In-situ electrochemical Fe(VI) for removal of microcystin-LR from drinking water: comparing dosing of the ferrate ion by electrochemical and chemical means

K. L. Dubrawski, M. Cataldo, Z. Dubrawski, A. Mazumder, D. P. Wilkinson and M. Mohseni

ABSTRACT

Harmful algal blooms (HAB) release microtoxins that contaminate drinking water supplies and risk the health of millions annually. Crystalline ferrate(VI) is a powerful oxidant capable of removing algal microtoxins. We investigate in-situ electrochemically produced ferrate from common carbon steel as an on-demand alternative to crystalline ferrate for the removal of microcystin-LR (MC-LR) and compare the removal efficacy for both electrochemical (EC) and chemical dosing methodologies. We report that a very low dose of EC-ferrate in deionized water (0.5 mg FeO_4^{2-} L^{-1}) oxidizes MC-LR ($MC-LR_0 = 10\,\mu g\,L^{-1}$) to below the guideline limit ($1.0\,\mu g\,L^{-1}$) within 10 minutes' contact time. With bicarbonate or natural organic matter (NOM), doses of 2.0–5.0 mg FeO_4^{2-} L^{-1} are required, with lower efficacy of EC-ferrate than crystalline ferrate due to loss of EC-ferrate by water oxidation. To evaluate the EC-ferrate process to concurrently oxidize micropollutants, coagulate NOM, and disinfect drinking water, we spiked NOM-containing real water with MC-LR and Escherichia coli, finding that EC-ferrate is effective at 10.0 mg FeO_4^{2-} L^{-1} under normal operation or 2.0 mg FeO_4^{2-} L^{-1} if the test water has initial pH optimized. We suggest in-situ EC-ferrate may be appropriate for sporadic HAB events in small water systems as a primary or back-up technology.

Key words | advanced oxidation, algal toxin, disinfection, ferrate, MC-LR, micropollutants

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INTRODUCTION

Cyanotoxins, released from cyanobacteria during harmful algal blooms (HABs), are of concern globally due to increasing eutrophication and global warming. Microcystins (MCs) are hepatotoxic cyanotoxins, with one variant, microcystin-LR (MC-LR), accounting for 46–99% of all MCs in HABs (Vasconcelos et al. 1996). The World Health Organization has established a guideline drinking water limit of $1\,\mu g\,L^{-1}$ MC-LR (WHO 2004), although meeting this can be challenging for conventional water treatment plants, e.g., MCs in Lake Erie left 500,000 people without drinking water in August 2014 (Tanber 2014). Chlorine alone is capable of MC-LR removal (Rodriguez et al. 2007; Acero et al. 2008),

but can lead to disinfection by-products in natural organic matter (NOM)-containing waters and lead to potential increases in toxicity due to MC-LR by-products (Kull et al. 2004; Rodriguez et al. 2008). Ozone and permanganate are capable of MC-LR oxidation (Onstad et al. 2007; Rodriguez et al. 2007), but are often not practical as back-up units for sporadic and seasonal events such as HABs. The iron-based ferrate(VI) (FeO_4^{2-}) ion has attracted recent attention as an oxidant in water treatment since it has one of the highest oxidation potentials of oxidants suitable for water treatment (Jiang & Lloyd 2002; Sharma et al. 2005), can achieve disinfection over a wide pH range (Acero et al.

2005; Zong *et al.* 2013), reduces to relatively environmentally benign ferric oxyhydr(oxides) (Jiang & Lloyd 2002; Filip *et al.* 2011), and can act as a combined oxidant, disinfectant, and coagulant in a single dose (Sharma *et al.* 2005; Yates *et al.* 2014). Applying ferrate as an oxidant has been shown to significantly reduce concentrations of micropollutants in municipal wastewater (Lee *et al.* 2009), disinfection by-product precursors (Noorhasan *et al.* 2010; Casbeer *et al.* 2013), and endocrine disrupting chemicals (Yang *et al.* 2012a). Ferrate has also been shown to be promising for MC-LR oxidation in drinking water (Yuan *et al.* 2002; Jiang *et al.* 2014a; Sharma *et al.* 2017). Most previous work on ferrate utilizes powdered chemically derived crystalline ferrate(VI) salts (e.g., K_2FeO_4). The use of electrochemical (EC) technologies to generate electrochemical ferrate (EC-ferrate) has been less explored, despite its potential as a lower cost and more convenient alternative to crystalline ferrate, since it can be produced on-demand and dosed *in situ*, making it especially useful as a back-up technology for sporadic events such as HABs or for use in small remote communities as a single-dose oxidant, disinfectant, and coagulant. Much of the EC-ferrate research focuses on the optimization of electrochemical conditions leading to a high purity precipitate salt (Yu & Licht 2008; Sánchez-Carretero *et al.* 2011; Híveš *et al.* 2016), since an efficient electrochemical pathway would be useful as an alternative to the relatively complicated wet or dry oxidation methods for producing solid ferrate salts (Jiang & Lloyd 2002). However, electrochemically produced and dried crystalline ferrate salts suffer from similar shortcomings as chemically produced ferrate salts, namely, stability issues at lower purities, logistical issues of transportation and storage as a hazardous substance, complexity in the measurement and dosing of solid salts for practical use in water treatment, and disposal requirements for reagents and electrolytes (Jiang & Lloyd 2002; Sharma *et al.* 2005). To overcome these shortcomings, aqueous ferrate ions could be electrochemically generated *in situ* in a direct or slipstream process, greatly reducing or eliminating storage, stability, and transportation concerns. Only a small number of studies have looked at the efficacy of aqueous EC-ferrate, namely, for sewage treatment (Lapicque & Valentin 2002; Jiang *et al.* 2009), sulfides, arsenic, and cyanides (Licht & Yu 2005), chromium (Sylvester *et al.* 2001), methyl mercaptan

