Nicholas MELAS - FW: Disinfection of drinking water

PCB 7

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To: <melasn@ipcb.state.il.us>
Date: 6/17/2008 4:54 PM
Subject: FW: Disinfection of drinking water

Dear Mr. Melas:

It was a great pleasure to meet you yesterday and a privilege to share some of my views with you regarding a cleaner Chicago River. I attach the first research report on the novel zerovalent iron approach. I hope you find it interesting. I like it, not only for its virus-eliminating features, but for its low cost and low-energy requirements. I look forward to future conversation around this idea. If you have additional questions regarding this approach please call on me.

Again my thanks for your work for Illinois waterways and for the future of Chicago.

Very Cordially,

David M. Solzman, Ph.D

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Removal and Inactivation of Waterborne Viruses Using Zerovalent Iron

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A daunting challenge facing the water industry and regulators is how to simultaneously control microbial pathogens, residual disinfectant, and disinfection byproducts in drinking water, and to do so at an acceptable cost. Of the different pathogens, viruses are especially problematic due to their small size, high mobility, and resistance to chlorination and filtration. In the past decade, zerovalent iron has been used to treat a wide variety of organic and inorganic contaminants from groundwater. However, iron has not been tested against biological agents. This study examined the effectiveness of commercial zerovalent iron to remove two viruses, ϕX174 and MS-2, from water. Removal of these viruses by iron granules in batch reactors was first-order, and the rate was likely controlled by external mass transfer. Most of the viruses removed from solution were either inactivated or irreversibly adsorbed to iron. In a flow-through column containing zerovalent iron (with 20 min of iron contact time), the removal efficiency for both viruses was 4-log in an initial pulse test, and over 5-log in the second pulse test after passage of 320 pore volumes of artificial groundwater. We assume that the improved efficiency was due to continuous formation of new iron (oxyhydr)oxides which served as virus adsorption sites. To our knowledge, this is the first demonstration of biological agent removal from water by zerovalent iron. Results of this study suggest zerovalent iron may be potentially useful for disinfecting drinking water and wastewater, thereby reducing our dependence on chlorine and reducing the formation of disinfection byproducts.

Introduction

Microbial pathogens in drinking water present a serious threat to public health. Sources of microbial contamination include leaking septic tanks and sewer lines, landfills, land disposal of biosolids, wastewater discharge and reuse, and runoff and infiltration from animal waste-amended fields (*1*, *2*). The EPA Science Advisory Board (*3*) cited drinking water contamination as one of the highest remaining environmental risks and microbial contamination as the greatest challenge in health risk management for drinking water suppliers. The Surface Water Treatment Rule (SWTR) and Interim Enhanced SWTR were established to regulate microbial contaminants in drinking water systems using surface water or groundwater under direct influence of surface water. The 1986 and 1996 Safe Drinking Water Act (SDWA) Amendments required EPA to establish national primary drinking water regulations requiring disinfection to control microbial contaminants for all public water systems, including systems supplied by groundwater sources (*4*). More recently, the EPA promulgated Long Term 1 Enhanced SWTR and proposed Long Term 2 Enhanced SWTR to specify treatment requirements for reducing microbial pathogens in drinking water (*5*, *6*).

Despite continued efforts to regulate water quality and improve treatment practices, microbial pathogens continue to threaten drinking water safety. Epidemiological studies (*7*–*9*) have found a link between gastrointestinal diseases and tap water, even when water quality guidelines were met. The occurrence of illnesses was found to correspond to short-term turbidity breakthrough from individual filters in the water treatment plant (*10*). In addition, data collected by the Centers for Disease Control and Prevention (CDC) and EPA (*4*) indicate that almost as many waterborne disease outbreaks were reported between 1971 and 1996 for systems with disinfection that was inadequate or interrupted (134 outbreaks) as for systems without disinfection (163 outbreaks) during the same period.

Viruses have been shown to be responsible for approximately 80% of disease outbreaks for which infectious agents were identifiable (*11*). A recent study by Abbaszadegan et al. (*12*) on the occurrence of pathogens in groundwater analyzed samples collected from 448 sites in 35 states in the United States for various indicators of fecal contamination, including total coliform, *E. coli*, somatic and male-specific coliphages, and human viruses. It was found that 31.5% of the samples were positive for one or multiple pathogenic viruses using polymerase chain reaction (PCR), and human viruses were detected by cell culture in 4.8% of all the samples. Although viruses are not the only pathogens found in water supplies, they are far smaller (~0.01–0.1 μm) than bacteria and protozoan cysts and thus are removed to a lesser extent by filtration. As a result, viruses can travel much longer distances in the subsurface (*13*, *14*), and treatment processes such as filtration are generally less effective in removing viruses (*15*). In addition, chlorination, which is the dominant disinfection method used in the United States, has been shown to be less effective against viruses and protozoa than bacteria (*16*, *17*).

