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Removal of estrogenic compounds via iron electrocoagulation: impact of water quality and assessment of removal mechanisms

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Water Impact Statement

Estrogens pose a range of human and ecological health risks, as they are not readily removed through conventional water treatment technologies. Electrocoagulation (EC) is an emerging drinking water technology that generates *in-situ* coagulants and redox reactions. While this research revealed estrogen removal is due to both oxidation and sorption mechanisms, EC is likely better served as a pretreatment method to other oxidation processes for removal of estrogens due to impractical conditions required for removal.

Keywords: 17β-estradiol (E2), 17α-ethynylestradiol (EE2), drinking water, coagulation, oxidation, adsorption

Abstract

Estrogenic compounds pose a range of ecological and public health risks. They are not readily removed via conventional drinking water treatment and are thus listed on the EPA Contaminant Candidate List. Electrocoagulation is an alternative drinking water treatment process that generates coagulations *in-situ* and offers potential for removal of organic micropollutants via redox reactions and anodic oxidation. An iron electrocoagulation bench-scale batch reactor was used to investigate the influence of water quality parameters and removal mechanism of four estrogenic compounds, estrone (E1), 17β-estradiol (E2), estriol (E3), and 17α-ethynylestradiol (EE2). High pH (pH 9.5) yielded greater removal than neutral and low pH (pH = 5.5). Turbidity and dissolved organic carbon had minimal impact on removal of estrogenic compounds. Removal mechanisms were elucidated via a series of experiments to identify the role of adsorption and oxidation; direct anodic oxidation at the anode surface was likely the primary removal mechanism. Oxidation, including at the anode surface and from reactive oxygen species, accounted for an estimated 55% to 68% of removal. Using the oxidant scavenger's tert-butyl alcohol and methanol it was determined that reactive oxygen species, possibly hydroxyl radicals and ferryl iron, likely contributed to ≤22% of estrogen removal. Examination of transformation products confirmed E1 was a transformation product of EE2. Removal due to adsorption to electrocoagulation iron flocs was ≤ 5% for E1, E2, and E3, and accounted for 22% of EE2 removal. Conventional jar tests revealed that estrogen removal due to enmeshment in flocs accounted for <9% removal of E1, E2, and E3 and approximately 30% for EE2 with ferric sulfate and <24% for E1, E2, and E3 and approximately 42% for EE2 with ferrous sulfate. Electric energy per order was much larger for EC compared to other oxidation technologies reported in the literature.

1.0 Introduction

Public health concerns have been raised over the presence of steroidal estrogenic compounds - estrone (E1), 17β-estradiol (E2), estriol (E3), and 17α-ethynylestradiol (EE2) - in drinking water, surface water, groundwater, and wastewater ranging in concentration from ng L^{-1} to µg L^{-1}.[1–9] A number of studies have shown that estrogenic compounds persist through conventional drinking water treatment at concentrations around 0.5 ng L^{-1}.[5,8,10] Concentrations in surface water are typically at the ng L^{-1} level, although concentrations as high as 4381 ng L^{-1} have been reported.[11] The average concentrations of estrogenic compounds in wastewater are typically in the ng L^{-1} range and are highly variable. Wastewater concentrations range from 1.3 to 670 ng L^{-1} for E1, 0.5 to 138 ng L^{-1} for E2, 2 to 470 ng L^{-1} for E3, and 1.5 to 155 ng L^{-1} for EE2.[10,12] In addition, estrogenic compounds may undergo transformations in water treatment systems. When natural estrogens are deconjugated, the compounds can become more resistant to oxidation, but also have less estrogenic activity.[9,12] The occurrence of estrogenic compounds at these levels has heightened awareness in terms of their ecological and human health impacts and the need for technological advances in water treatment.[3,8]

Hormones and hormone-like compounds are able to mimic, increase, or inhibit other hormones.[13,14] Hormones altering the function of the endocrine system can potentially trigger health complications by interfering with synthesis, metabolism, and binding or cellular response of natural hormones.[14] For example, estrogenic compounds are capable of feminizing fish and affecting puberty in humans.[14–16] These estrogenic compounds are 18-C steroids that have the most potent estrogenic activity (EE2>E2>E1>E3 [17]) resulting from the presence of the phenolic moiety.[18]

As a result, estrogenic compounds, including E1, E2, E3, and EE2, are listed on the U.S. Environmental Protection Agency's (USEPA) Contaminant Candidate List (CCL) version 4 (2016). The CCL includes contaminants that are not currently regulated by drinking water standards but are likely to occur in public drinking water systems.[19] These CCL contaminants are considered emerging contaminants of interest in regards to public health concerns related to exposure from drinking water, meaning that more research is needed to fill knowledge gaps prior to regulatory determinations.[19]

Not all drinking water treatment facilities are equipped with technologies capable of effectively removing estrogenic compounds and, as a result, their removal is highly variable. Specifically, the physical-chemical coagulation/flocculation/sedimentation treatment process conventionally used to treat surface water was not designed to remove estrogenic compounds. While using alum and ferric chloride for coagulation/flocculation/sedimentation, Westerhoff et al. (2005) reported that E1, E2, and EE2 were removed by only 5%, 2%, and 0%, respectively.[8] Accordingly, alternative unit operations have been investigated for removal of estrogenic compounds as part of point-of-use, emergency, and municipal treatment systems. Electrocoagulation (EC) may be a good candidate for estrogen removal due to *in-situ* coagulant generation coupled with redox reactions.[20–22] EC employs sacrificial electrodes, typically either aluminum or iron, to produce metal hydroxide flocs.[20,21]

Organic and inorganic contaminants may be oxidized in EC through anodic oxidation (direct oxidation) reactions at the surface of the anode as well as indirect redox reactions. These oxidants could include reactive oxygen species (ROS) such as hydroxyl radicals (●OH) and superoxide radicals, or high valence iron species, such as ferryl iron (Fe(IV)), via intermediate iron reactions.[20–26] Through the combination of physical adsorption in flocs and oxidative degradation, EC has been shown to efficiently remove a variety of pollutants, including turbidity, chemical oxygen demand, biochemical oxygen demand, phosphate, and color in wastewaters.[27] In drinking water applications, EC is capable of removing heavy metals,[22,28] polyfluoroalkyl acids (PFAAs),[29] and some pharmaceuticals including sulfamethoxazole and trimethoprim.[30–32]

Our previous work discovered that EC was capable of removing estrogenic compounds, but the impact of water quality parameters and the removal mechanisms remain unknown.[33] The specific research objectives of this research were to 1) assess the impact of water quality parameters (pH, turbidity, and dissolved organic carbon [DOC]) on the removal of estrogenic compounds (E1, E2, E3, and EE2) and 2) estimate the relative contribution of different mechanisms (e.g., adsorption, oxidation) responsible for removal of estrogenic compounds via EC.