(Yang *et al.* 2012b), phenol (Sun *et al.* 2016), and disinfection in drinking water (Jiang *et al.* 2014a). Only two studies have compared EC-ferrate to a baseline technology, namely, ferric sulfate in wastewater treatment (Stanford *et al.* 2010), and $FeClSO_4$ and poly-aluminum chloride in drinking water treatment (Jiang *et al.* 2014a). Previous studies of EC-ferrate have not investigated the impacts of pH or co-occurring solutes in treatment efficacy. Nor has there been any comparison of aqueous EC-ferrate to chemically derived crystalline ferrate, to determine the impact and viability of dosing *in situ*. Further, no study has looked at EC-ferrate as a single step oxidant, disinfectant, and coagulant, which could be especially helpful as a primary or back-up technology for small communities facing sporadic HAB events. To these ends, the objectives of our current study were to: (i) use a robust method to accurately quantify *in-situ* EC-ferrate; (ii) investigate the kinetics of removal of MC-LR by EC-ferrate and the impact of dose, dosing method, and co-occurring solutes; (iii) investigate the impact of optimum pH on the removal of MC-LR by EC-ferrate; and (iv) investigate EC-ferrate as a single step oxidant, disinfectant, and coagulant with MC-LR and *Escherichia coli* spiked NOM-containing natural water.

METHODS

Preparation of ferrate

Ferrate was synthesized by both electrochemical and chemical means for quantification of EC-ferrate and comparison of treatment efficacy. Chemical ferrate, defined here as high purity (>98%) crystalline potassium ferrate, was prepared by the method of Li *et al.* (2005), a version of the Delaude & Laszlo (1996) method. Chemical ferrate produced in the current study was tested for purity by chromite titration (Schreyer *et al.* 1950), stored in a vacuum desiccator, and re-tested for purity prior to use. For oxidation experiments, chemical ferrate was either added in crystalline form or dissolved in pH 7, 9, or 14 solutions (18 MΩ purity deionized (DI) water and reagent grade KOH solution, 45% w/w, Fisher Scientific) and used immediately. EC-ferrate was produced via iron electrolysis in alkaline conditions. Equations (1) and (2) summarize

the half-cell reactions for the anode and cathode, respectively:

$$FeO_4^{2-} + 4\,H_2O + 6\,e^- \rightleftharpoons Fe(0) + 8\,OH^- \tag{1}$$

$$6\,H_2O + 6\,e^- \rightleftharpoons 6\,OH^- + 3\,H_2 \tag{2}$$
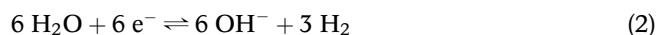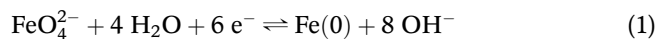
The electrochemical system was a three-electrode cell with a carbon steel anode (McMaster Carr AISI 1008, 0.10% C), stainless steel cathode, and Hg/HgO reference electrode (Figure S1, available with the online version of this paper). Carbon steel was chosen as it has been shown to have greater ferrate yield than high purity iron anodes (Mácová *et al.* 2009). The anode was kept at 10 mA cm^{-2} in galvanostatic mode (Solartron potentiostat/galvanostat) until the desired charge had passed. The solution pH was 14, and KOH was chosen as an electrolyte over NaOH due to a greater current efficiency for anodic ferrate production, as has been previously reported (Sánchez-Carretero *et al.* 2011). EC-ferrate was generated as concentrated as possible before precipitation of solids occurred, and was dosed directly into the solution (after spectrophotometric quantification) to be treated without modification to represent an *in-situ* or slipstream EC-ferrate treatment system. For practical evaluation and comparison, we chose this methodology to model realistic chemical and EC-ferrate dosing systems. Preparing identical solutions of both chemical and EC-ferrate (identical ferrate ion with identical pH and dosing methodology) would have only led to identical results, we thus chose our methodology to evaluate an online EC-ferrate system compared to a baseline crystalline chemical ferrate dosing system as accurately as possible.

