dose of sand was changed from 40 g of sand alone to 20 g of sand when the ZVI is present. By substituting Eq. (10) into the material balance equation with $W = 20 \text{ g}$, we can get $c_e = 34.4 \text{ mg/L}$. The calculated curve with the fitted parameters is shown in Fig. 1.

From the model calculations, the first-order reduction rate constant was found to increase about 35 times when 20 g of sand was present together with the 20 g of ZVI, compared with the presence of only 20 g of ZVI (i.e., $k_{Fe} = 0.509 \text{ hr}^{-1}$ vs. $k_{Fe}^0 = 0.0147 \text{ hr}^{-1}$). The first-order adsorption rate constant decreased to about 70% of the value obtained when only sand was present due to the presence of reduction product Cr(III) ($k_s = 0.203 \text{ hr}^{-1}$ vs. $k_s^0 = 0.292 \text{ hr}^{-1}$).

In conclusion, we could quantify the enhancement of Cr(VI) reduction when sand was added to the ZVI, through the introduction of a series of simple mathematical models in each physical/chemical step.

ACKNOWLEDGMENT

This research was supported by Kyungpook National University Research Team Fund (KNURTF), 2003.

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