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Rates of Cr(VI) sorption on a column of zero-valent Iron of ground water

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Abstract
The aim of this study was to generate removal rate coefficients that would be applicable to the Reactive Well Technology, a groundwater remediation technology that replaces the sand in a filter pack of a conventional well with a reactive material such as zero-valent iron, Fe(0). The removal rate of Cr(VI) from the aqueous phase by Fe(0) under flow conditions was measured. The removal pseudo-first order rate coefficients measured under flow conditions were comparable to those previously measured under batch conditions that had significantly greater ratios of solution volume to Fe(0) surface area. Between the range of 20 and 100 wt-% Fe(0), there was little measurable change in the reaction kinetics. Thus, it may be possible to include sand into the reactive filter packs in the event it is necessary to increase filter pack porosity or to decrease the accumulation of secondary reaction products that may lead to filter pack plugging. Background water chemistry had only marginal effects on reaction rate coefficients. A rank ng of the background solutions based on their pseudo-first order rate coefficients is: 0.2 M $NaHCO_2$ > distilled water > a carbonate-dominated groundwater. The reduction rates measured in this study indicated that an 'e(0) filter pack could be used to lower Cr(VI) concentrations by several orders of magnitude in a once-through mode of operation of the Reactive Well Technology.

Keywords: Chromium sorption, removed, column, zero-valent Iron, ground water

Introduction

Under common environmental conditions, chromium has two stable oxidation states, Cr(VI) and Cr(III). Cr(VI), a known carcinogen, forms relatively soluble precipitates and does not adsorb readily. Cr(VI) is a diprotic acid with pK_a values of 0.8 and 6.5. Thus under environmentally relevant pH values, Cr(VI) exists as chromate, CrO_2^- and dichromate, $HCrO_4^-$ Both oxyanion species are highly mobile and strong oxidants with reduction potentials (E°) greater than 1 V. Cr(III) is a micronutrient and it forms sparingly soluble precipitates, commonly $Cr(OH)_3$ or $Fe(OH)_3$, rendering it immobile under most environmental conditions.

Reduction of Cr(VI) to Cr(III) by reaction with Fe(0), and subsequent precipitation of Cr(III) oxyhydroxides occurs through the reaction:

$$3/2Fe^0_{(a)} + CrO2_{(aq)} + 5H^+_{(aq)} \rightarrow 3/2Fe^{2+}_{(aq)} + Cr(OH)_{3(s)} + H_2O)_{(1)}$$

The extent and rate of Cr(VI) removal by Fe(0) has been evaluated extensively in laboratory [2, 3, 4] and field demonstrations. The results of these studies indicate that the rate of Cr(VI) reduction by Fe(0) and removal through precipitation is sufficiently rapid for use in permeable reactive barriers used for groundwater remediation.

The reactivity of Fe(0) varies greatly as its surface becomes pacified with secondary mineral coatings formed when Fe(0) is oxidized [5, 6]. The secondary phases form on the surface of the Fe(0) have been characterized under several experimental conditions and by several different analytical methods[7,4]. These secondary phases include magnetite (Fe_3O_2), green rust [Fe^{II}_4 $Fe^{III}_2(OH)_{12}SO_3$ H_2O], goethite (FeOOH), and ferric hydroxide [$Fe(OH)_3$). There are several different Fe phases formed primarily because of the steep Eh gradient that generally exists between the Fe(0) surface and the surrounding water. Minerals with Fe in a lower oxidation state such as magnetite and green rust, are generally found near the Fe(0), whereas minerals with Fe in a higher oxidation state such as goethite, are generally found closer to the water interface [6]. A number of carbonate mineral including calcite ($CaCO_3$), aragonite ($CaCO_3$) and siderite ($FeCO_3$) are also commonly reported on Fe(0) surfaces. Carbonate minerals form because the concentrations of dissolved carbonates increase as the pH increases due to the proton consuming nature this redox reaction.

As the Fe(0) surfaces become increasingly covered with secondary precipitates not surprisingly, the contaminant removal rates change. Most often, removal rates are showed to decrease [5]. (Johnson *et al*., 1998) [5, 6]. For instance,[1] Sass *et al*. (1998) reported that the half life of TCE degradation in a Fe(0) column increased from 2.0 to 2.6 h after 35 pore volumes had been passed through the column. The reaction rates may initially decrease, they eventually increase again over extended durations. They attributed this chemical behavior to the semiconductor nature and the increased adsorptive capacity of the solid phase as magnetite and green rust are formed. Together, these processes may contribute to enhance the overall removal of Cr(VI) from the aqueous phase, e.g., magnetite and green rust may increase the amount of Cr(VI) sorbed to the solid phase and then it may behave as a semiconductor to facilitate electron transfer to the sorbed Cr(VI).