Model and real waters

Model waters were composed of 18 MΩ purity DI water (Barnstead Easypure UV) with 122.0 mg L^{-1} HCO$_3^-$, 192.1 mg L^{-1} SO$_4^{2-}$ or 80.2 mg L^{-1} Ca$^+$ (as NaHCO$_3$, Na$_2$SO$_4$, and CaCl$_2$, respectively, reagent grade, Fisher Scientific), or DI water with an NOM standard (Suwannee River reverse osmosis standard, International Humic Substances Society). NOM was added at concentrations of either 1.8 or 7.2 mg L^{-1} dissolved organic carbon (DOC), measured by a UV/persulfate oxidation total organic carbon (TOC) analyzer (Shimadzu TOC-VCPH) after

membrane filtration at 0.45 μm. Initial pH was adjusted to allow a final mixing pH = 8 (Denver Instruments ATC UB-10) by NaOH or H$_2$SO$_4$ (reagent grade, Fisher Scientific), except for experiments that examined the impact of initial pH, where initial pH was varied from 1 to 14. All waters were allowed to equilibrate to 20 ± 1 °C before use, pH was monitored throughout each experiment. Tests were done both in DI water and with bicarbonate as a buffer to elucidate the impact of ferrate itself acting as a buffer when reduced (Equation (1)). MC-LR stock solution (10 mg L^{-1}) was made by hydrating MC-LR powder (Enzo Life Sciences) with 18 MΩ purity DI water and bringing testing concentrations to 10 μg L^{-1}. The stock solution was stored at 5 °C; the concentration was analyzed prior to all experiments and reformulated when the concentration dropped by >2%. Elk Lake (EL) natural water was collected from Elk Lake, Victoria, Canada as representative poor-quality (high DOC and UV$_{254}$) surface water (DOC = 6.3 mg L^{-1}; UV$_{254}$ = 0.262 cm^{-1}; pH = 6.4; alkalinity = 18 mg L^{-1} CaCO$_3$; MC-LR$_0$ < 0.01 μg L^{-1} – method detection limit). The EL natural water was also spiked with *E. coli* in select tests to determine co-oxidation and disinfection capabilities of EC-ferrate. The inocula were prepared as previously described (Chandran *et al.* 2013). Briefly, *E. coli* inocula was grown in rehydrated Tryptone Soy Broth (Hi-Media) at 37 °C for 24 hr. After incubation, the cells were concentrated by centrifugation and washed twice with sterile distilled water. Washed cell suspensions inoculated the ferrate reactors to bring the initial *E. coli* count to 1.5 × 10^4 dL^{-1}. The enumeration of culturable bacteria was carried out by serial dilution, 0.45 μm membrane filtration, incubation, and counting of colony forming units (CFUs) using a spread plate technique on Tryptone Soy Agar (Hi-Media).

Experimental and analytical techniques

All analytical reagents (Fisher/Alfa) were of reagent grade or higher. To measure removal efficacy, samples of 50–1,000 mL of MC-LR contaminated model or EL waters were placed in glass flasks on a magnetic stir plate (IKA Works) and mixed at 60 rpm with identical doses of EC-ferrate or chemical ferrate. Controls showed no loss of MC-LR by aeration or due to contact with plastic, which is known to adsorb MC-LR (Hyenstrand *et al.* 2001). Ferrate

(VI) is an identical ion in both EC-ferrate and chemical ferrate; however, because the dosing methodology of *in-situ* generation and addition of crystalline chemical was investigated for efficacy, we sought to ensure the same mixing pH between EC-ferrate and chemical ferrate. The initial pH of the model or EL water in EC-ferrate experiments was lowered with H_2SO_4 (reagent grade, Fisher) to ensure the same conditions (mixing pH = 8) for both EC-ferrate and chemical ferrate experiments. Control experiments examining the impact of pH adjustment showed no contribution to MC-LR removal. Quenching Fe(VI) to Fe(III) by addition of H_2SO_4 prior to contact with MC-LR also showed negligible removal of MC-LR by Fe(III) precipitates. MC-LR was extracted from samples by solid-phase extraction (SPE). SPE cartridges (Waters Sep-Pak C18 200 mg, 37–55 μm) were first washed with 50 mL methanol and 50 mL DI water. Samples were passed through the SPE cartridges after the allotted mixing time, liquid permeation of the supernatant in the cartridge was at 20 mL min^{-1}. Cartridges were then washed with a 9:1 water to methanol solution. MC-LR was then eluted with 3 mL methanol with 0.1% tri-fluoro-acetic acid (reagent grade, Caledon), dried to 1 mL in a nitrogen manifold, and subjected to high-performance liquid chromatography (HPLC) analysis in a method similar to other studies (Yuan *et al.* 2002; Sangolkar *et al.* 2006; Klein *et al.* 2013). A HPLC (Dionex 600, Dionex Photodiode Array Detector, PDA-100) was equipped with a constant-flow pump and variable-wavelength UV detector operated at 240 nm. The separation was performed on an Acclaim-120 C_{18} (I.D.4.6 × 150 mm) reverse-phase column and the mobile phase was a methanol-0.05 mol L^{-1} phosphate buffer (60:40, Sigma-Aldrich, HPLC grade, pH 3.0) (Harada *et al.* 1988). MC-LR was identified by UV spectra and retention times, which were calibrated with purified standards in methanol (CRM-MC-LR, 10.2 μM 1:1 v/v in methanol, National Research Council of Canada). Our method detection limit (MDL) was 0.5 μg L^{-1} in a 20 mL sample size, 0.1 μ L^{-1} in 100 mL, and 0.01 μg L^{-1} in 1,000 mL, with elution and detection of >98% MC-LR in all reference experiments. To quantify and monitor EC-ferrate after generation and prior to dosing, we required an accurate methodology without interference from precipitates to maintain dosing consistency in comparing to crystalline ferrate. We thus used an indirect 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS)