2.0 Materials and Methods

2.1 Chemicals

Stock solutions of E1, E2, E3, and EE2 were prepared in HPLC-grade methanol (≥99%) purchased from Alfa Aesar (West Hill, MA). E1 (≥99% purity), E2 (≥98%), E3 (≥97%), EE2 (≥98%), sodium bicarbonate (≥99%), sodium sulfate (≥99%), and tert-butyl alcohol (t-BuOH) (≥99%) were purchased from Sigma-Aldrich (St. Louis, MO). Ferric sulfate (81%) and ferrous sulfate (>99%) were purchased from J.T. Baker Chemical Company (Phillipsburg, NJ) for use in conventional coagulation jar tests. Fine test dust (ISO 12103-1, A2 Fine Test Dust) was purchased from Powder Technology, Inc. (Burnsville, MN) for turbidity experiments. Dissolved organic carbon (DOC) was purchased as Suwannee River natural organic matter (NOM) isolate (RO isolation) from the International Humic Substances Society (IHSS, St. Paul, MN). Sulfuric acid (96.6%) was purchased from Fisher Scientific International, Inc. (Fair Lawn, NJ).

2.2 Reactor Operation

EC batch experiments were performed in a 500-mL glass reactor equipped with two electrodes with an interelectrode distance of 1 cm.[33] This interelectrode distance was selected based on Naje et al.[34] The electrodes used in EC tests were iron (mild steel) plates with an active anode surface area of 60 cm^2. The experiments were conducted at a current density of 16.7 mA/cm^2 with applied potential fluctuating from 11 to 16 volts and a stir rate of 500 rpm.[33] Power was supplied using a compact benchtop DC power supply (Sorensen XPH75-2D, 300W, 0-75W, 0-2A, dual output, universal input 110VAC to 240VAC). A current alternator (kindly provided by A/O Smith Corporation, Brookfield, WI) alternated the polarity between the electrodes every 30 seconds. Previous tests determined that 30 seconds was the ideal polarity reversal time to reduce electrode passivation and improve estrogen removal.[33] A multi-position magnetic stirrer was used to completely mix the reactors during batch tests. Tests were conducted for two hours, with 1-mL samples collected at 0, 5, and 120 min. This time was sufficient to achieve less than 10% variation in effluent concentrations, as indicated by kinetic tests completed previously.[33] The 1-mL samples changed the reactor volume by 0.4%, and thus had negligible impact on treatment conditions.

To eliminate organic contamination or residual estrogenic compounds from previous adsorption to the reactor surfaces, all glassware, stir bars, and caps were rinsed three times with methanol. The 4-mL glass amber sample vials were baked at 550°C for 45 minutes and cooled to remove any residual organics. Preliminary control tests indicated less than 5% of the estrogenic compounds adsorbed to the glassware. Between experiments, the electrodes were acid washed in a 2-M sulfuric acid, rinsed with Milli-Q water, and cleaned with Alconox®. The electrodes were then scoured with an abrasive scrubber, followed by sanding with 320 grit fine sand paper, and sonicated in methanol for 20 minutes. A minimum of triplicate tests were conducted to account for variation in electrode pitting and to ensure reproducibility of EC performance. Samples were collected, digested and analyzed for total dissolved iron via inductively coupled plasma mass spectrometry (ICP-MS, 7700 Series, Agilent Technologies, Santa Clara, CA, USA).

For all experiments, the test water was prepared in Milli-Q (Millipore, Burlington, MA) water with a conductivity of 18.2 MΩ at 22 ± 1°C. The water was augmented with an additional electrolyte concentration of approximately 4.51 mM (1000 µS/cm) using sodium sulfate (Na_2SO_4), alkalinity at 85 mg L^{-1} as $CaCO_3$ using sodium bicarbonate, and pH adjustment using sodium hydroxide or sulfuric acid. The pH was adjusted to approximately 7 for all tests with the exception of the pH tests with different target values, as shown in Table 1. All estrogenic compounds (E1, E2, E3, and EE2) were added at a nominal concentration of 200 µg L^{-1} in a methanol solution. Table S1 in Section S1 of the Electronic Supplemental Information (ESI) includes the physical-chemical characteristics of the estrogenic compounds. Cosolvent effects from methanol were negligible as the volumetric fraction of methanol to water was 0.05%.[35]

Table 1. Water quality parameters test matrix

Parameter	Range	Means of Adjustment
pH	5.5 - 9.5	Sulfuric acid and sodium hydroxide
Turbidity (NTU)	0 - 60	ISO 12103-1, A2 fine test dust
DOC (mg L^{-1})	0 - 15	Suwannee River NOM isolate

2.3 Influence of water quality parameters

EC experiments were conducted in the batch-scale reactor described in section 2.2 to investigate the impact of pH, turbidity, and DOC on the removal of estrogenic compounds (Table 1). The pH was measured using an Orion 4 Star pH meter (Thermo Scientific, USA) and turbidity was measured using a 2100AN Turbidimeter (Hach, Loveland, CO, USA).

2.4 Investigation of removal mechanisms

2.4.1 Role of adsorption

Three types of experiments were conducted to evaluate the relative importance of adsorption as an estrogenic compound removal mechanism during EC: (1) surface adsorption to pre-formed EC flocs, (2) entrapment of estrogenic compounds during iron floc formation tested via conventional coagulation jar tests using ferric sulfate ($Fe_2(SO_4)_3$) and ferrous sulfate ($FeSO_4$), and (3) estrogen extraction from iron oxide floc. All iron oxides were analyzed and identified using X-Ray Diffraction (XRD), in accordance with methods reported by Maher et al. 2019.[33]

To test adsorption to pre-formed EC flocs, the test water for the EC reactor was prepared without estrogenic compounds. After 120 minutes of EC to produce *in-situ* flocs, the power source was turned off and estrogenic compounds were spiked into the reactor at approximately 200 µg L^{-1}. The solution was mixed for 120 minutes to replicate a standard EC test, but with no power input.