Reaction rates are typically measured in batch mode, a mode that tends to concentrate the reaction products thereby promoting the formation of precipitates. Consequently, the reaction rates are measured while several reactions with the solute of interest may be occurring. One of the advantages of measuring reaction rates in a flow system, as exist in most Fe(0) remediation applications, is that the reaction products are less likely to form precipitates because the

concentrations of the a vacation products are lowered by dilution. As the dw rate increases, the concentration of reaction products will decrease, thereby reducing the tendency for secondary precipitate to form. Furthermore, under flow conditions, the elevated reactant coricentrations may be too short lived to permit the formation of the precipitate, i.e., precipitate formation may be kinetically hindered. For example, dolomite, Ca, $Mg(CO_3)_2$, is commonly predicted based on thermodynamic considerations to form in Fe(0) permeable reactive barriers, but is rarely found. The cause for this is that dolomite requires a relatively long time to form, on the order of years.

The overall objective of this study was to measure under flow conditions, Cr(VI) removal rates from the aqueous phase by Fe(0). The specific objectives were to determine the influence of the following on Cr(VI) removal rates: 1) adding sand to a reactive Fe(0) bed, a potential engineering solution to prevent clogging of a bed from secondary precipitates, and 2) background solution chemistry. The intent of this study was to generate removal rate data that would be applicable to the Reactive Well Technology [9] (Gilmore *et al.*, 1998) [9]. This technology modifies the typical groundwater well by replacing the filter pack sand with a chemically reactive substrate which could include absorbents, bio-amendments, oxidants, or reductants. These reactive substrates detoxify or sorb the targeted contaminant during the operation of a recirculating well. The effectiveness of the technology depends on the zone-of-influence which is largely controlled by geological conditions (e.g., intrinsic permeability), pumping rate and he rate of reaction between the contaminant and the reactive material in the filter pack. Greater the reactivity, the more rapidly the contaminants are removed from the aqueous phase and the fewer times that the groundwater needs to be recirculate through the reactive filter pack to achieve a targeted clean up level.

The experimental approach used in this study was to introduce a Cr(VI)-spiked solution into a column of Fe(0) at different flow rates (and therefore different contact times). Once the column came to steady state with respect to in-line measurements of redox potential and/or dissolve oxygen concentration, the Cr(VI) effluent concentration was measured. The flow rate and therefore the contact time, was changed at least 6 times for each experiment, providing a series of Cr(VI) concentrations as a functions of contact times. Pseudo first-order rate constants with respect to Cr(VI) concentration then calculated from this data.

Materials and methods

The reaction rates of Cr(VI) removal by Fe(0) were measured using a flow-through column technique. The two variables of interest were the concentration of Fe(0) mixed into sand and background solution chemistry. Three sand-Fe(0) mixtures, 20, 50, and 100 wt-% Fe(0) and three types of aqueous phases, deionized water, a 0.2-M $NaHCO_3$ aqueous solution and an Agra groundwater (Table 1), were evaluated. The columns used in this study were made of PVC and had a 2.5-cm diameter and a 10-cm length. Polyethylene screens were used to hold the sand- Fe(0) mixture in the columns. In-line platinum and O_2 electrodes were placed in the effluent tubing. The columns were brought to hydrological and chemical steady state by slowly introducing at a slow flow rate an unspiked background solution (deionized water, 0.2 M $NaHCO_3$, or groundwater) overnight into the bottom of the column. The flow rate was then increased and a 5 mg L^{-1} Cr(VI) spiked solution (made from $K_2Cr_2O_7$) was introduced into the column. Once in-line measurements of redox and O_2 stabilized, suggesting steady-state had been achieved, an effluent sample was collected for Cr(VI) analysis. The flow rate was then lowered and once the redox and O, values restabilized, another effluent sample was collected for Cr(VI) analysis. The flow rate was decreased 5 to 10 times per column to obtain residence times that ranged between 0.1 to 20 min (representative of pumping rates in the field of between 4.0 and 40 L min^1).