For the past decade, zerovalent iron has been used in subsurface permeable reactive barriers (PRBs) for groundwater remediation (*18*, *19*). While initially proposed to treat chlorinated solvents in contaminated aquifers, zerovalent iron has since been shown to be effective in removing a broad range of organic and inorganic pollutants, including heavy metals, Freons, radionuclides, pesticides, and nutrients (*20*). Zerovalent iron can remove contaminants from water through one of two processes: reduction or adsorption. For contaminants such as chlorinated solvents, the treatment involves primarily reduction (*21*), whereas for phosphate and arsenic, the main removal mechanism appears to be adsorption to iron oxides and hydroxides, which are formed during iron corrosion in water (*22*, *23*). Iron corrosion initially forms amorphous iron hydroxides, which then transform into more stable oxides and oxyhydroxides such as magnetite, goethite, and lepidocrocite, depending on the solution composition and redox conditions (*24*–*26*).

A number of studies have shown that iron oxides can remove and inactivate viruses in water (*11*, *27*–*29*). Although

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the mechanism for the removal and inactivation is not fully understood, the process has been suggested to involve adsorption of virus particles to iron (oxyhydr)oxides through electrostatic attraction (*11, 30*). This is followed by inactivation of adsorbed viruses due to the strong attachment force, which causes the viruses to disintegrate or become noninfective (*11, 27*). These studies suggest an intriguing possibility that zerovalent iron may continuously remove and inactivate viruses in water through corrosion and formation of (oxyhydr)oxides at the iron surface. Although zerovalent iron has been tested against a large number of organic and inorganic contaminants, it has never been shown to remove biological agents from water. This study was prompted to assess the effectiveness of zerovalent iron to remove and inactivate waterborne viruses and evaluate its potential for water and wastewater treatment applications.

Materials and Methods

Virus Selection and Assay. Two bacteriophages, MS-2 and ϕX174, were selected as model viruses for this study because they have been used as surrogates for human enteric viruses in previous studies due to their structural resemblance to many human enteric viruses and their ease of use (*31, 32*). MS-2 is an icosahedral single-stranded RNA phage with a diameter of 26.0–26.6 nm (*33*) and an isoelectric point (pH_{iep}) of 3.9 (*34*). MS-2 was obtained from the American Type Culture Collection (ATCC 15597B1) and grown on bacterial lawns of *E. coli* (ATCC 15597). ϕX174 is a spherical single-stranded DNA phage with a diameter of 23 nm and a pH_{iep} of 6.6 (*35*). It was grown on an *E. coli* host (ATCC 13706). Concentrations of infective ϕX174 and MS-2 particles were determined by the plaque-forming unit assay using the agar overlay method (*36*). Briefly, 1 mL of host culture and 1 mL of diluted virus sample were added to a trypticase soy agar (TSA) tube, and the mixture was poured onto a TSA plate. The plates were solidified for 15 min and placed in a 37 °C incubator for 5 and 12 h for ϕX174 and MS-2, respectively. Viable virus concentration was determined by counting the plaques in the host lawn and reported as plaque-forming units per milliliter (pfu/mL). Only dilutions that resulted in 10–300 plaques per plate were accepted for quantification (i.e., the limit of quantification was set to be 10 pfu/plate for this study). All virus assays were performed in duplicate.