This test was performed to estimate the fraction of compounds adsorbed onto flocs after formation. The flocs formed in the reactors were similar, i.e., dosed at the same rate, and formed using the same electrode material, as the iron flocs formed in a typical EC experiment.

The flocs were characterized using XRD at 5, 15, 30, 60 and 120 minutes to assess the chemical nature of the floc material over the course of the 120-minute EC run. Pre-formed floc adsorption experiments were conducted to address weak hydrophobic forces to the exterior of the floc. The experimental approach eliminated any estrogenic compound removal due to electrochemical reactions, the influence of electrophoretic movement, or removal due to enmeshment in the flocs during floc formation.

Physical removal and enmeshment of the estrogenic compounds was assessed by performing conventional coagulation tests in the EC reactors without electricity. Enmeshment was calculated by subtracting the estrogenic compound removal from adsorption during conventional coagulation tests from adsorption to the preformed floc. Each reactor was dosed with approximately 200 $\mu g\ L^{-1}$ of estrogenic compounds and 2800 $mg\ L^{-1}$ as ferric iron, using ferric and ferrous sulfate, which was equivalent to the iron dose generated during the 2-hour EC tests, as calculated using Faraday's Law and confirmed as total iron via ICP-MS analysis. The iron dose was based on the time required for the estrogens to reach less than 10% variation in concentration. After coagulant addition, the pH of the reactor was adjusted to 7.0 using sodium hydroxide. The reactors were mixed at 500 rpm for two hours. These experiments eliminated any impacts of electrophoretic movement or removal due to intermediate electrochemical reactions. While these iron flocs are not the same as those generated during EC (ESI S2, Figure S1), they were used as a surrogate to assess estrogen removal via enmeshment in the floc when no electrochemical oxidation or reduction reactions are occurring. Differences in flocs generated during conventional coagulation and EC will certainly exist due to differences in the thermodynamics of the system and subsequent EC floc species generated. To further explore such differences, the flocs formed in conventional coagulation tests were examined via XRD to determine if they have a similar oxidation state as the EC generated iron floc.

Ultrasonic-assisted extraction of estrogenic compounds from the iron oxide floc was completed to examine the mass adsorbed using established methods.[36,37] Experiments for extraction were spiked with 500 μg L^{-1} of E1, E2, E3, and EE2 for enhanced detection with liquid-chromatography mass spectrometry (LC-MS). Equal volumes of samples were mixed with methanol extraction solvent. Samples were sonicated with a Q500 QSonica Ultrasonic Homogenizer (QSonica, Newton, CT) at 20 kHz and 500 W in pulse mode for 5 minutes (15 sec pulse and 45 sec rest). The samples were processed at room temperature and kept in an ice bath during homogenization. The percent recoveries for this process were 137±19 for E1, 116±9 for E2, 126±8 for E3, and 108±7 for EE2.

2.4.2 Role of oxidation

Oxidant scavenger batch experiments were conducted to evaluate the relative importance of i) indirect oxidation (dissolved oxidants such as Fe(IV), ROS [$\bullet O_2^-$, $\bullet OH$, H_2O_2, and $\bullet SO_4^-$] and carbonate radical ($\bullet CO_3^-$) formed during EC) and ii) direct oxidation (anodic oxidation due to direct electron transfer at the anode or surface-bound ROS at the electrode surface) as estrogen removal mechanisms.[25,38,39] Oxidant scavengers, like saturated alcohols (t-BuOH), do not readily react with the electrode surface, however they do react rapidly with dissolved oxidants (likely ●OH or $●CO_3^-$) and, as a result, provide insight into the importance of solution-phase intermediates.[38]

Sulfate radical production could be evaluated from the direct oxidation experiments because methanol is also a well-established sulfate radical scavenger.[40] However, sulfate radical production was unlikely in the absence of peroxodisfulate or peroxomonosulfate during EC.[41]

The indirect ROS oxidants were scavenged by t-BuOH by dosing in excess every 10 minutes during an EC test to achieve an overall concentration of 0.25 M [42–44]. t-BuOH is a well-known efficient scavenger of ●OH, but is less reactive with high valence iron species such as Fe(IV).[45–49] Tests under these conditions eliminated the influence of ROS to better probe its influence on estrogenic compound removal during EC. In other tests, excess methanol was dosed incrementally for an overall concentration of 0.59 M to scavenge all oxidants present including both ROS and high valence iron species such as Fe(IV).[50,51] The impact of other oxidants (free chlorine and hydrogen peroxide) was negligible because no chloride/chlorine was present in these tests, and hydrogen peroxide has been shown to be non-reactive with estrogenic compounds.[52]

Oxidation transformation products were examined by conducting EC experiments dosed with each compound separately. These samples were then analyzed for E1, E2, and E3 to test if EE2 had been transformed to these products. These specific byproducts were evaluated here as an indication of degradation via oxidation.

2.5 Analytical Methods and Quality Assurance/Quality Control (QA/QC)

All analytical methods, sample preparation methods, spike and recovery experiments, standard curve requirements, limit of detection (LOD), limit of quantification (LOQ) and QA/QC were previously reported.[18,33] Estrogenic parent compound removal was analyzed via LC-MS, as previously reported.[18,33] The standards for each test were prepared in the same manner as the test water used; with electrolyte, pH adjustment, alkalinity, and estrogenic compounds. Briefly, each experiment was completed in at least triplicate, alongside one control reactor operated under same conditions but with no power input. During each test, a blank water sample (no estrogens) was collected prior to the addition of the estrogen stock solution to ensure clean glassware. Methanol was sampled and analyzed to ensure no contamination. Instrument blanks were analyzed approximately every six samples during LC-MS runs to ensure no carryover on the column between samples.