spectrophotometric method (Lee *et al.* 2005) and measured absorbance at 415 nm (Ultrospec 2000, Pharmacia Biotech), which was preferred to measuring absorbance directly at 510 nm for EC-ferrate due to the lower likelihood of interference from any potential co-generation of iron oxyhydr-(oxides), as well as higher molar absorptivity to avoid exceeding the buffering capacity due to the highly alkaline solutions of EC-ferrate (Rush *et al.* 1996; Lee *et al.* 2005). All experiments were performed in duplicate (or triplicate for kinetics experiments), vertical error bars represent standard error in all figures. Ferrate doses in MC-LR removal experiments are reported as [FeO_4^{2-}] in mg L^{-1}. To quantify the rate of MC-LR oxidation by EC-ferrate, experimental kinetics were determined for select experiments. First, we found pseudo-first-order rates for Fe(VI) degradation in excess MC-LR, corrected for Fe(VI) self-decay, and then determined apparent second-order rate constants (k_{app}) where Fe(VI) was in excess by plotting $\ln(MC\text{-}LR/MC\text{-}LR_0) = -k_{app} \int_0^t [Fe(VI)]$ dt as done elsewhere (Jiang *et al.* 2014b). Stability experiments were performed at different pH values of concentrated EC-ferrate solution, adjusted by H_2SO_4 (reagent grade, Fisher Scientific), and monitored by the ABTS method.

RESULTS AND DISCUSSION

Quantification of EC-ferrate

EC-ferrate quantification was calibrated by the ABTS method, seen in Figure 1. This calibration was done to ensure that the dose of EC-ferrate to make an accurate comparison with crystalline ferrate was known. The ABTS
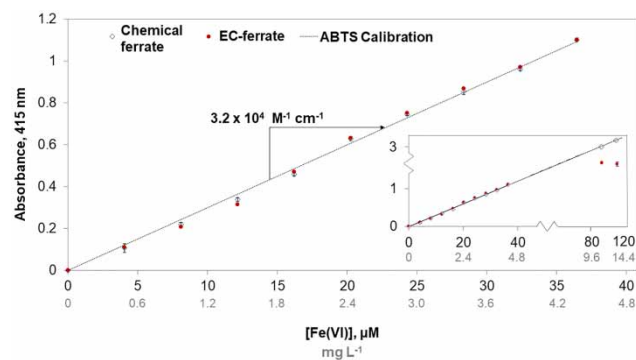

Figure 1 │ Quantification of EC-ferrate with ABTS; inset: showing breakdown of linearity at higher concentrations of EC-ferrate.

method measures Fe(VI) selectively, and forms a green radical cation ABTS•+ that is measured spectrophotometrically at 415 nm (Lee *et al.* 2005). Our calibration curve was created with high-purity potassium ferrate (>98%) corrected for purity by chromite titration (Schreyer *et al.* 1950), giving a slope of $3.2 \times 10^4 \, M^{-1} \, cm^{-1}$ ($R^2 > 0.99$), similar to the previous reported slope of $3.4 \times 10^4 \, M^{-1} \, cm^{-1}$ (Lee *et al.* 2005) for crystalline ferrate. The agreement suggests that the higher pH of the EC-ferrate solution did not impact the resulting ABTS oxidation to ABTS•+ at [Fe(VI)] below 4.4 mg L^{-1}, excess OH^- in the EC-ferrate electrolyte was neutralized by the pH 4.2 buffer system (Lee *et al.* 2005). At higher concentrations of EC-ferrate (>9.6 mg L^{-1}), EC-ferrate no longer followed the linear ABTS calibration curve, showing significantly lower absorbance than expected (see inset in Figure 1). This was likely due to the higher pH at greater concentrations and lower availability of ABTS (Lee *et al.* 2014), causing a significant decrease in Fe(VI) reactivity. For this reason, we suggest quantification of EC-ferrate by series dilution until [Fe(VI)] is below 9.6 mg L^{-1}. This allowed us to quantify the EC-ferrate generated in our electrochemical reactor (Figure S1) in the ranges of 400–600 mg L^{-1} (measured as $[FeO_4^{2-}]$), and indicated that the faradaic current efficiency of EC-ferrate was approximately 40% (calculated as the ratio of actual charge that oxidized Fe(0) to Fe(VI) compared to the theoretical value in Equation (1)). Furthermore, this allowed direct quantification instead of crystallization and purification, during which some loss of ferrate would be likely. We also found that the ABTS method provided greater accuracy than colorimetric quantification (especially at higher EC-ferrate concentrations >9.6 mg L^{-1}) since the EC-ferrate solution is diluted by approximately three orders of magnitude before spectrophotometric analysis, reducing interference by anodically co-generated iron oxyhydr(oxides) (Dubrawski *et al.* 2015) or other constituents in natural water. This also allowed high quantification accuracy when comparing low doses of EC-ferrate to crystalline ferrate in our study.

