PILOT-SCALE IRON ELECTROCOAGULATION FOR NATURAL ORGANIC MATTER REMOVAL

Avskiljning av naturligt organiskt material med järnelektrokoagulering i pilotskala

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Abstract

A scaled-up, continuous iron electrocoagulation reactor was built for drinking water treatment research. The impact of current density (*i*), metal loading (ML) and inter-electrode gap (δ) on the removal of natural organic matter (NOM) was studied at 1.35 L/min. Removal performance was evaluated using UV-abs-254 and DOC analysis. Larger δ provided the greatest reductions in DOC. When considering UV-abs-254 analysis, the largest and smallest δ , 10 and 1 mm respectively, provided the greatest reductions. The effects of *i* on DOC and UV-abs-254 yielded the least clear results; however, it could be surmised that lower *i* provided greatest reductions of both DOC and UV-abs-254. The parameters providing the most substantial reduction on both DOC and UV-abs-254 reductions was ML. At the highest ML, both reductions in DOC and UV-abs-254 were observed, however continued work must be dedicated to further reducing the latter. Although DOC reductions were observed at ML < 51.1 mg/L, increased absorbance was observed through all factors and treatments. These increased absorbance results are due to dissolved iron species introduced during the EC process and present during UV-spectrophotometric analysis.

Key words - Electrocoagulation; water treatment; natural organic matter; pilot-scale; iron; coagulation

Sammanfattning

I denna artikel användes en uppskalad försöksreaktor med järnelektrokoagulering för att producera dricksvatten med järnelektrokoagulering. Påverkan av strömtäthet (*i*), metallbelastning (ML) och elektrodavstånd (δ) på avskiljning av naturligt organiskt material (NOM) studerades vid ett flöde av 1,35 L/min. Avskiljningen utvärderades med UV-abs-254 och DOC-analys. Större δ gav den största reduktionen av DOC. För UV-abs-254, den högsta och minsta δ , 10 och 1 mm, gav den största reduktionen. Effekten av *i* på DOC och UV-abs-254 gav ett något oklart resultat, men antagligen ger en lägre *i* störst reduktion av både DOC och UV-abs-254. Parametern som gav högst reduktion av både DOC och UV-abs-254 var ML. Vid den högsta ML var reduktionen av både DOC och UV-abs-254 störst, men mer forskning behövs för att studera hur man ytterligare kan reducera den senare. Fastän DOC-reduktion observerades vid ML < 51.1 mg/L så observerades en ökning i absorbansen för alla typer av behandling. Dessa resultat beror på en ökning av löst järn under EC-processen som påverkar analysen med UV-spektrofotometri.

Introduction

Canada is a vast country with an endless array of geographies including semi-arid desserts, coastal islands, mountain ranges and deciduous rainforests. Although the major city centers, like Vancouver and Toronto, have access to clean, treated drinking water, a large number of boil water advisories are a reality for the small and remote communities distributed throughout the country. In 2013, 80% of the issued boil water advisories were for drinking systems provided to communities of 500 people or less (Environment Canada). Moreover, 74% of those advisories were put in place as a precautionary measure due to equipment or treatment issues (Environment Canada). The equipment and process issues that propagate this inordinate amount of advisories can be distilled into numerous aspects. One such aspect involves the appropriateness and applicability of traditional water treatment technologies to unconventional applications (i.e., small-scale and inaccessible communities). The inaccessibility of the remote communities presents difficulties for supplying the needed chemicals involved in the treatment process, as well as the need for skilled operators to oversee the treatment process. One such water treatment unit process requiring a constant supply of chemicals and operator supervision is coagulation. It is for this reason that alternative processes are needed in order to simplify the process and minimize or eliminate the chemical supply chain necessary for current water treatment practices in remote communities. One such alternative technology is electrocoagulation (EC), which utilizes an electrochemical process to produce chemical coagulants in-situ on demand.

Electrocoagulation

In current water treatment practices, the most common process to remove dissolved organics is by coagulation and flocculation followed by sedimentation and/or filtration (Crittenden *et al*, 2012). The coagulation process involves the addition of coagulant chemicals, usually iron or aluminum based, to water. These coagulants compress the diffuse layer of the charged dissolved and undissolved contaminants present in the water. The particle-particle electrostatic repulsion is minimized due to the compression of the diffuse layer of the contaminants, whereby Van der Waals forces begin to predominate and promote particle-particle attraction (Mollah, 2001).