2.6 Statistical and Data analysis

Statistical data analysis was performed with Graphpad Prism 7® (Graphpad Software, La Jolla, CA). A one-way analysis of variance (ANOVA) was performed for each compound for each water quality parameter. A one-way ANOVA was also performed for conventional coagulation jar tests, adsorption tests and oxidant scavenger treatment tests. A Student's t-test was performed for the comparison of the EC test to the adsorption test using the pre-formed iron floc. All data transformations were conducted in the same manner as Maher et al., 2019.[33] Post-hoc tests were performed with the Fisher's least significant difference (LSD) test and all error bars on figures represent the standard error of the mean. Any potential outliers were examined using the Grubb's Test and were then excluded[53]

The treatment effectiveness was evaluated based on the electrical energy per order (E_{EO}; kWh m^{-3} $order^{-1}$) - a measure of the amount of energy required to reduce the concentration of the compounds by one order of magnitude in a unit volume.[54–57] This commonly used metric is a convenient value to compare treatment processes and was calculated for each compound using Equation 1.[43,50]

Equation 1: $$E_{EO} = \frac{1000P * t}{V * log\left(\frac{C_i}{C_f}\right)}$$

P is the rated power (kW), t is the time (hour), V is the volume (L), C_i is the influent estrogen concentration (µg L^{-1}), and C_f is the final estrogen concentration.

3. Results and Discussion

3.1 Influence of water quality parameters

3.1.1 Effects of pH

Estrogenic compound removal generally increased as pH increased for E1, E2, and E3, with greatest removal at pH 9.5 (Figure 1; ANOVA p-value < 0.0001; see ESI, Section S3, Table S3 for post-hoc p-values). The pH is an important characteristic for the EC system as it impacts the speciation and oxidation rate of iron oxides and estrogenic compounds (see ESI, Section S1, Table S1 for pKas).[51,60,61] Fe(II) oxidation is strongly pH dependent and higher pH is likely to increase the rate of Fe(II) oxidation to Fe(III), decrease the competition of aqueous Fe(II) for intermediate oxidants (Fe(IV)), and decrease the formation of ferric oxides.[24] As a result, the increased rate of oxidation of Fe(II) to Fe(III) may increase the rate of indirect oxidant production and direct electron transfer with the anode and thus increase the rate of estrogenic compound degradation. As a result of alkaline conditions being more favorable, the formation of higher valence iron species offers greater potential for the formation of indirect oxidants and would explain the increase in removal as a function of pH.[24]

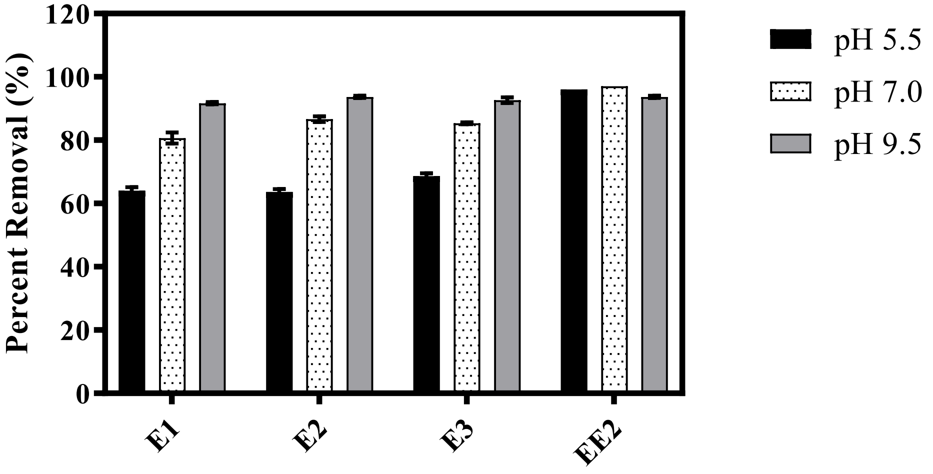

Figure 1. Impact of pH on removal of E1, E2, E3, and EE2.The percent removal for each estrogenic compound was significantly different between pH values. Error bars represent the standard error of the mean, n = 3 for all tests.

Additionally, the pKa values of estrogenic compounds are all greater than 9.5, ranging from 10.3 to 10.8; thus at pH values below the dissociation constant, all compounds trend toward full protonation and neutral charge. As the pH of the system approaches the pKa values, larger fractions of the compounds are partially dissociated and their negatively charged components are more likely attracted to the positively charged anode surface where they may be oxidized via anodic oxidation, which could increase removal.

With respect to adsorption, pH plays an important role in electrochemical coagulation processes by dictating the formation of complexes via hydrolysis and polymerization.[21] The optimal pH for insoluble floc formation of iron oxide species is between pH 6 and 9.[62] In these reactors, the iron oxyhydroxide generated in-situ was lepidocrocite (γ-FeOOH),[33] the speciation of which is pH dependent with pKa values of 6.4 and 8.3.[63] Lepidocrocite remained the major species at pH values 5 and 9.5 (see ESI Section S2, Figure S2). The point of zero charge (PZC) of lepidocrocite from literature ranges from 6.7 to 7.45.[62] The PZC was previously measured on the EC iron oxide floc formed in these experiments as 5.6±0.018.[33] Therefore, at neutral pH, the surface charge of this iron oxide floc is negative. The estrogenic compounds are neutrally charged at neutral pH, so the iron floc and the estrogenic compounds are not oppositely charged and will not attract at neutral pH, with the exception of a small fraction deprotonated estrogenic compounds at higher pH values.

3.1.2 Effects of Turbidity

Turbidity had a statistically significant but minor impact on the removal of E1 and E2 (Figure 2, ANOVA p-values < 0.05; see ESI, Section S3, Table S4 for post hoc p-values) and did not impact E3 removal (ANOVA p-value =0.06). The decrease in percent removal was not greater than 11% for E1, E2, and EE2 between no added turbidity (0.0 NTU) and 2.0 NTU, and there was no difference in removal between 0.0 NTU tests and 60 NTU tests (Figure 2).The dose of iron generated *in-situ* during the 2-hr EC tests was much larger than the relatively minor variations in turbidity and it was not expected to decrease estrogen removal. The increase in turbidity was expected to increase adsorption of estrogens to the iron oxide floc due to the likelihood of larger floc formation and enmeshment.[64] With an initial turbidity of zero, there was likely no oxidation inhibition. With the addition of a small amount of turbidity (2.0 NTU), the test dust may have scavenged oxidants, thereby inhibiting oxidation of estrogenic compounds. For the highest turbidity tested (60.0 NTU), adsorption of estrogens to the flocculated particles may have been enhanced by the higher number of particles present.[64] While there were statistically significant variations, there was no consistent trend between compound removal and turbidity for any of the compounds. EE2 was consistently removed to the detection limit in all tests.