Iron and Sand. The zerovalent iron used for this study was commercial iron particles (ETI8/50) obtained from Peerless Metal Powders & Abrasive (Detroit, MI). The iron was used as received without pretreatment. The specific surface area of the Peerless iron was 1.67 m^2/g, as measured by the Brunauer–Emmett–Teller (BET) adsorption method with nitrogen. This value is within the range reported by other authors for Peerless iron [e.g., 1.50 m^2/g by Alowitz and Scherer (*37*) and 2.53 m^2/g by Su and Puls (*22*)]. In addition to zerovalent iron, the Peerless iron also contained magnetite, maghemite, and graphite, as determined by X-ray powder diffraction with Cu Kα radiation using a Philips/Norelco diffractometer. Accusand (Unimin, Le Sueur, MN) with the following particle size distribution was used for the column experiment: 9% of 0.1–0.25 mm, 69.8% of 0.25–0.5 mm, and 21.2% of 0.5–1.0 mm. The properties of Accusand have been well-characterized in a laboratory study (*38*). It consisted essentially of quartz with trace levels of organic matter and metal oxide coating. The sand was treated to remove metal ions and oxides using a citrate buffer solution containing 44.1 g/L of sodium citrate ($Na_2C_6H_5O_7 \cdot 2H_2O$) and 10.5 g/L of citric acid, following a procedure modified from Mehra and Jackson (*39*). The detailed treatment procedure is given in Chu et al. (*27*). After the treatment, the iron content decreased from 32.5 mg iron/kg sand to below the detection limit (0.02 mg iron/kg sand), as determined by extraction with 0.05 M sodium dithionite ($Na_2S_2O_4$) and 0.4 M sodium citrate and quantification using inductively coupled plasma (ICP).

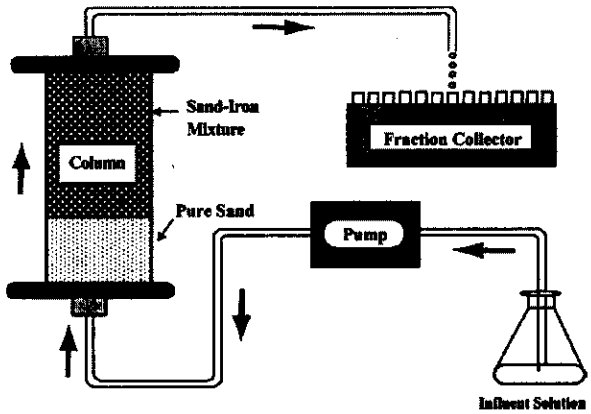

FIGURE 1. Schematic diagram of column experiment setup.

Artificial Groundwater. An artificial groundwater (AGW) was used as the background solution; it contained 0.075 mM of $CaCl_2$, 0.082 mM of $MgCl_2$, 0.051 mM of KCl, and 1.5 mM of $NaHCO_3$ (ionic strength $\approx$ 2 mM). After autoclaving and vacuum degassing, the pH of the AGW was adjusted to 7.5 using 0.1 M NaOH or HCl prior to use.

Batch Experiments. Both batch and column experiments were conducted in a large refrigerator at 5 ± 1 °C to avoid inactivation of the viruses due to high temperature. Batch experiments were conducted to study the kinetics of virus removal by Peerless iron particles. Stock solutions of ϕX174 and MS-2 were diluted in AGW to the desired titer ($\sim 10^5$ pfu/mL). Experiments were performed using 250-mL amber borosilicate bottles prepared in duplicate. Following addition of 1.0 g of iron particles, the bottles were filled completely (free of headspace) with virus solution and sealed immediately with an open-hole screw cap and a Teflon-lined silicone septum (10/90 mil, Alltech, Deerfield, IL). Care was taken to prevent trapping of air bubbles during filling and capping of the bottles as viruses can be inactivated at the air–water interface (*40, 41*). The sealed bottles were shaken end-over-end at 20 rpm in a refrigerator. At different elapsed times, 1.0 mL of virus-free AGW was injected into the bottle through a fully inserted 5.5-in. stainless steel side port needle (Popper & Sons, New York), and simultaneously a 1-mL sample was displaced through an inserted 2-in. stainless steel side port needle (Alltech). The different needle lengths were used to ensure spatial separation of injection and sampling points to prevent sample dilution. Side port needles were used to minimize damage to septa and avoid introduction of air. The 1-mL sample was analyzed immediately for viable virus concentration by the plaque assay.

To determine whether virus removal was due to reversible adsorption to iron or irreversible adsorption and inactivation, solution was discarded after the last sample was taken and 250 mL of 3% beef extract solution (BEX, pH 9.5) was added to the bottle to extract viruses from iron particles. BEX is a high-ionic strength enzyme digest of beef protein and has been shown to effectively detach viruses adsorbed to various surfaces (*42*). The bottle was then shaken at 5 °C for 30 min and concentrations of viable viruses in BEX were measured. Controls (without iron) were set up in an identical fashion to assess any background adsorption and/or inactivation of the viruses during the experiment.