Electrocoagulation (EC) is an alternative treatment technology to conventional chemical coagulation, which operates under the same fundamental principles described above. EC is comprised of one or more electrochemical cells containing sacrificial metal anodes and inert cathodes in the water to be treated. By use of an external DC power supply, current is passed through the electrochemical cell initiating the slow dissolution of metal cations (Me^{z+}) into the solution (R.1) at the anode-solution interface. On the cathode side, the electrolysis process reduces water molecules to hydroxide anions (OH^{-}) and hydrogen gas (H_2) (R.2). Metal cations and hydroxide anions interact and combine to form metal oxides and hydroxides, collectively referred to as metal hydr(oxides). These metal hydroxides function as coagulant species in the EC process.

Anode: $Me_{(s)} \rightleftharpoons Me_{(aq)}^{z+} + ze^{-}$ (R.1)

Cathode: $x_w H_2 O_{(l)} + ze^- \rightleftharpoons y_H H_{2(g)} + zOH_{(aq)}^-$ (R.2)

Coagulant:
$$Me_{(aq)}^{z+} + zOH_{(aq)}^{-} \rightleftharpoons Me(OH)_{z(s)}$$
 (R.3)

As more electrical current is provided to the system, the dissolution of metal cations also increases and therefore the dosing of coagulant. The term metal loading (ML) describes the dosing of coagulant, and can be determined using Faraday's Law (E.1.):

$$ML = \frac{\varphi \cdot I \cdot MW}{Q \cdot z \cdot F} \tag{E.1}$$

where φ , *I* and *MW* respectively represent the current efficiency, operating current and molecular weight of the anode metal. The denominator terms *Q*, *z* and *F* represent the operating flowrate, the number of transferred electrons and Faraday's constant (96,485 C/mol·e⁻), respectively.

The predominating published EC research has been focused around two metal types: aluminum (Al) and iron (Fe). Although both metal types have been shown to be effective for the removal of a number of contaminants, some research has suggested that Fe provides the lowest residual metal concentration post-EC (Dubrawski et al, 2013b). Iron has also shown to be superior to Al and Zn by yielding greater removal of NOM (Dubrawski, 2012). Moreover, when compared to Al and Zn, iron is the least costly and most available material. In total, there are 16 different iron hydr(oxides) species (Cornell et al, 2003), each having a varying affinity to function as a coagulant chemical. There are several factors that can influence the selectivity of an EC process to predominantly produce one species in greater quantities than others. These factors include anode potential, pH, temperature, dissolved oxygen, the [Fe(II)]:[Fe(III)] ratio, and co-occurring solute concentration and ratios (Dubrawski et al, 2013a).

A higher level of complexity is associated with electrocoagulation when implemented into a drinking water treatment process due to the inherently low conductivities of most surface waters. Low water conductivity correlates to a greater electrical resistance through the water, therefore requiring higher operating potentials and power consumption. This relationship is mathematically described by Ohm's Law:

$$I = \frac{V}{R} \tag{E.2}$$

where R represents the resistivity of the water, I is the applied current, and V is the potential. As opposed to wastewater and brine water treatment processes, which are either highly ionic or can be made to be, drinking water treatment processes cannot increase ion concentrations as they would need to be removed downstream.

EC for drinking water treatment has been an area of interest for many researchers, with many investigations involving Al and Fe electrocoagulation. Successful Al electrocoagulation for defluoridation and the effects of

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temperature, *i* (Mameri et al, 1998), charge loading and pH (Zhu et al, 2007) has been achieved by other researchers. A significant body of work has also been contributed in the area of Fe EC for drinking water treatment. In particular, the removal of arsenic from groundwater and the effects of competitive co-occurring solutes such as phosphate, silicate and bicarbonate was researched (Addy, 2008). The research yielded promising results for the effectiveness of arsenic removal, reducing high concentrations of arsenic laden groundwater from Bangladesh to World Health Organization safety standards. Thorough research has also been conducted in the area of NOM removal by means of Fe electrocoagulation. Studies investigating reactor design parameters (*i* and charge loading rate) for NOM removal in a bench-scale batch reactor found a decrease in current efficiency with an increase in *i*, negatively affecting NOM removal (Dubrawski et al, 2013c).

Other relevant research investigated the iron hydr(oxide) speciation phenomena during an EC process on natural waters, where species where identified in-situ using Raman spectrophotometric analysis. In particular, the impact of *i*, charge loading rate and dissolved oxygen on speciation was investigated. The three most predominate iron species were identified to be green rust (GR), lepidocrocite and magnetite. GR speciation occurred at low current density, while magnetite was found to predominate during processes at high current density. All other conditions yielded the formation of lepidocrocite. Further analysis compared the varying effectiveness of the three species as a coagulant chemical. It was suggested that GR is a preferred iron species due to its ability to most effectively reduce NOM concentrations (Dubrawski et al, 2013a).