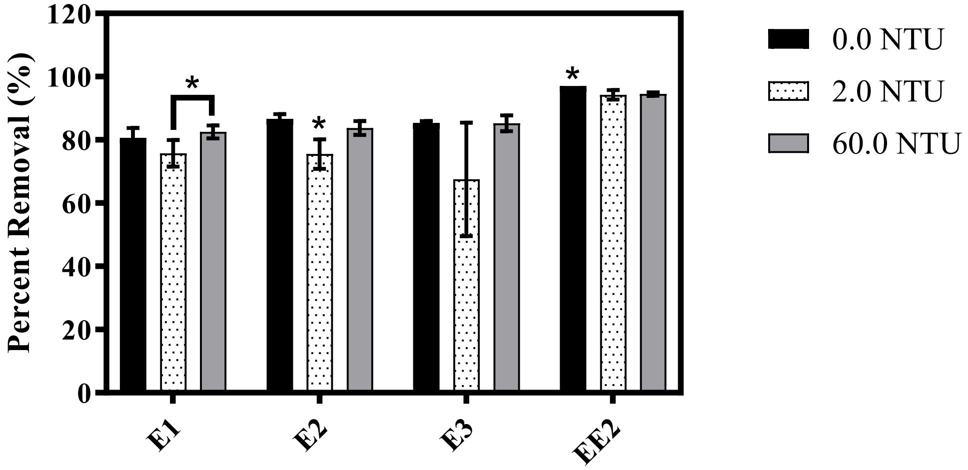

Figure 2. Impact of turbidity on removal of estrogens (0.0 NTU, n=3; 2.0 NTU, n=4; 60 NTU, n=4). The error bars represent the standard error of the mean. Asterisks indicate significant difference between all other conditions within a single estrogenic compound. Bars indicate difference between specific conditions.

3.1.3 Effects of Dissolved Organic Carbon

The DOC concentration did not significantly impact removal of E1, E3, or EE2 (Figure 3; p-value > 0.11). Removal of E2 did vary with DOC concentration as the percent of E2 removal decreased between 0.5 and 15 mg L^{-1} DOC (ANOVA p-value = 0.025; see ESI, Section S3, Table S5 for post hoc p-values). DOC has been shown to inhibit estrogenic compound degradation that occurs from high valence iron species [65] indicating that DOC may have interfered with estrogenic compound oxidation. Some studies have shown an increase in sorption of E1, E2, E3, and EE2 to iron oxide flocs in the presence of total organic carbon,[66–68] but this trend was not observed indicating that removal by sorption likely played a smaller role than removal by oxidation. The average percent removal decreased for E1, E2, and E3 at DOC concentrations of 15 mg L^{-1}. Although this decrease was not statistically significant, it was expected, as Khan et al. previously reported that DOC scavenges oxidants, which would then interfere with estrogenic compound oxidation.[69] However, Khan et al.'s research was based on removal due to hydroxyl radicals and not due to anodic oxidation. Compounds that have high molecular weights, such as humic and fulvic substances, have been shown to be more resistant to anodic oxidation.[70] Therefore, the small decrease in estrogenic compound removal may be due to competition from DOC scavenging indirect oxidants. These results imply anodic oxidation may be the major removal mechanism due to the lack of DOC's interference in estrogen removal and DOC's resistance to anodic oxidation.

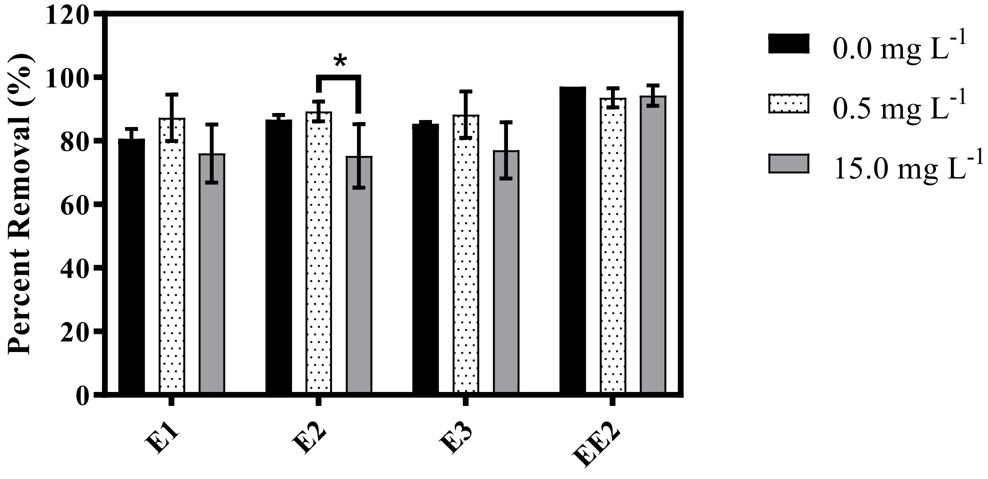

Figure 3. Impact of DOC on removal of estrogens (0.0 mg L^{-1}, n=6; 0.5 mg L^{-1}, n=4; 15.0 mg L^{-1}, n=4). The error bars represent the standard error of the mean. Asterisks indicate significant difference between all other conditions within a single estrogenic compound. Bars indicate difference between specific conditions.

3.2 Investigating Mechanisms

3.2.1 Role of adsorption

The physiochemical characteristics of the estrogenic compounds (ESI Section S1, Table S1) reveal that natural estrogenic compounds (E1, E2, and E3) have solubility limits of 13 mg L^{-1}, and the synthetic estrogenic compound (EE2) has a solubility of 4.8 mg L^{-1}.[71] All of the compounds have low vapor pressures, indicating low volatility.[71] These properties demonstrate that the estrogenic compounds are hydrophobic organic compounds with low volatility and high adsorption potential.[71] However, estrogenic compounds are not charged at neutral pH and are moderately polar; thus, it is expected the adsorption mechanisms are likely due to weak attractive forces.[64,72] At higher pH estrogenic compounds and iron oxide flocs are negatively charged and would likely repel each other limiting adsorption capabilities.