Column Experiments. Column experiments were conducted to evaluate the effectiveness of iron to remove viruses from water under continuous, saturated flow conditions and over an extended operation time. The experiment was performed using a setup (Figure 1) similar to that in our previous studies (*43, 44*). Two identical glass chromatography

columns of 3.8-cm i.d. and 10-cm length were used. The control column was wet-packed with oxide-removed sand by pouring sand into an AGW-filled column at 1-cm increments while stirring with a glass rod to remove any attached air bubbles (*43*). The iron column was packed in a similar manner with 3 cm of oxide-removed sand followed by 7 cm of 1:1 (v/v) mix of oxide-removed sand and Peerless iron particles. The iron mass in the packed iron column was approximately 150 g.

Each column was flushed with 10 pore volumes (10 PVs) of autoclaved and degassed AGW at a flow rate of 0.5 mL/min. The flow rate was then increased to 1 mL/min and flushing was continued for another hour to establish a steady-state flow condition prior to virus introduction. This gives a residence time of 41 min in the sand column and 58 min in the iron column. Given the iron content of 35 vol %, the effective contact time with iron in the iron column was 20 min.

For each pulse test, a solution containing ~10^5 pfu/mL each of ϕX174 and MS-2 and 50 ppm of bromide was introduced into both columns at approximately 1 mL/min for 5 PVs using a peristaltic pump. Effluent samples from both columns were collected in 6-mL tubes at 5-min intervals (i.e., 5 mL of sample/tube) using a fraction collector. After the 5-PV slug input, the influent was switched back to the virus-free background solution (sterilized, degassed, and pH-adjusted AGW), and effluent samples were collected for another 5 PVs. Pumping of the background solution was continued at ~1 mL/min for 10 days (>320 PVs) before the second pulse test was conducted. The effluent concentrations of the viruses and bromide were determined by the plaque assay and ion chromatography (Doinex, Sunnyvale, CA), respectively.

Results and Discussion

Batch Experiments. Figure 2 shows the removal of MS-2 and ϕX174 from the solution in batch reactors containing 1.0 g of iron particles. The aqueous concentrations of viable MS-2 and ϕX174 decreased continuously over 2 h, and the removal appeared to follow first-order kinetics. In contrast, in the absence of iron, no removal of either virus was observed at 5 °C during the same time period (data not shown). This indicates that both viruses were removed from solution by iron particles. Result of the BEX recovery test shows that only 0.13% of the MS-2 and 0.16% of the ϕX174 adsorbed were viable and could be recovered from the iron particles. Therefore, most of the viruses removed from solution were either irreversibly adsorbed or rendered noninfective. Using eq 1, the first-order rate constants for MS-2 and ϕX174 removal at pH 7.5 were estimated to be 0.0231 ± 0.0038 and 0.0130 ± 0.0020 min^{-1}, respectively.

$$\ln [\text{virus}] = \ln [\text{virus}]_o - k_1 t \quad (1)$$

In eq 1, [virus] is the infective virus concentration in solution at time t, $[\text{virus}]_o$ is the initial virus concentration measured before iron addition, and k_1 is the apparent first-order virus removal rate constant.

Because removal of virus from water by iron particles in a batch reactor involves multiple steps, the observed first-order rate constants may reflect the rate of any one of these processes or their combination: mass transfer of virus from bulk solution to the exterior surface of an iron particle, diffusion of virus in pores within an iron particle, and adsorption of virus to a surface site. Although kinetic data for the intraparticle diffusion and adsorption of viruses are not available, it is possible to estimate the external mass transfer rate constant (k_{MT}, s^{-1}), using the procedure described by Arnold et al. (*45*). k_{MT} is the product of mass transfer coefficient (k_L, m/s) and the ratio of particle geometric surface

