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Mechanisms of virus control during iron electrocoagulation–Microfiltration of surface water

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ABSTRACT

Results from a laboratory-scale study evaluating virus control by a hybrid iron electrocoagulation – microfiltration process revealed only 1.0–1.5 log MS2 bacteriophage reduction even at relatively high iron dosages (~13 mg/L as Fe) for natural surface water containing moderate natural organic matter (NOM) concentrations (4.5 mg/L dissolved organic carbon, DOC). In contrast, much greater reductions were measured (6.5-log at pH 6.4 and 4-log at pH 7.5) at similar iron dosages for synthetic water that was devoid of NOM. Quantitative agreement with Faraday's law with 2-electron transfer and speciation with phenanthroline demonstrated electrochemical generation of soluble ferrous iron. Near quantitative extraction of viruses by dissolving flocs formed in synthetic water provided direct evidence of their removal by sorption and enmeshment onto iron hydroxide flocs. In contrast, only approximately 1% of the viruses were associated with the flocs formed in natural water consistent with the measured poor removals. 1–2 logs of virus inactivation were also observed in the electrochemical cell for synthetic water (no NOM) but not for surface water (4.5 mg/L DOC). Sweep flocculation was the dominant destabilization mechanism since the ζ potential did not reach zero even when 6-log virus reductions were achieved. Charge neutralization only played a secondary role since ζ potential → 0 with increasing iron electrocoagulant dosage. Importantly, virus removal from synthetic water decreased when Suwanee River Humic Acid was added. Therefore, NOM present in natural waters appears to reduce the effectiveness of iron electrocoagulation pretreatment to microfiltration for virus control by complexing ferrous ions. This inhibits (i) Fe^{2+} oxidation, precipitation, and virus destabilization and (ii) virus inactivation through reactive oxygen species intermediates or by direct interactions with Fe^{2+} ions.

1. Introduction

Disinfection of contaminated waters to reduce enteric diseases continues to be one of the most important aspects of drinking water purification (Madaeni, 1999). Enteric viruses have been identified as causative agents for over 40% of childhood diarrhea in developing countries (Ramani and Kang, 2009). It has also been suggested that viruses are the etiologic agents responsible for the majority of unidentified outbreaks since they are typically more difficult to analyze than bacterial pathogens (Environmental Protection Agency, 2006). While microfiltration alone is highly efficient for the

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control of pathogenic protozoa and bacteria, it is not well-suited for removing viruses since they are substantially smaller than membrane pore sizes (Jacangelo et al., 1995; Madaeni et al., 1995; Urase et al., 1996; Mi et al., 2005; Pontius et al., 2009). Although sorption onto microfilters can transiently increase virus removal (Madaeni et al., 1995; van Voorthuizen et al., 2001), hydrophobic, electrostatic, and other non-specific interactions leading to their attachment onto the membrane material cannot reliably remove viruses during water purification especially during long-term (pseudo steady-state) operation. However, virus removal by microfiltration can be significantly improved by chemical coagulation pretreatment, with several studies demonstrating >99.99% or 4-log removals (as required under the Surface Water Treatment Rule) using alum or iron salts e.g. (Zhu et al., 2005b, 2005a; Fiksdal and Leiknes, 2006; Shirasaki et al., 2009). Alternately, electrocoagulation can also be employed for micro- and ultrafiltration pretreatment.

Electrocoagulation is a process in which metal-ion coagulants are directly added to the feed water by *in situ* electrochemical dissolution of an anode. The burgeoning interest in applying it for water and wastewater treatment can be attributed to its many potential advantages such as (i) portability, (ii) reduced use of corrosive chemicals, (iii) availability of optimized module configurations that have decreased energy consumption and increased capacity, (iv) suitability for use in predesigned packaged plants, and so on (Mollah et al., 2004; Cañizares et al., 2007; Moreno et al., 2009).