The Fe(0) particles had a flat plate shape with an average particle size of 2.5 x 2.5 x 0.4 mm (length x width x thickness) and a BET surface area of 0.0605 m^2 g. The sand used in these experiments consisted of approximately 90% quartz, 9% Na-, K- and Cafeldspar and 1% mica as determined by XRD. The sand fraction used in this study could passed through a 20-mesh sieve (850 µm), but was retained by a 40-mesh sieve (425 µm). The sieving procedure produced a sand with a mean grain size of 650 µm (based on SEM analysis) and a BET surface area of 0.107 m^2 g^{-1}. The groundwater used in this study was collected from an uncontaminated aquifer in Agra and analyzed by standard methods and results are shown in Table – 1.

The influent Cr(VI) concentrations were periodically monitored during each experiment. Additionally, the amount of Cr(VI) adsorbed by the experimental apparatus (the influent reservoir, tubing, PVC column, quarried sand and sampling tube) was monitored by introducing at the start and end of each experiment the influent Cr(VI) solution into a control column containing 100% sand. These control samples indicated that there was no loss of Cr(VI) to the experimental apparatus throughout the study.

The total Cr(VI) concentrations in the sample extracted with perchloric acid (after removing silica with HF as silica can adsorb metals) were determined with Perkin Elmer AAnalyst 100 AAS by calibrating it with K_2CrO_4 standards.

Results and discussion

Before and during the study, a number of control tests were conducted to evaluate the experimental approach. A negative control was conducted several times during the study in which the Cr(VI)-spike! Influent solution was passed through a column of pure sand to monitor whether Cr(VI) sorbed to the sand or to the column assembly. In all cases, there was no indication of Cr(VI) loss in these samples. It was also assumed that these tests could be replicated well. Finally, a test was conducted to determine if there was a hysteresis effect, i.e., determine whether Cr(VI) removal rates were dependent on whether the residence times were achieved by incrementally increasing or decreasing the flow rate during the test. The operational limitations of batch and column solute experiments have been reviewed.

The experimental data for the reduction of CrO_4^{2-} were analysed using four sorption kinetic models: the pseudo first order, the Ritchie second order, the modified second order and the Elowich equations. The values of specific rate coefficient k was calculated for all the sorbents and they were found constant when calculated using the first order equation:

$k = 2.303/t \times \log a/(a-x)$.....(1)

where a mol/l is initial arsenate concentration from which x mol/l has been removed after t seconds. By assuming that the reactivity of the Fe(0) remains constant and hydrogen ion concentration remains constant, the Equation (1) can be simplified. The assumption the Fe(0) remains constant is reasonable because the number of moles of Fe(0) greatly exceeds the quantity of oxidants. The assumption that the hydrogen ion concentration remained constant is less reasonable because the pH varied from 7.9 to 8.4 during and between the experiments. Given these assumptions and caveats, a pseudo-first-order rate coefficients, k', can be defined as in equation – 2.

$k = k[Fe(0)]^{3/2}[H^+]^5$.....2

The data indicate that it does not follow the first- order model throughout the evaluation period. This has been attributed to more than one reaction occurring in the system, including Cr(VI) sorption to several different and changing surfaces, and Cr(VI) reduction by Fe(0) and different Fe(II)-bearing minerals. The pseudo-first-order rate coefficients k, were remarkably similar for all treatments (Table 2). With the exception of the 20% Fe(0) - distilled water column, the k values ranged from 0.167 ± 0.028 to 0.340 ± 0.149 min¹. The overlap of the 95% confidence levels of this range suggests that the k' values are not significantly different. The k' values tended to be somewhat greatest in the $NaHCO_3$ background solution, followed by distilled water, and then the groundwater (Table-2). Expressed differently, the Cr(VI) half-life, the duration required for Cr(VI) concentrations to decrease by half, tended to be shortest in the $NaHCO_3$ solution, followed by distilled water, and then the groundwater (Table-2). The significant decreases in Cr(VI) removal by Fe(0) as the ionic strength was incrementally increased through the addition of Na_2SO_4[11].
The general similarity between the magnitude of the k', irrespective of Fe(0) concentrations, suggests that Fe(0) concentrations between 20 and 100 wt- were not limiting Cr(VI) removal. However, inspection of the data suggests that the rate of Cr(VI) removal is not greatly influenced by Fe(0) concentration.
The rate coefficients report here do not differ greatly from those reported [2] who measured Cr(VI) removal rates by the batch method with a very high solution volume to surface area ratio. They reported a pseudo-first order rate constant of 0.128 min¹ (half life of 5.4 min). This k' value is within the range of values presented in Table-2. A volume to surface area ratio of 2.1 x 10 cm² whereas a ratio between 1.1 x 10 to 5.3 x 10 cm³ was used in this study. This difference may also be attributed to differences in reactivity of the Fe(0) [2].
Since surface area da a is 1.0t always provided, it is useful to make qualitative comparison of rate coefficients from other studies by normalizing to the initial spike concentration. For the initial Cr(VI) concentration of 5 mg L^{-1} (96 m M), a Cr(VI) reduction rate of 2.1 x 10^{-5} M min¹ was calculated from the average k' in this study, 0.214 min^{-1}. Rates of Cr(VI) removal in the presence of Fe(0) is in the order of 10^{-6} M min[2] aqueous Fe(II) is 10^{-6} M s^{-1} (for 1 m M Fe(II) at pH 7;[12] magnetite is 10 M s¹, and green rust is 10^{-5} M s^{-1}[12]. Although it is important not to over interpret these results given differences in experimental conditions among the various studies, it can be seen that the rates generally follow the reduction potentials of the reductant, more specifically the difference in enthalpies between the reductant and CriVI). Due to the highly negative reduction potential of Fe(0), it has a relatively faster rate of reduction than other iron-bearing reluctant.