Oxidation of MC-LR in DI water and impact of co-occurring solutes

Results of MC-LR oxidation experiments in DI water show high levels of removal with low doses of EC-ferrate (>99%

removal with MC-LR$_0$ = 10 µg L^{-1}, $[FeO_4^{2-}]$ = 0.5 mg L^{-1}), shown in Figure 2(a). For both the EC-ferrate and chemical ferrate dosing methods, MC-LR removal to 1 µg L^{-1} was observed with 0.5 mg L^{-1} ferrate (after 10 minutes' contact time) and 1.0 mg L^{-1} ferrate (after 5 minutes' contact time). MC-LR reduction seen here is consistent in DI water with other studies using crystalline (chemical) ferrate (Yuan *et al.* 2002; Jiang *et al.* 2014b). EC-ferrate was slightly less effective than chemical ferrate – despite identical Fe(VI) ion concentration, contact time, and mixing pH. This difference can be explained by the differential pH between the ferrate solution and the test water to which it is added. The EC-ferrate concentrate had a higher pH than the chemical ferrate solution (due to alkaline electrochemical generation), thus the test water to which it was added
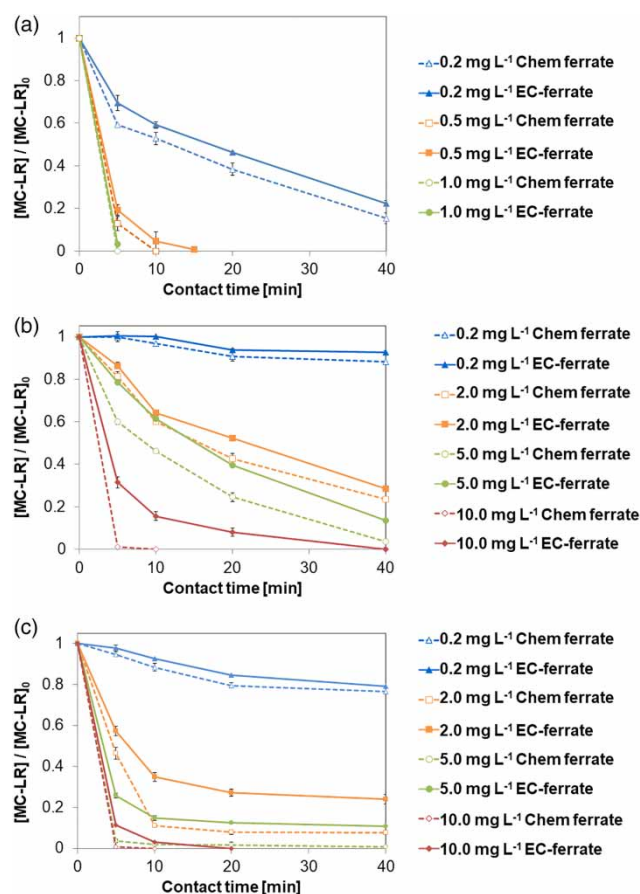
Figure 2 │ Kinetic rate experiments of MC-LR oxidation by EC-ferrate and chemical ferrate in synthetic test water. [MC-LR]$_0$ = 10 µg L^{-1}, guideline limit is [MC-LR]/[MC-LR]$_0$ = 0.1 (1 µg L^{-1}) for (a) DI water, (b) 122.0 mg L^{-1} HCO$_3^-$, (c) [DOC$_0$] = 1.8 mg L^{-1}.

required a lower pH value to ensure the same mixing pH, necessitating an initial pH difference between chemical ferrate and EC-ferrate test waters. The greater pH differential in EC-ferrate caused some Fe(VI) to oxidize water and undergo rapid reduction to a Fe(III) hydr(oxide) species, as noted elsewhere (Lee *et al.* 2002; Yuan *et al.* 2002), instead of oxidizing MC-LR. This led to the slightly lower MC-LR removal observed with EC-ferrate – the effect of this pH differential is further discussed in subsequent sections. Experiments with chemical ferrate dissolved at a higher pH produced almost identical results to EC-ferrate, supporting our hypothesis, and suggesting there was little error in our quantification of EC-ferrate by the ABTS method. In DI water, for $MC-LR_0 = 10\ \mu g\ L^{-1}$, $k_{app} = 3.2 \pm 0.05 \times 10^2$ $M^{-1}\ s^{-1}$ for EC-ferrate and $3.6 \pm 0.02 \times 10^2\ M^{-1}\ s^{-1}$ for chemical ferrate (pH = 8). These were both greater values than the only reported rate constant for MC-LR and ferrate, where k_{app} was reported as $\sim 1 \times 10^2\ M^{-1}\ s^{-1}$ for pH 7.5 (Jiang *et al.* 2014b).

A lower mixing pH likely contributed to the faster kinetics seen in our experiments, since faster kinetics are generally reported for ferrate at lower pH values (Lee & Gai 1993). Jiang *et al.* (2014b) also used a test water with 300 times greater initial MC-LR, which would substantially contribute to the slower second-order rate kinetics. Alternatively, the phosphate buffer used by Jiang *et al.* (2014b) may have slowed MC-LR oxidation, as phosphate has been shown to sequester ferrate products and retard decomposition (Jiang *et al.* 2015). The impact of common co-occurring solutes (sulfate, calcium, bicarbonate, and NOM) on MC-LR oxidation is shown in Figure S2 (available with the online version of this paper) at $[FeO_4^{2-}] = 1.0\ mg\ L^{-1}$. Little impact on MC-LR oxidation was seen with the addition of sulfate or calcium, whereas bicarbonate and NOM showed significant reduction in removal; we thus focused subsequent experiments on bicarbonate and NOM only, which are shown in Figures 2(b) and 2(c). Our results show a more significant impact with bicarbonate than reported elsewhere (Jiang *et al.* 2014b). However, Figure 2(b) shows data using a dose of $[FeO_4^{2-}] = 1.0\ mg\ L^{-1}$, while Jiang *et al.* (2014b) used a dose of $[FeO_4^{2-}] = 5.0\ mg\ L^{-1}$. At $[FeO_4^{2-}] = 5.0\ mg\ L^{-1}$, we found >90% reduction in MC-LR, which was consistent with previous work. Kinetics of MC-LR oxidation were