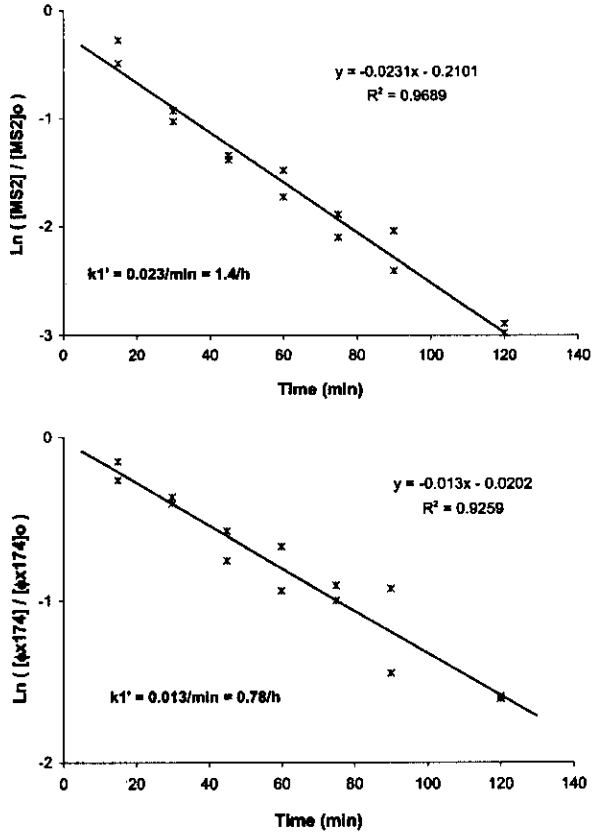

FIGURE 2. Pseudo-first-order removal of the bacteriophages MS-2 and ϕX174 in AGW in batch reactors containing 1.0 g of Peerless iron granules. Initial virus concentrations ≈ 10^5 pfu/mL. Shaking speed = 20 rpm.

area to solution volume (a, m^{-1}). If external mass transfer is slow relative to the other processes, the overall rate constant (k_1) would be comparable to k_{MT}. Conversely, if another process is rate-limiting, k_{MT} would be significantly larger than k_1.

The mass transfer between bulk solution and suspended particles in a mixed batch system is controlled largely by the velocity of the particles relative to the fluid; that is, the particles' terminal velocity (*46*). Using the semi-theoretical eq 2 (*46*, *47*) for mass transfer to spherical particles moving at their terminal velocity with a Reynolds number greater than 1, the minimum mass transfer rate coefficient (k_L^*) can be calculated, as shown below.

$$Sh = (k_L^* d_p / D_w) = 2 + 0.6\ (\text{Re})^{0.5}\ (\text{Sc})^{0.33} = 2 + 0.6\ (d_p u/\nu)^{0.5}\ (\nu/D_w)^{0.33} \quad (2)$$

In eq 2, Sh, Re, and Sc are dimensionless Sherwood number, Reynolds number, and Schmidt number, respectively, k_L^* is the minimum (uncorrected) mass transfer coefficient (m/s), d_p is iron particle diameter (~5×10^{-4} m), D_w is the diffusion coefficient of the viruses in water (m^2/s), u is the terminal velocity of the iron particles (m/s), and ν is the kinematic viscosity of water at room temperature (1.02E−6 m^2/s). Using a corrected Stokes' Law (*48*), the terminal velocity of iron particles (u) was calculated to be 0.18 m/s, with a corresponding Re of 87. The D_w values of the two viruses are expected to be similar because of their similar sizes. Using an assumed diameter of 23 nm for both viruses and either the Stokes−Einstein equation (*49*) or an empirical equation proposed by Wilke and Chang (*50*), D_w was calculated to be

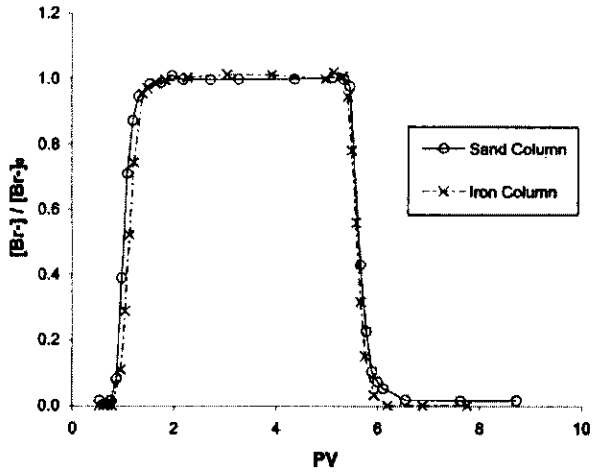

FIGURE 3. Breakthrough curves of bromide tracer from columns packed with oxide-removed sand only and oxide-removed sand plus iron granules.