Natural Organic Matter

Methods

A problem communities using natural surface waters as a source for drinking water often face is natural organic matter (NOM), which is the product of degrading plant and animal matter. Although NOM is not an acutely harmful contaminant, it is considered to be a disinfection by-product (DBP) precursor. DPBs such as trihalomethanes and haloacetic acids are formed during chlorine disinfection, a common unit operation in drinking water treatment facilities. It is these DPBs that are potentially harmful and hence are subject to increasingly stringent regulations.

The efficacy of EC as a potential alternative to chemical coagulation for specialty markets such as small and remote communities was investigated using a thorough

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scale-up process. These efforts included a systematic factorial design approach in order to fully understand the processes' ability to remove the target contaminant, NOM. The primary research involved scaling up the iron electrocoagulation process, while understanding the process in a continuous operating mode and gaining a thorough knowledge of NOM removal efficiency. In order to do so, three operating parameters were varied: *i*, ML and δ . A knowledge of the process power and energy requirements was also attained through the monitoring of electrical potential data for all experiments. Finally, operational conditions effects on the downstream process of flocculation were determined.

A pilot-scale continuous reactor was built to accommodate 10 L/min. The reactor incorporated a baffled inlet to ensure well-distributed flow through all of the electrochemical cells. Synthetic water was composed of distilled water and humic acid (HA) at 40 mg/L, corresponding to an initial DOC of ~10 mg/L and UV-abs-254 of 1.01 cm⁻¹. Given the large-scale operations of the research, HA was used as a surrogate species to NOM. This is a reasonable substitution because NOM is primarily composed of humic and fulvic substances and its similar chemical structure to NOM. Two-liter samples were collected at the outlet of the unit after steady-state operations had been achieved, and were then placed in a Bird and Phipps jar-testing unit to allow flocculation to occur for 0, 5, 30 and 60 minutes. Samples of roughly 40 mL were collected and filtered using a 0.45 µm PVDF syringe filter and analyzed with UV-abs-254 spectroscopy and DOC. All treatments were performed in duplicates. Four ML (25.5, 38.3, 51.1, 63.8 mg/L) were applied at a range of $i (0.5-15 \text{ mA/cm}^2)$. One, two and four cells were assembled to achieve the *i*. At these conditions, three δ (1, 3 and 10 mm) were studied at ~1.5 L/min.

Results and Discussion

Flocculation Effects

A constant parameter monitored throughout all treatments and levels of experimentation was the effect of flocculation time on the removal of HA. All samples were filtered and analyzed for DOC and UV-abs-254 immediately after electrocoagulation, as well as after 5, 30 and 60 min of steady-state flocculation at 35 rpm. Throughout all levels of the factorial design, no trends were observed with respect to flocculation time and reduction of DOC or UV-abs-254. It was observed that any reductions in DOC and UV-abs-254, or increases for the latter in some cases, occurred immediately after electrocoagulation and only small fluctuations in either parameter existed throughout the 60 minutes of flocculation, as seen in Figure 1.



Figure 1. Flocculation time effects on DOC (a) and UV-abs-254 (b); i = 2.15, $3.22 \& 5.36 \text{ mA/cm}^2$, $\delta = 1 \text{ mm}$.

It can be observed that for each respective ML dose in Figure 1(a), all significant reductions occurred immediately after electrocoagulation and only small changes in DOC occurred during the 60 min of flocculation. In Figure 1(b), all increases or reductions of absorbances occurred immediately after the EC treatment, without any significant changes as flocculation progressed. Irrespective of current density, inter-electrode gap or metal loading doses, no conclusive evidence was found for flocculation effects ameliorating HA removal post-electrocoagulation. From these results, it can be concluded that any dissolved HA contaminants present in the inlet water which are later removed during filtration became undissolved either during the electrolysis process of EC, or while exiting the reactor immediately after passing through the electrodes.

Metal Loading Effects

The one factor yielding the most obvious impact on HA reductions is the effect of ML. Throughout all the factors and levels of experiments, there was a clear relationship between ML, DOC and UV-abs-254. Intuitively, as

the ML increases from 25.5 mg/L to 63.4 mg/L (corresponding to 2.0 A and 5.0 A of current respectively, for all number of cell configurations), significant decreases in DOC were observed [see Figure 2]. At 25.5 mg/L, the lowest ML tested, a decrease in HA is indicated by the decrease in DOC concentration. Roughly only a 30 -50 % decrease were observed for all current densities and inter-electrode gaps at the lowest ML. When the ML was increased to 38.2 mg/L, corresponding to a 3.0 A operations, further average DOC reductions were increased to 70-80% for all factors and treatments investigated. When ML was further increased to 51.1 and 63.4 mg/L, applying 4.0 and 5.0 A respectively, DOC reduced below 1.5 mg/L in nearly all cases, corresponding to a \geq 85% reduction from initial conditions. These two highest ML levels provided very similar final results and no significant differences were observed between them for any set of operating parameters tested.