significantly slower in the presence of bicarbonate ($k_{app} = 12.2 \pm 0.02\ M^{-1}\ s^{-1}$ for EC-ferrate). Slower kinetics were not likely a result of direct Fe(VI) scavenging by bicarbonate, as seen with UV-based MC-LR removal by OH radicals (Pelaez *et al.* 2011), but can instead be explained due to the stabilizing effect of bicarbonate on the Fe(VI) decomposition product of Fe(III), which reduces the autocatalytic activity of Fe(VI) (Jiang *et al.* 2015). NOM also had a significant impact on MC-LR oxidation, even a modest concentration ($DOC_0 = 1.8\ mg\ L^{-1}$, Figure 2(c)). The significant impact of NOM on MC-LR removal ($k_{app} = 47.1 \pm 0.05\ M^{-1}\ s^{-1}$ for EC-ferrate for $DOC_0 = 1.8\ mg\ L^{-1}$) was likely due to both ferrate oxidation of NOM, which acts as a ferrate scavenger (Jiang *et al.* 2014b), and NOM stabilizing freshly formed Fe(III) colloids (Jiang *et al.* 2015), retarding decomposition similarly to bicarbonate. DOC removal was 34% and 36% for chemical ferrate and EC-ferrate, respectively ($DOC_0 = 1.8\ mg\ L^{-1}$), while neither showed any detectable residual ferrate. The likely primary mechanism of DOC removal was via coagulation by the ferrate decomposition product of Fe(III) and resulting ferric oxyhydr(oxides) as seen elsewhere (Jiang & Wang 2003), and not NOM mineralization by ferrate. We observed iron flocs at higher ferrate doses only, whereas no flocs occurred at lower doses ($1.0\ mg\ L^{-1}$ $[FeO_4^{2-}]$) even for extended contact times. The lower MC-LR removal with EC-ferrate suggests that ferrate reduction to Fe(III) occurred more quickly than chemical ferrate, allowing less time for MC-LR oxidation, although similar DOC removal was due to similar Fe(III) concentration and coagulation products to remove NOM. Kinetics with both bicarbonate and NOM were also likely reduced due to pH buffering, as seen in other studies (Jiang *et al.* 2015). The impact of pH is further discussed in the next section. Interestingly, the test water with bicarbonate slowed kinetics to the point of approaching pseudo-zero-order. This might either be due to a rate-limiting redox interplay of Fe(V) or Fe(IV) with Fe(VI), as noted elsewhere (Lee *et al.* 2014), or due to a complexing of Fe(VI) by excess bicarbonate. While bicarbonate had an impact of only slowing MC-LR oxidation, NOM had an impact of both slowing oxidation and scavenging ferrate, as noted previously. This effect can be seen by the plateau trend in MC-LR removal after 20 minutes of contact time with NOM. Real waters with NOM may thus require

initial reduction of DOC, possibly through *in-situ* electro-coagulation using the same carbon steel anode (Dubrawski & Mohseni 2013), or conventional coagulation-flocculation (Jiang *et al.* 2016) followed by EC-ferrate.

## Impact of pH on oxidation of MC-LR

As noted in the previous sections, bulk and localized pH have a significant impact on MC-LR oxidation. The impact of initial solution pH is shown in Figure 3(a), showing that EC-ferrate has a significantly lower optimum initial pH (pH = 3 for $[FeO_4^{2-}] = 0.5$ mg L^{-1}) than chemical ferrate (pH = 5).

The difference in optimal initial pH is due to the highly alkaline EC-ferrate solution, compared to the relatively neutral stock solution of crystalline ferrate. Both methodologies' optimum initial pH result in a final mixing pH ≈ 8, similar to the optimum mixing pH other researchers found with ferrate and other pollutants (Jiang *et al.* 2007; Sharma 2011). However, the lower initial pH of the test water in the EC-ferrate experiments increases the pH differential between the test solution and the concentrated EC-ferrate; more EC-ferrate is thus lost to the localized oxidation of water upon rapid initial mixing. This explains the consistent results
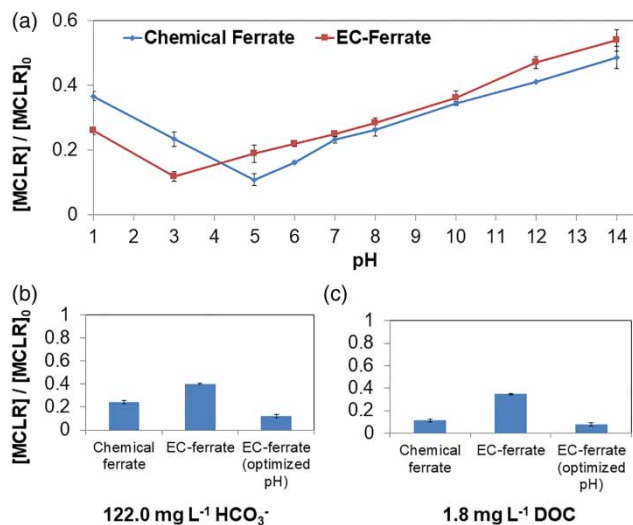
Figure 3 | (a) Impact of initial solution pH on MC-LR oxidation by EC-ferrate and chemical ferrate in synthetic test water. [MC-LR]$_0$ = 10 μg L^{-1}, guideline limit is [MC-LR]/[MC-LR]$_0$ = 0.1 (1 μg L^{-1}), ferrate dose for both chemical and EC-ferrate is $[FeO_4^{2-}] = 5.0$ mg L^{-1}; (b) impact of pH optimization on MC-LR oxidation with bicarbonate (optimized EC-ferrate initial pH = 2.5); (c) impact of pH optimization on MC-LR oxidation with NOM (optimized EC-ferrate initial pH = 3).