3.2.1.1 Adsorption to pre-formed EC flocs.

Less estrogenic compound removal occurred during adsorption tests with pre-formed iron floc compared to EC (Figure 4, t-test p-values <0.0001), indicating that estrogenic compounds do not adsorb well to the flocs formed during EC. These results corroborate the findings of low estrogenic compound removal via adsorption to iron from conventional coagulation experiments.[8] Estrogenic compound removal in the pre-formed floc experiments was due to physical adsorption to the floc surface because the experimental approach eliminated any estrogenic compound removal due to electrochemical reactions, the influence of electrophoretic movement, or removal due to enmeshment in the flocs during floc formation. As previously mentioned in Section 3.1.1, the major iron precipitate was γ-FeOOH (PZC measured = 5.7).[33]

Lepidocrocite remained the major species throughout the entire electrolysis time, at varying pH values, and for the pre-formed floc which was identified previously by Maher et al. (see ESI Section S2, Figure S2).[9] Therefore, at neutral pH the charge of the floc is net negative while the estrogenic compounds are uncharged. Consequently, attraction due to coulombic attraction would be unlikely.

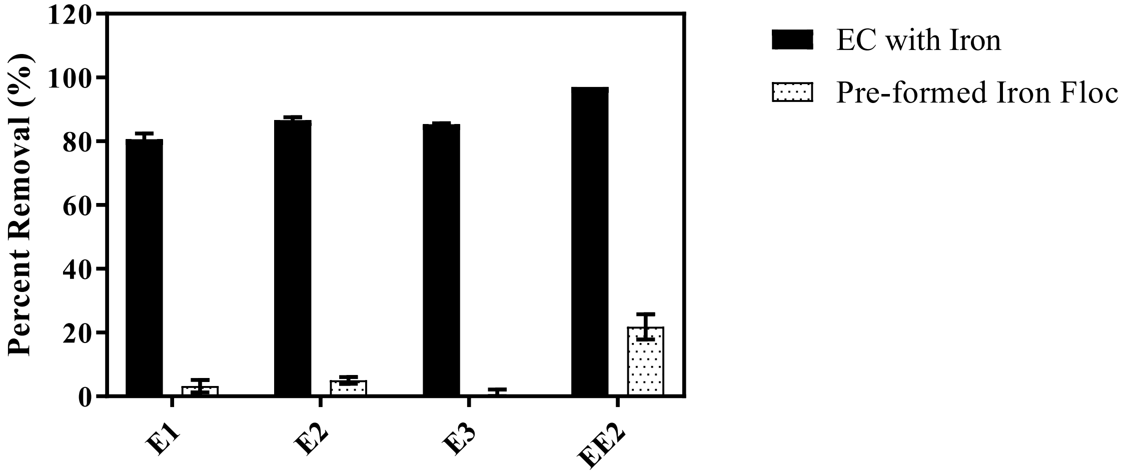

Figure 4. Removal of estrogens via electrocoagulation (EC with Iron, n=3) compared to removal via adsorption using iron floc formed from electrocoagulation (Pre-formed Iron Floc n=5). Pre-formed iron flocs were prepared using standard operating parameters (1000 µS cm^{-1}, 16.7 mA cm^{-2}, 120 minutes and pH 7). After floc formation, the electricity input was stopped, the electrodes were withdrawn, and estrogens were spiked at 200 µg L^{-1} followed by 120 minutes of mixing to test for removal via adsorption. The percent removal for each estrogenic compound was significantly different between EC with Iron and pre-formed iron floc values. The error bars represent the standard error of the mean.

3.2.1.2 Adsorption or enmeshment to flocs formed during ferric sulfate ($Fe_2(SO_4)_3$) and ferrous sulfate ($FeSO_4$) conventional coagulation jar tests

During the conventional coagulation experiments, estrogenic compound removal via adsorption accounted for <9% removal of E1, E2, and E3 and approximately 30% for EE2 with $Fe_2(SO_4)_3$ and <24% for E1, E2, and E3 and approximately 42% for EE2 with $FeSO_4$ (Figure 5). $Fe_2(SO_4)_3$ and $FeSO_4$ were both used in the conventional coagulation jar tests because both iron oxidation states (Fe(III) or Fe(II)) may be present during EC and form precipitates.[73] XRD analysis suggested that $Fe_2(SO_4)_3$ produced flocs consisting of a mixture of goethite (α-FeOOH) and natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) (ESI Section S2, Figure S1). The formation of natrojarosite may be due to the hydrolysis and co-precipitation of $Fe_2(SO_4)_3$ and Na_2SO_4 that was used as the electrolyte in the coagulation experiments.[74,75] In contrast, magnetite was identified as the predominant product in the flocs generated from $FeSO_4$, indicating a partial oxidation of Fe(II) to Fe(III) during the coagulation process.

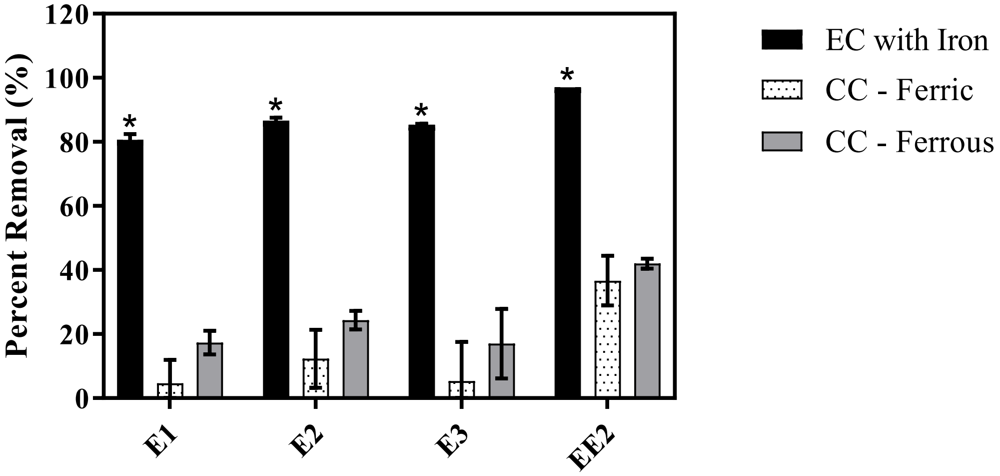

Figure 5. Removal of estrogens via electrocoagulation (EC with Iron, n=3) compared to removal via conventional coagulation jar tests using ferric (CC – Ferric, n = 3) or ferrous sulfate (CC – Ferrous n=3). The error bars represent the standard error of the mean. Asterisks indicate significant difference between all other conditions within a single estrogenic compound. Bars indicate difference between specific conditions.