Although clear decreases in DOC were observed in all experiments after electrocoagulation, the UV-abs-254 yielded different trends. For all experiments, the smallest two ML levels produced increases in UV-abs-254, sug-



Figure 2. ML effects on DOC and UV-abs-254; δ = 1 mm, i = 6.43, 9.65, 12.87 & 16.09 mA/cm².

gesting the introduction of dissolved Fe contaminants in the water during the EC process. An inspection of samples producing higher absorbances generally showed a dark orange color compared to inlet waters, a visual characteristic sometimes associated with rust/Fe. Although spectrophotometry is conducted at a 254 nm wavelength, targeting aromatic-structured organics like NOM and HA, the only explanation for the increase in absorbance is the presence of dissolved iron species not participating as a coagulant and passing through the 0.45 µm filter. Ultraviolet-visible absorption bands for several iron hydr(oxide) species are found in lower ranges near 254 nm, including goethite (250 nm), hematite (270 nm) and maghemite (250 nn). More notably, lepidocrocite and magnetite have absorption band positions at 239 and 300 nm, respectively (Cornell, 2003); iron hydr(oxides) that have been previously identified as the predominate species during iron EC (Dubrawski et al, 2013) in similar operating ranges to those used in these experiments. It is not possible to accurately determine the concentration of Fe purely based on the DOC and UV-abs-254 results, and therefore it is unknown whether higher absorbance at 25.52 mg/L ML compared to 38.30 mg/L is associated with more dissolved Fe. Further spectral and chemical analysis is required to conclusively investigate the increases in absorbance and will be conducted in future work. DOC results outlined above indicate lower HA concentrations at 38.2 mg/L ML, it is unknown how much absorbance is associated with Fe versus HA in either sample.

When ML parameters were increased above 38.2 mg/L, absorbance reductions were yielded [see Figure 2]. When ML was administered at 51.1 mg/L, an average UVabs-254 reduction of 31.2 % was realized. Much larger reductions were observed with the highest tested ML = 63.4 mg/L, yielding an average UV-abs-254 reduction of 57.7 %. Despite reducing UV-absorbance below half of its initial value, further reduction is required for EC to be considered as viable drinking water treatment.

Inter-Electrode Gap Effects

Three inter-electrode gaps were investigated: 1, 3 and 10 mm. Unlike metal loading, the effects on DOC reductions with respect to inter-electrode gap are not as evident. DOC data from all three inter-electrode gaps for two constant metal loadings and current densities (38.2 mg/L and 3.22 mA/cm², and 63.4 mg/L and 5.36 mA/cm², respectively) are seen in Figure 3(a) and (b), respectively. On average, for all MLs and current



Figure 3. Inter-electrode effects on DOC, potential and UV-abs-254; (a), (c) ML = 38.2 mg/L, $i = 3.22 \text{ mA/cm}^2$, (c), (d) ML = 63.4 mg/L, $i = 5.36 \text{ mA/cm}^2$.

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densities investigated, a greater reduction was achieved with a 10 mm gap compared to the 1 and 3 mm gaps. Furthermore, for all factors and levels investigated, a 1 mm gap yielded slightly greater DOC reductions than the 3 mm gap experiments. For two-cell configuration experiments [shown in Figure 3] these reductions were so slight that they were within the uncertainty range of each respective error. However, for half-cell, single-cell and four cell configuration experiments [not shown], the 1 mm inter-electrode gap experiments provided conclusively greater DOC reductions compared to the 3 mm experiments.

Results for UV-abs-254 followed similar trends to those outlined above for DOC reductions with respect to increasing inter-electrode gaps. Similarly to the description above for DOC, the 3 mm gap experiments provided the least reductions in UV-abs-254, while the 1 and 10 mm gaps the highest reductions. As opposed to the DOC results, experiments conducted with a 1 mm inter-electrode gap provided substantially differing results from 3 mm gap experiments. Interestingly, as ML increased from 25.5 to 63.4 mg/L, differences in 1 mm and 3 mm UV-abs-254 results increased, while 1 mm reductions surpassed 10 mm reductions at the highest ML. For half- and single-cell experiments, electrical potential requirements exceeded 10 V for higher ML experiments and were therefore not pursued due to power availability. Future experiments may utilize higher power DC supplies in order to investigate these omitted process parameters.