of slightly greater efficacy of chemical ferrate throughout our experiments. Operating at an optimum initial pH would result in some loss of EC-ferrate due to this pH differential effect, but would have the faster kinetics of MC-LR removal at lower pH. Engineered treatment systems could thus have an operational choice of using less EC-ferrate with an optimized pH, or more EC-ferrate without adjusting initial pH, depending on the capability of the system and the size of community served. Figures 3(b) and 3(c) show the impact of optimizing initial pH in the presence of bicarbonate and NOM, respectively. Optimizing initial pH showed significant improvement of EC-ferrate efficacy compared to chemical ferrate, with an additional 11% and 2% removal of MC-LR by EC-ferrate in the presence of bicarbonate and NOM, respectively. The impact of pH buffering from bicarbonate and NOM was also reduced due to the pH adjustment in the optimized-pH EC-ferrate system, which overwhelmed their proton buffering capacity and led to the faster observed kinetics. These results indicate that, in systems where pH adjustment of initial water is feasible (e.g., smaller volumes of water in small systems with appropriate infrastructure), EC-ferrate can perform better than chemical ferrate, and require less ferrate input. However, as seen in Figure 3(b), buffered waters have a similar optimum mixing pH ≈ 8, but may require even greater initial pH reduction (initial pH = 2.5 for 122.0 mg L^{-1} HCO$_3^-$), limiting the practicality of optimizing initial pH for these waters. Other waters of low initial pH (e.g., acidic industrial wastewaters) might also utilize alkaline EC-ferrate without initial pH adjustment. These specific application instances may remain niche circumstances – suggesting efficient generation of EC-ferrate in neutral solutions is likely required for widespread use. However, the undesirable aspects of neutral generation persist: the higher oxidation potential of ferrate would lead to more oxidation of water (Lee *et al.* 2014) and faster self-decay (Lee & Gai 1993), both reducing the $[FeO_4^{2-}]$ available to oxidize MC-LR. Oxidation of water by the ferrate ion is the reason it is not possible to simply adjust the pH of the EC-ferrate solution after generation – Figure 4(a) shows the impact of changing the pH of the concentrated alkaline EC-ferrate solution. The reduction in ferrate concentration is significant – adjusting the initial pH of the EC-ferrate concentrate from 14 to 12.2 reduces $[FeO_4^{2-}]$ by over 60% due to water oxidation.
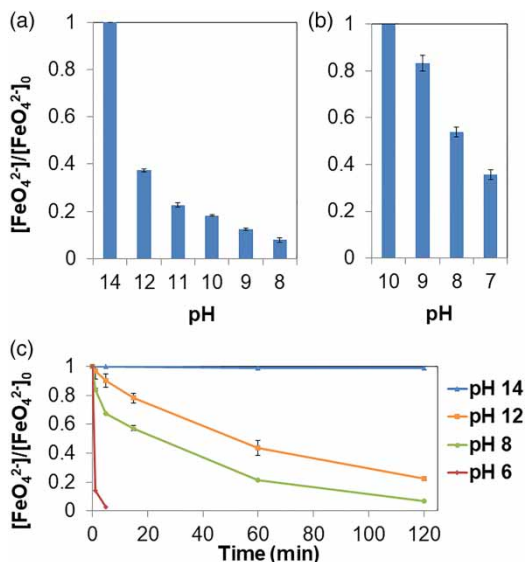
Figure 4 | (a) Impact of pH on concentrated EC-ferrate $[FeO_4^{2-}]_0 = 591.4$ mg L^{-1}; (b) impact of pH change on dilute EC-ferrate, $[FeO_4^{2-}]_0 = 2.0$ mg L^{-1}; (c) impact of pH on EC-ferrate stability over 120 min, $[FeO_4^{2-}]_0 = 2.0$ mg L^{-1}.

The impact was slightly reduced, although still significant, at lower initial ferrate concentrations, as seen in Figure 4(b) at $[FeO_4^{2-}]_0 = 2$ mg L^{-1}. The rapid decrease in $[FeO_4^{2-}]$ upon lowering pH can be explained by the added H$^+$ creating a localized region of higher ferrate redox potential, allowing oxidation of H$_2$O with faster kinetics, as noted elsewhere (Lee & Gai 1993; Jiang *et al.* 2014b). Ferrate subsequently liberates OH$^-$ when oxidizing H$_2$O (Equation (1)), creating a buffering effect that maintains a high pH and effectively neutralizes any attempt at pH adjustment without significant decrease in $[FeO_4^{2-}]$. Practically speaking, adding a buffer after EC-ferrate treatment would result in a similar problem – as the buffer releases protons to compensate for the excess of hydroxide ions, ferrate would oxidize water and liberate hydroxide ions. Figure 4(c) shows the impact of pH on the stability of EC-ferrate, showing significantly higher stability at pH = 14, and almost complete reduction to Fe(III) within 5 minutes at pH = 6. These results suggest that, with generation of EC-ferrate at neutral pH, the lower stability of ferrate would require immediate dosing and rapid mass-transfer to oxidize pollutants and avoid self-decay. While generating EC-ferrate in acidic medium by oxidation of Fe(II) with boron-doped diamond (BDD) anodes has been reported (Lee *et al.* 2002), EC-ferrate produced in this low pH system would rapidly oxidize water, as the rate in