Although $Fe_2(SO_4)_3$ and $FeSO_4$ produced different flocs, estrogenic compound removals were not significantly different from each other (ANOVA $p\text{-value} > 0.1$; see ESI, Section S3, Table S6 for post-hoc test p-values), and both were significantly less than removal with EC ($p\text{-value} < 0.007$). Both chemical coagulation and EC typically produce iron oxides and/or iron oxyhydroxides,[63,64,76] but EC can form much larger floc that contains less bound water and is typically more stable than conventional coagulation flocs.[21] Alternately, Lee and Gagnon observed that conventional coagulation flocs were larger as well as more dense and stable than EC floc.[77] Iron oxide flocs vary widely, and are strongly dependent upon the test matrix.[77] The small fraction of estrogenic compounds that adsorbed to the floc likely stemmed from hydrophobic interactions,[78] as at pH 7 the estrogenic compounds are in their neutral, more hydrophobic form (see pKa and LogK_{ow}'s listed in ESI, Section S1, Table S1). Estrogenic compound removal using EC was much greater than with conventional coagulation jar tests and pre-formed floc experiments. These results indicate removal was not solely due to adsorption because of the low estrogenic compound removal during the pre-formed floc and conventional coagulation experiments; nor was it solely enmeshment because of the much greater removal in EC than in conventional coagulation jar tests.

3.2.1.3 Estrogen extraction from iron oxide floc

Ultrasonic-assisted extraction was used to estimate the fraction of estrogenic compounds adsorbed to the iron oxide floc. The extraction experiments indicated any removal due to adsorption was undetectable (i.e. below the instrument detection; see ESI, Section S4, Table S8).

3.2.2 Role of oxidation

The contributions to estrogenic compound removal due to oxidants formed in solution were isolated by indirectly targeting the oxidant through the addition of selected scavengers (Figure 6). In previous studies, the dissolution of zero-valent iron led to production of ROS and Fe(IV).[23–26,45–47] In EC, Fe(II) is released from the iron electrodes, making Fe(II)/O_2 reactions relevant.[76]

Fe(II) is oxidized to Fe(III) via several intermediate reactions that may form ●OH or Fe(IV) (reactions 1 through 7).[23,24]

$$\mathrm{Fe(0)} \rightarrow \mathrm{Fe(II)} + 2e^- \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \tag{2}$$

$$\mathrm{Fe(II)} + O_2 \rightarrow O_2^{\cdot -} + \mathrm{Fe(III)} \tag{3}$$

$$\mathrm{Fe(II)} + O_2\bullet^- + 2H^+ \rightarrow \mathrm{Fe(III)} + H_2O_2 \tag{4}$$

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \text{Intermediate Reactions (IR)} \tag{5}$$

$$\mathrm{IR} \rightarrow \bullet\mathrm{OH} \tag{6}$$

$$\mathrm{IR} \rightarrow \mathrm{Fe(IV)} \tag{7}$$

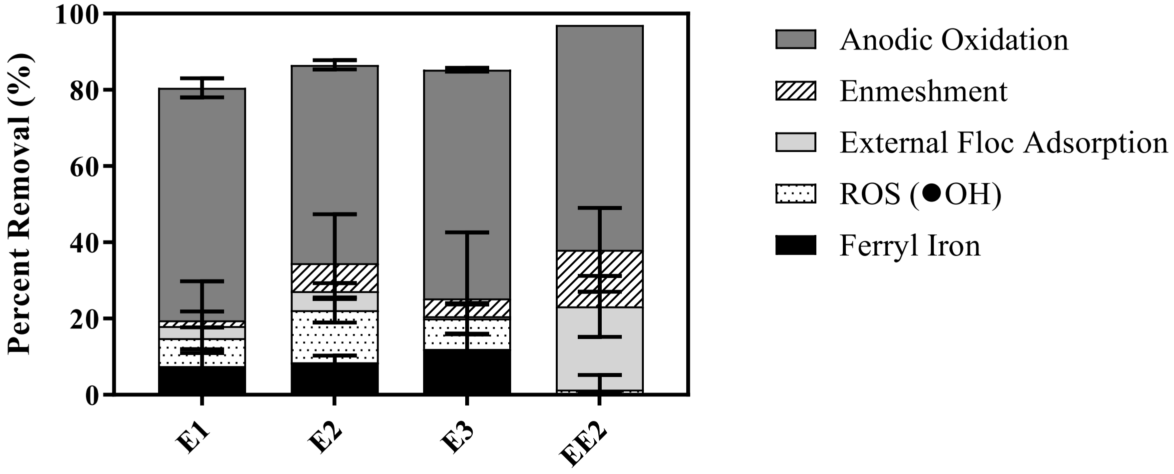

Figure 6. Estimation of removal mechanisms contributing to estrogen removal in electrocoagulation. Contributions were calculated using averages derived from previously described mechanism isolation tests and error bars represent standard error of the mean.

The potential oxidation of estrogenic compounds via ROS and Fe(IV) during EC was examined by adding oxidant scavengers, t-BuOH and methanol (MeOH), in separate tests (see ESI, Section S5, Figure S3). t-BuOH was added to scavenge ROS including ●OH,[45] while MeOH was added to quench high valence iron species, including Fe(IV).[46,50,51] Less estrogenic compound removal was observed for tests with t-BuOH for E1, E2, and E3 (ANOVA p-values < 0.007; see ESI, Section S3, Table S7 for post hoc tests), indicating that a portion of removal may be due to the presence of ROS. The difference in removals between the t-BuOH results and standard EC tests were 7% for E1, 14% for E2, and 8% for E3. EE2 was always removed below detection limit indicating that indirect oxidation played a negligible role on EE2 removal.