2.0×10^{-11} m²/s. The Sherwood and Schmidt numbers based on this D_w are 5.4×10^{-4} and 206, respectively. k_L^* can then be calculated to be 7.8×10^{-6} m/s using eq 2. Harriott (*46*) suggested that, in a mildly stirred batch system without an impeller, the actual mass transfer coefficient (k_L) is likely to be 1.2 to 1.5 times k_L^*. Because 1.5 was used as a correction factor in an earlier study to estimate k_L and a good agreement with experimental data was observed (*45*), we used 1.5 to obtain an estimated k_L of 1.2×10^{-5} m/s. Finally, based on the iron mass (1.0 g) and liquid volume (250 mL) used, an assumed spherical particle geometry, and an estimated nominal density of 6500 kg/m³ for the iron, we calculated the geometric surface area-to-solution volume ratio (a) to be 7.4 m⁻¹. Therefore, the external mass transfer rate constant $k_{MT} = k_L a = 8.7 \times 10^{-5}$ s⁻¹, or 0.0052 min⁻¹.

This calculated k_{MT} value is a factor of 2−4 lower than the apparent removal rate constants for MS-2 and ϕX174 (Figure 2). Since k_1 must be smaller than or equal to k_{MT}, this underestimation is most likely due to the assumptions and uncertainties involved in our calculations, especially those related to the estimation of diffusivity D_w (since viruses are much larger and more massive than dissolved molecules) and surface area concentration a (which was probably underestimated since the iron particles were not spherical). Nonetheless, the estimated k_{MT} argues that external mass transfer was probably the rate-limiting process that controlled the overall rate of virus removal from solution in our batch reactors.

Column Experiments. The bromide breakthrough curves from the sand column and the iron column are shown in Figure 3. The two breakthrough curves essentially overlap, indicating that the water flow conditions in both columns are very similar. These curves are well-described by the equilibrium convection−dispersion equation (*51*), indicating that there was no physical nonequilibrium in either column. Using the bromide breakthrough data, we calculated the pore volumes of the sand and iron columns to be 41 and 58 mL, respectively.

The breakthrough curves of MS-2 and ϕX174 from the sand column and the iron column are shown in Figure 4. Although MS-2 was retained slightly in the sand column, as indicated by the greater tailing than the bromide tracer breakthrough curves, complete breakthrough of MS-2 was observed in both pulse tests, with 108% and 94% recovery, respectively. ϕX174 was retained more significantly than MS-2, with approximately half of the input viral particles retained in the sand column (49% and 42% recovery from the two pulse tests, respectively). Similar retention of ϕX174 by the same type of sand has been found to be reversible, and adsorbed ϕX174 could be recovered completely when eluted with beef extract solution (*43*). While the mechanism for the more pronounced retention of ϕX174 by clean sand is unclear, it may be related to the higher pH_{iep} of ϕX174 (6.6) than MS-2 (3.9). The higher pH_{iep} probably resulted in a lower net negative charge of ϕX174 than MS-2 in AGW (pH 7.5) and thus a weaker electrostatic repulsion between ϕX174 and sand particles, which could be overcome more easily by the van der Waals attraction. Although MS-2 and ϕX174 behaved differently in terms of their retention in the sand column, the overall removal of both phages by clean sand was limited.

In sharp contrast, the breakthrough concentration of MS-2 from the iron column in the first pulse test, conducted shortly after packing, was only about 0.01% of the influent concentration, barely above the limit of quantification (10 pfu/plate) for the plaque assay. The breakthrough concentration of MS-2 in the second pulse test conducted 10 days later was even lower, with all data points more than 10 times below the limit of quantification. These breakthrough concentrations correspond to 4-log (i.e., 99.99%) removal of MS-2 by Peerless iron in the first pulse test and more than 5-log (>99.999%) removal in the second test after 320 PVs of AGW had passed the iron column. The breakthrough curves of ϕX174 tell essentially the same story: Removal of ϕX174 by iron in the first pulse test was approximately 4-log and increased to over 5-log in the second pulse test after passage of 320 PVs of AGW. If we assume first-order kinetics (eq 1) for virus removal in the iron column, a 4-log removal would correspond to a rate constant of 0.3 min⁻¹ in the (7-cm) section of the column that contained 50% Peerless iron.