decomposition of ferrate is approximately three orders of magnitude faster at pH 1 compared to pH 7 (Rush *et al.* 1996). Thus, neutral, or slightly basic EC-ferrate would be preferable.

Efficacy in natural water spiked with MC-LR and *E. coli*

Removal of MC-LR in spiked natural water is shown in Figure 5. As observed in test waters, the NOM and alkalinity in the natural water required higher doses of EC-ferrate for adequate MC-LR removal. At a dose of $[FeO_4^{2-}] = 2.0$ mg L^{-1}, only optimized-pH EC-ferrate was capable of MC-LR removal to <1 µg L^{-1}, confirming that optimized-pH EC-ferrate can be more effective than chemical ferrate if adjusting initial water pH is feasible for the water system. As with NOM in test waters, DOC removal was similar with both chemical and EC-ferrate, iterating that NOM removal is mainly via Fe (III) coagulation. The buffering capacity of the natural water led to the decreased efficacy as seen previously with bicarbonate and NOM. Other solutes, such as carbonates and phosphates present in natural water, also suppress Fe (VI) decomposition, as seen elsewhere (Jiang *et al.* 2015). EC-ferrate also showed capability as a co-oxidant and disinfectant in *E. coli*-spiked natural water. As with MC-LR oxidation, optimized initial pH EC-ferrate showed the
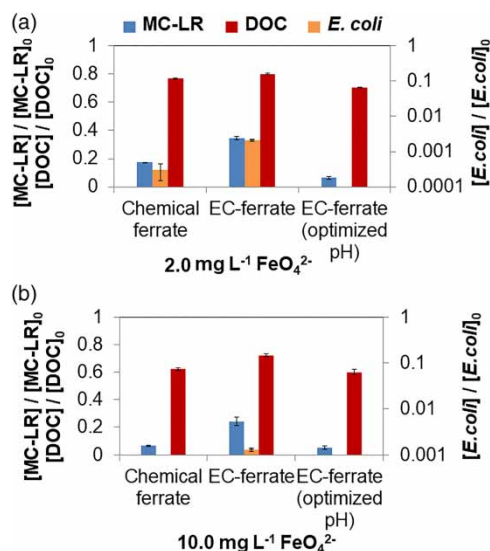
Figure 5 | (a) Co-oxidation of MC-LR ($[MC-LR]_0 = 10$ µg L^{-1}), coagulation of DOC, and inactivation of *E. coli* in natural water with EC-ferrate: (a) $[FeO_4^{2-}] = 2.0$ mg L^{-1}, (b) $[FeO_4^{2-}] = 10.0$ mg L^{-1} (optimized pH = 4).

greatest reduction (non-detect) compared to 3.5 log removal for chemical ferrate. *E. coli* inactivation was slightly less than reported elsewhere with chemical ferrate (Jiang *et al.* 2007), as the NOM and buffering capacity of the natural water in our study likely scavenged a significant amount of ferrate. In water treatment systems considering ferrate as a primary or back-up technology, *E. coli* deactivation results shown in Figure 5 suggest that EC-ferrate without initial pH adjustment may not be effective for adequate disinfection. Larger municipal systems may immediately dismiss initial pH adjustment as prohibitively expensive, whereas medium and smaller systems might consider pH adjustment due to the smaller quantities involved, or may already have pH-adjustment capabilities for coagulation.

Systems utilizing EC-ferrate as both a disinfectant and coagulant, or as an oxidant with UV disinfection (without subsequent microfiltration) may not have an adequate barrier to intracellular MC-LR. Further testing is required to determine whether EC-ferrate is capable of removing intracellular MC-LR at the same efficacy levels and kinetic rates as observed with extracellular MC-LR in this study. Further pilot testing is required to ultimately decide the feasibility of on-line EC-ferrate for MC-LR removal or co-oxidation, disinfection, and coagulation in such systems, although results here demonstrate promise that EC-ferrate, synthesized from only common carbon steel, is capable of MC-LR oxidation to $<1 \mu g L^{-1}$ in both synthetic test waters and spiked natural waters when initial pH is adjusted.

CONCLUSIONS

In this work, we investigated the use of the on-line production of electrochemically generated ferrate with a common carbon steel anode for MC-LR removal from test and natural drinking waters and compared this dosing methodology of the same ion in crystalline form. Initial water pH adjustment allowed for the highest removal at the lowest EC-ferrate dose. This was also the case for EC-ferrate as a co-oxidant/disinfectant/coagulant to simultaneously remove MC-LR, *E. coli*, and coagulate NOM. Aqueous EC-ferrate, generated in alkaline solution as described here, could be considered a simple and viable candidate for community water systems.

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