Table 1: Chemical composition of the groundwater (< 0.45 - $\mu m\ filter$) used in this study

Constituent	Concentration (mg/L)
pH	8.3 (unit less)
Cl^-	2
EC ($\mu mhos/com$)	255
NO_3^-	22
SO_4^{2-}	128
Total organic C	0.95
Total alkalinity (as CO_3^{2-})	70.5
Al	0.24
B	0.15
Ba	0.069
Ca	97.5
K	30.3
Mg	26.4
Mn	0.049
Na	47.6
Si	26.2
Sr	0.38

Table 2: Pseudo – first order rate coefficients

Fe (0) in sand (wt -%) (1)	Aqueous phase (2)	No. obs. (3)	k (min^{-1}) (4)	$t_{\frac{1}{2}}$ (min) (5)	Probability ($P \leq x$) (6)	R^2 (7)
20	$NaHCO_3$	9	0.200 ± 0.86	3.46 ± 0.86	0.001	0.88
20	Distilled water	8	0.167 ± 0.028	4.14 ± 1.19	0.001	0.86
20	Ground water	6	0.091 ± 0.007	7.65 ± 1.40	0.001	0.97
50	$NaHCO_3$	9	0.323 ± 0.046	2.15 ± 0.54	0.001	0.88
50	Distilled water	7	0.185 ± 0.030	3.74 ± 1.17	0.01	0.84
50	Ground water	6	0.182 ± 0.035	3.82 ± 1.27	0.01	0.90
100	$NaHCO_3$	6	0.241 ± 0.060	2.88 ± 1.18	0.01	0.80
100	Distilled water	6	0.340 ± 0.060	2.04 ± 1.12	0.1	0.57
100	Ground water	6	0.200 ± 0.077	3.48 ± 1.80	0.05	0.63

Conclusions

The flow-through technique of measuring the reactivity of Fe(0) has the advantage that it more closely simulates expected under groundwater remediation conditions and it minimizes the build up of pacifying cheatings on the reactive surface. In this study, the flow rates were appreciably faster than those that have been previously tested to simulate permeable reactive barriers. The faster flow rates were used to simulate conditions expected during the deployment of the Reactive Well Technology. The measured reaction rates were comparable to those reported [2], who used the batch method with a significantly greater ratio of solution, volume to Fe(0) surface area. The reaction rates measured in this study indicate that Cr(VI) concentrations would be significantly reduced in a once-

through mode of operation (assuming 15-cm thick filter pack, an initial Cr(VI) concentration of 4000 µg L^{1}, final Cr(VI) concentration of the maximum allowable concentration, <50 µg L^{-1} and a pumping rate of 38 L min^{1}). Background water chemistry had little, if any, effect on Cr(VI) removal, Also, the amount of Fe(0) mixed into the sand did not greatly change the reaction kinetics. Thus it may be possible to include sand into the reactive filter packs in the event it is necessary to increase filter pack porosity or to decrease the accumulation of secondary reaction products that may lead to filter pack plugging. However, by decreasing the concentration of Fe(0), the useful life-span of the filter pack will be diminished and the ability of the system to remove coexisting contaminants with a longer half life such as DCE, TCE, PCE, U(VI) and As(III/V) was compromised.

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