The virus removal in the iron column most likely occurred via interactions with the iron oxides, such as magnetite and maghemite, present in the iron. Adsorption and inactivation of viruses by iron oxides, as well as other metal oxides, have been widely reported. Murray and Laband (*52*) found that poliovirus was adsorbed to aluminum and iron oxides. Both magnetite and hematite have been shown to adsorb a variety of viruses (*28, 53, 54*). In field and laboratory experiments, Ryan et al. (*11*) observed inactivation of the viruses MS-2 and PRD1 on the surface of iron oxide-coated quartz sand. In our previous study using oxide-removed sand and Ottawa sand containing metal oxides (identified as primarily goethite), we found significant differences in the transport and survival of MS-2 and ϕX174 (*27*). In a recent study using goethite-coated sand, we further showed that 90% of MS-2 and 95% of ϕX174 were removed (*55*) and the removal was due mainly to inactivation rather than reversible adsorption (*27, 55*). The additional 1- to 2-log removal in the second pulse test was most likely due to formation of new iron oxides (i.e., new adsorption sites) resulting from corrosion of zerovalent iron during the 10-day period. Although removal via filtration could not be completely excluded, it was probably negligible since the iron column had a higher porosity than the sand column, where virus removal was minimal, and no pressure buildup or flow rate reduction was observed over this period.

To our knowledge, this is the first demonstration of biological agent removal from water by zerovalent iron. The batch experiments show that removal of two bacteriophages by commercial iron was rapid, with rates approaching the limit of external mass transfer. The removal appeared to be largely due to irreversible adsorption or inactivation of the viruses. The column study illustrates that in a flow-through system, over 5-log removal of both viruses could be achieved within an effective contact time with iron of 20 min. Furthermore, the column data suggest that, as water flowed through the iron column, new iron (oxyhydr)oxides were formed continuously to serve as new adsorption sites, and