From the experimental results outlined above, it is observed that for both DOC and UV-abs-254 reductions, the greatest results were obtained at the highest and lowest potentials. A possible explanation for this phenomena is the specific speciation which occurs at the respective operating potentials. As outlined above, different iron species have a given affinity to function as a coagulant. In order to confirm these suspicions, further speciation experiments are to be conducted, doing UVspectral analysis.

Current Density Effects

Another parameter investigated was the effect of current density, *i*, on the removal of HA. Under constant current, adding or eliminating the number of cells used in the EC configuration will dictate the current density. It should be noted that although EC configurations existed in half-, single-, double- or four-cell setups, if the same current is provided to each system the same ML will be yielded. However, although the ML remains constant if the current remains constant, the current density changes for each setup.

Figure 4 summarises the DOC results obtained from

half-, and four- cell setups, whereby the abscissa represents the respective *i* for a constant ML. In agreement with literature, the lowest *i*, on average, consistently produced the greatest reduction in DOC (Addy, 2008; Dubrawski, 2013). Many fluctuations were observed with respect to *i* and DOC reduction for different ML parameters making it difficult to determine conclusive trends. However, it was observed that higher *i* operation consistently yielding the poorest DOC reductions for each respective ML. When considering the initial $DOC_0 = 10.0 \pm 0.7 \text{ mg/L}$, current densities did not produce substantial differences in reduction when compared to the effects of MLs.

As seen in Figure 4(c,d), the lowest and highest *i* investigated consistently yielded greater UV-abs-254 reductions when compared to the intermediate *i*. The highest and lowest *i* correspond to half-cell and four-cell configurations, respectively. Although the two intermediate ML parameters (38.2 and 51.1 mg/L) did occasionally display significant UV-abs-254 reductions with respect to the high and low current density experiments, it was observed that poor UV-abs-254 reductions frequently occurred within the range of $5 \le i \le 9$ mA/cm².

Although higher reductions in UV-abs-254 at high i yielded poor DOC reductions, a possible explanation could be attributed to iron speciation. The predominating iron hydr(oxides) synthesized at higher i may have a greater affinity to remove larger HA structures with many aromatic rings. Since UV-spectrophotometry at 254 nm selectively absorbs aromatic organics, selective removal of these structures would reduce the UV-abs-254. DOC analysis account for all organic carbon and does not selectively measure aromatic structures, therefore this phenomena would not necessarily be reflected in DOC analysis results.

Conclusion

The research here addresses the field of drinking water treatment and related remote community water challenges. The continued efforts towards this work will help to determine the efficacy of EC as a possible technology suited for small and remote communities in Canada and abroad. More specifically, by investigating *i*, δ and ML effects on NOM removal at a scaled-up pilot capacity, a more thorough understanding of the processes' ability as an implementable technology will be better known.

From the research already conducted at a low flowrate, it is known that flocculation time has little effect on the continued or increased reductions of either DOC or UV-abs-254. The larger δ provided the greatest reductions in DOC at the cost of being the most energy inten-



Figure 4. Current density effects on DOC, potential and UV-abs-254; $\delta = 1 \text{ mm}$ (a) and (c) ML = 25.5 mg/L, (b) and (d) ML = 63.4 mg/L; average initial $DOC_0 = 10.03 \pm 0.7 \text{ mg/L}$.

sive, due to greater resistivity associated with the lower conductivity of the water. UV-abs-254 was most greatly reduced while operating at the largest and smallest gaps (10 and 1 mm, respectively). Current density effects on DOC and UV-abs-254 were the greatest at the lowest operating conditions, a phenomenon in agreement with literature (Addy, 2008; Dubrawski, 2012). The effect that provided the most substantial reductions of DOC and UV-abs-254 was ML. As ML increased, both reductions in DOC and UV-abs-254 increased, however continued work must be dedicated to further reducing the latter. Although DOC reductions were observed at ML < 51.1 mg/L, increased absorbance's were universally observed through all factors and treatments. It is believed that these increased absorbance results are due to dissolved iron species introduced during the EC process and present during UV-spectrophotometric analysis. In addition to continued research directed towards the reduction of UV-abs-254, scale-up efforts to a pilot-scale must be undertaken. Using the same methodology employed in this outlined research paper, scaled-up flowrates of 10 L/min should be tested.

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