Electrocoagulation alone has been shown to be effective in removing oil and grease, chemical oxygen demand (COD), dyes, heavy metals, turbidity, and bacteria from drinking water and wastewaters (Chen et al., 2000; Jiang et al., 2002; Bayat et al., 2006; Cañizares et al., 2007; Lakshmanan et al., 2010; Ricordel et al., 2010; Durante et al., 2011; Wan et al., 2011). Electrocoagulation has also been combined with microfiltration and shown to be highly effective for *synthetic waters*, achieving ~90% energy savings, ~99% removals of heavy metals (Se, Pb, Zn, Cu, Cd, and As) and >99.999% removal of viruses (Zhu et al., 2005a; Mavrov et al., 2006; Ben Sasson and Adin, 2010). In contrast, iron electrocoagulation appears to be less promising for pretreating *natural waters* prior to low-pressure membrane filtration since chemical coagulation with $FeCl_3$ has consistently outperformed it. For example, significantly greater fluxes were obtained following conventional chemical coagulation compared with iron electrocoagulation during seawater ultrafiltration (Timmes et al., 2010) as well as microfiltration of surface water from an inland lake (Bagga et al., 2008). Hence, it appears that experiments using synthetic waters cannot be directly used to extrapolate and predict electrocoagulation system performance for fouling control under real-world conditions. Therefore, a study was undertaken to determine whether the excellent (>5-log) removal of viruses measured from waters devoid of NOM by iron electrocoagulation – microfiltration (Zhu et al., 2005a) could be extended to surface water containing NOM.

The icosahedral F-specific ssRNA coliphage MS2 was employed to facilitate comparisons with earlier results of virus removals by low-pressure membranes e.g. (Jacangelo et al., 1995; van Voorthuizen et al., 2001; Mi et al., 2005; Zhu et al., 2005b, 2005a; Shirasaki et al., 2009). Its small size (approx. 30 nm) and low isoelectric point (3.9) reduce steric interactions and adsorption allowing a conservative estimate of virus removal by microfilters. Further, it has been shown to be a conservative surrogate for the treatability of human viruses such as coxsackievirus and echovirus by coagulation (Mayer et al., 2008). Since MS2 specifically infects the gastrointestinal bacterium *Escherichia coli*, it also captures similarities of origin and release of human enteric viruses into the aquatic environment. Additionally, being similar in size, shape, and nucleic acid composition to hepatitis A and polio virus, MS2 is an excellent surrogate for pathogenic human enteric viruses (Havelaar et al., 1993; Grabow, 2001; Mayer et al., 2008). Finally, bacteriophages facilitate experimentation since they are not hazardous to humans, avoid the need for animal cell lines, and are relatively easy to cultivate and dispose.

The objective of this study is to determine mechanisms of virus control from natural surface water by a combined iron electrocoagulation – microfiltration process. Comparisons were also made with experimental results using synthetic water and conventional iron chemical coagulation (with $FeCl_3$) to empirically demonstrate the role of natural organic matter (NOM) in inhibiting virus control during electrocoagulation. Virus removals were evaluated in a range of iron dosages (0–13 mg/L) and at pH 6.4 and 7.5. Results reported herein are part of our larger effort aimed at evaluating novel surface water treatment processes to meet the increased demands of a growing population in the greater Houston, Texas area and combating land subsidence associated with groundwater extraction.

2. Experimental work

2.1. Virus

The double-top agar layer technique was employed for MS2 (ATCC 15597-B1) propagation using *E. coli* (ATCC 15597) as the host. *E. coli* was first cultured overnight (18–24 h) in Tryptic Soy Broth (TSB; Difco, Detroit, MI) at 37 °C and later cultured TSB was added to a fresh TSB and grown to a mid-log phase for 3–6 h also at 37 °C. MS2 stock was serially diluted in Phosphate Buffered Saline (PBS; composition 137 mM NaCl, 2.7 mM KCl, 4.3 mM $Na_2HPO_4.7H_2O$, and 1.4 mM KH_2PO_4; pH 7.5). Next *E. coli* suspension (0.9 mL) and phage dilution (0.1 mL) were mixed in 3 mL 0.5% soft overlay agar and poured onto presolidified Trypticase Soy Agar plates (TSA 1.5%, Difco, Detroit, MI). The plates were incubated at 37 °C for 24 h. Plaques numbering from 20 to 300 were counted and MS2 concentrations are reported as plaque forming units/mL (PFU/mL). For filtration experiments, 1 mL of purified virus stock was added to 450 mL of feed surface water to obtain a feed concentration of $O(10^7–10^8)$ PFU/mL. All the natural water samples were centrifuged at 5,000 g for 20 min to remove any debris before plating and propagation.

Recently, quantitative real-time PCR (qRT-PCR) is gaining prominence for virus enumeration to calculate log-removals associated with water treatment unit processes to reduce potential issues associated with virus aggregation e.g. (Langlet