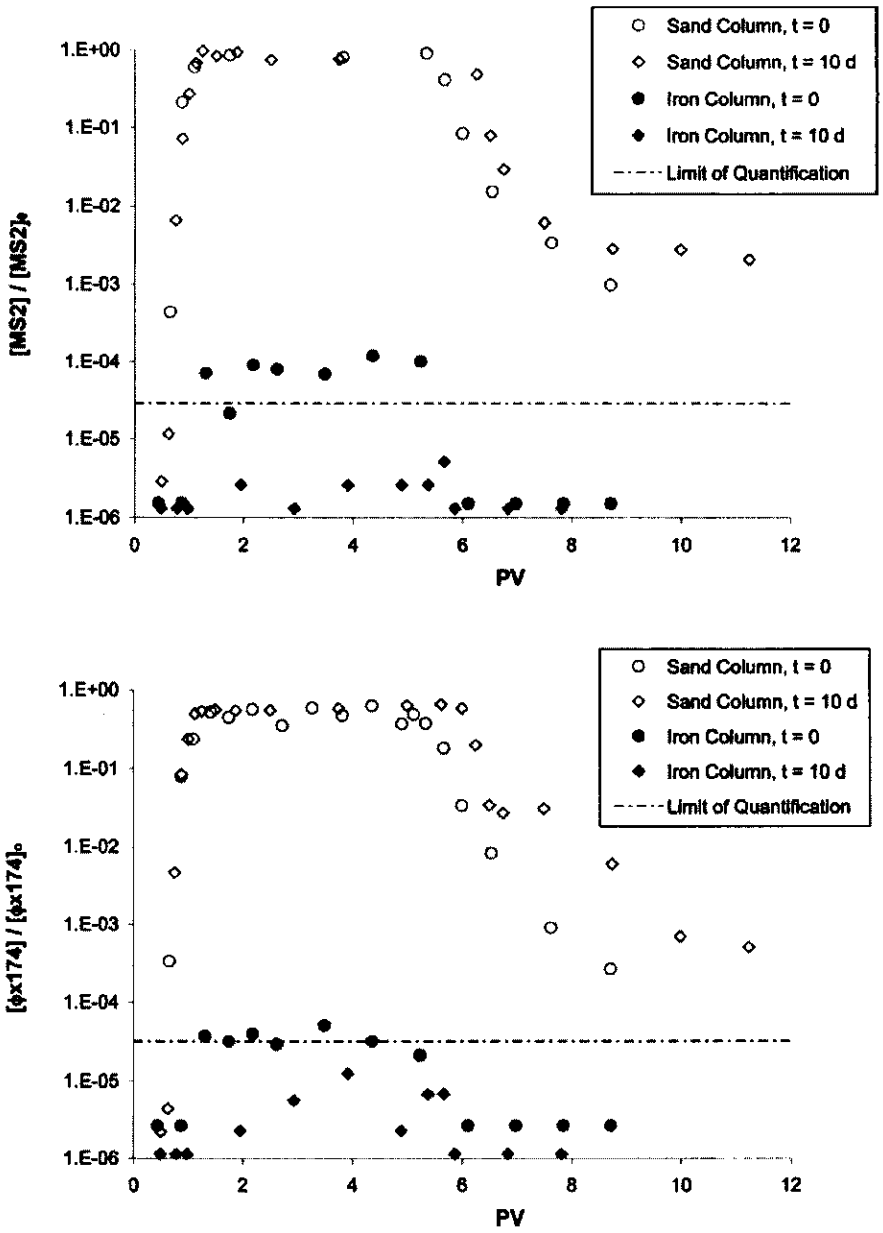

FIGURE 4. Breakthrough curves of MS-2 and φX-174 from sand and iron columns in two pulse tests conducted shortly after packing ($t = 0$) and after passage of over 320 PVs of AGW ($t = 10$ d). The limit of quantification corresponds to 10 pfu/plate of undiluted sample. Note that when a sample produced zero plaque, a calculated virus concentration corresponding to 1 pfu/plate was assigned for plotting purposes. These data points should be regarded as upper limits of the actual virus concentrations in the samples.

the capacity of iron to remove waterborne viruses could be sustained or even improved.

Potential Applications. These findings may have important implications for the treatment of water and wastewater. The greatest challenge facing the water industry and regulatory agencies today is, arguably, how to simultaneously control microbial pathogens, disinfection byproducts (DBPs), and residual disinfectant in drinking water—and to do so at an acceptable cost. Chlorine is by far the most common disinfectant in the United States to control microbial pathogens, used by approximately 80% of large water treatment facilities (serving over 10 000 people) and almost all of the smaller water systems (*56*). While largely effective to remove bacteria, chlorine was found to be less effective against viruses and protozoa (*16, 17*). Disinfection with chlorine also has many serious drawbacks, including formation of toxic DBPs, such as trihalomethanes and haloacetic acids, through reaction of chlorine with humic materials. In addition, accidental and deliberate release of chlorine gas can have catastrophic consequences, and is listed by the Homeland Security Council as one of the National Planning Scenarios (*57*). Moreover, some chlorine-manufacturing facilities still use mercury cell electrolysis, a process that can release large quantities of mercury. Therefore, it is desirable to minimize chlorine use and storage in water and wastewater treatment facilities and elsewhere. For these reasons, alternative disinfection technologies, such as UV and membrane filtration, have received considerable attention in recent years.

Zerovalent iron may help to disinfect water and wastewater and therefore reduce or eliminate chlorine use. For example, iron may be incorporated into a sand filter that precedes coagulation. Such an iron filtration system can predisinfect source water and may replace pre-chlorination,

which is practiced by many water treatment facilities. The corrosion products formed, namely ferrous and ferric ions, are common coagulants and can improve the efficiency of coagulation. Pretreatment of source water with zerovalent iron may enable water treatment plants to meet the disinfection goal by using lower chlorine dosage or replacing chlorine with another disinfectant such as chloramines, especially when viruses are the target agents that determine the disinfection requirement. For drinking water systems using membrane processes, zerovalent iron can help to ensure adequate removal of viruses, which are more difficult to filter out than other pathogens.

In addition to virus removal, a significant advantage of zerovalent iron is co-removal of natural organic matter, the precursor of DBPs. It has been shown that natural organic matter such as humic acid adsorbs to iron oxides (*58*, *59*). As source water flows through a medium containing zerovalent iron, iron oxides would be formed constantly through iron corrosion and humic acid would be removed from water continuously. Through removal of viruses and humic materials, iron may provide an economical option to simultaneously reduce risks associated with viral pathogens, disinfectants, and DBPs.

For wastewater treatment, zerovalent iron may also help to remove microbial agents in treated effluent and reduce chlorine use. These features, along with the ability of iron to effectively dechlorinate wastewater (*60*) and remove phosphate (*61*), strongly suggest the potential utility of zerovalent iron for pathogen, chlorine, and nutrient control in wastewater management.

While we believe this discovery represents an innovative and potentially cost-effective approach to disinfect water, much research is needed to understand the capacity and limitations of zerovalent iron and to develop this process further for large-scale applications. Among the important issues are long-term performance of zerovalent iron, its effectiveness to remove human viruses and other microorganisms such as bacteria and protozoa, and the impact of water chemistry (e.g., dissolved oxygen, pH, and buffering capacity) and constituents (humic and fulvic acids, and dissolved and suspended solids) on the functioning of iron. In addition, the exact mechanisms involved in adsorption and inactivation of viruses by zerovalent iron need to be better understood in order to ensure the robustness of the process and the safety of iron-disinfected water.

Acknowledgments

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