Because MeOH will quench ROS (specifically ●OH) at a greater rate ($k_{MeOH}^{OH\cdot} = 9.7 \times 10^{8}\ M^{-1}\ s^{-1} > k_{MeOH}^{Fe(IV)} = 5.72 \times 10^{2}\ M^{-1} s^{-1}$) [51] compared to Fe(IV), the percent removal due to Fe(IV) was estimated as the difference between the EC tests with MeOH and EC tests with t-BuOH. The addition of MeOH significantly decreased removal of E1, E2, and E3 (p-values < 0.05; see ESI, Section S3, Table S7 for post hoc tests) compared to EC Only and EC with t-BuOH. The decrease in removal indicates the possible presence of Fe(IV) or other high-valent iron oxidant species. The potential presence of high-valent iron species (such as Fe(IV)) accounted for 8% removal of E1, 9% of E2, and 12% of E3. This indicates some minor removal due to degradation from high-valence iron oxidation at neutral pH. There was no change in EE2 removal after the addition of either scavenger (p-values = 0.77).

EC experiments using only EE2 and E2 were completed to further probe the role of oxidation by analyzing samples for possible oxidation products of EE2 and E2. More specifically analyzing for only E1, E2, E3 and EE2. The results indicate oxidative transformation of EE2 to E1 occurred (see ESI, Section S5, Table S9) and complete oxidation of E2 to E3 (see ESI, Section S5, Table S10). As the tests proceeded, the EE2 concentration decreased to zero (non-detect) and

E1 appeared, confirming oxidation is a removal mechanism. The conversion of EE2 to E1 has been previously reported by two studies, Li et al. (2013) and Stump and Marschner (2009) with a proposed degradation pathway of E2/EE2 →E1→E3.[17,79] The conversion of EE2 to E1 was previously reported by Li et al. (2013) and Stump and Marschner (2009), with a proposed degradation pathway of E2/EE2 →E1→E3.[17,79] Our experiments indicated that EE2 was transformed to E1 (see ESI, Section S5, Table S9) and that E2 was transformed to E3 (see ESI, Section S5, Table S10). The oxidation transformation of estrogenic compounds has been shown to decrease estrogenic activity.[9,80] However, this depends on the oxidant and the degree of oxidation, as there is also potential to produce recalcitrant, estrogenically-potent intermediate organic by-products.[80,81] Confirmation of all oxidation byproducts was beyond the scope of this specific research, but future research should investigate the nature and estrogenicity of the remaining deconjugated compounds, their potential toxicity, and the extent of mineralization.

Overall, these results indicate that both ROS (e.g., ●OH) and high-valent iron oxidants (e.g., Fe(IV)) may be present at neutral pH with estrogenic compound removals ranging from 0 to 14% for ROS and 0 to 12% for high-valent iron oxidants. Accordingly, indirect oxidation stemming from ROS and high valence iron species was not the major removal mechanism for estrogenic compound removal during EC (Figure 6). Oxidation at the anode surface is diffusion limited. Previous tests on the impacts of polarity reversal and stir rate revealed that oxidation was a major removal mechanism.[33] A shorter polarity reversal time of 30 seconds increased estrogen removal by inhibiting the formation of the passivation layer and thus decreasing the rate of diffusion.[33] Stir rates of 50, 120, and 500 rpm were also evaluated in our previous research.[33] The results indicated a faster stir rate improved removal which was likely due to an increased velocity over the surface of the electrode enhancing the mass transport from the anode surface into solution.[58] Oxidation is favored because at higher stir rates the likelihood of floc break-up due to shear forces is greater, thus reducing the probability of adsorption as a major mechanism.[33] With adsorption responsible for approximately 0.6 to 21% percent removal from external floc adsorption and enmeshment, anodic oxidation appeared to be the major removal mechanism with removals ranging from 53% to 73%. Future experiments using cyclic voltammetry is recommended to fully explore the electron transfer processes occurring at the electrode surface.

3.3 Consistent Removal of EE2

The only synthetic hormone evaluated here, EE2, was removed to the detection limit in nearly all EC experiments conducted in this study regardless of the various parameters and scavengers. Minor differences in chemical structure and properties could account for the difference in removal. In general, E1, E2, E3, and EE2 are similar in structure (see ESI, Section S1, Table S1), with a tetracyclic network consisting of one phenolic ring, two cyclohexane rings, and one cyclopentane ring.[82] All are 18-C steroids that contain a phenolic moiety, making them estrogenic.[83] The oxidation of estrogenic compounds tends to occur at the phenolic moiety, depending upon the oxidant.[84] The major differences between these compounds are the groups located on the C16 and C17 position on the cyclopentane ring. E1 has a carbonyl group on C17, E2 has a hydroxyl group on C17, E3 has hydroxyl groups on C16 and C17, and EE2 has an ethynyl group on C17 and a hydroxyl group on C16.[82] As mentioned in Section 3.2.1, all of the estrogenic compounds have low vapor pressures indicative of low volatility and EE2 has a much lower Henry's law constant (see Table S8 in the SI) and less than half of the water solubility.[71] In addition, the Log K_{ow} of the estrogenic compounds indicates partitioning to solids for EE2 may be more likely than E1, E2, and E3.[71] Therefore, a combination of mechanisms could contribute to the greater and consistent removal of EE2. These could include better adsorption capabilities than E1, E2, and E3 (as seen in adsorption tests in Section 3.2.1.1 and 3.2.1.2). Moreover, oxidation reactions may be more likely to occur at the electron-rich ethynyl moiety.[84] Oxidation reactions could also be due to abstraction of hydrogen in an aliphatic ring or at the phenolic moiety due to the non-selective behavior of anodic oxidation and hydroxyl radicals.[84]

Finally, it is noted that removal was calculated as the difference between compounds detected at the end of the experiment from compounds present at the beginning. The oxidation of EE2 could lead to a formation and increase in E1 which decreases the overall removal of E1.

3.4 Electric Energy per Order

The electric energy per order (E_{EO}, Eq. 1) was calculated for each compound to facilitate comparison of the energy needed for estrogenic compound degradation using EC relative to other advanced treatment technologies. The E_{EO} value can be used to estimate energy and potential cost effectiveness of the treatment method and for potential scale-up.[56] For this batch system, the E_{EO} ranged from approximately 35 to 85 kWh m^{-2} $order^{-1}$ for the estrogenic compounds studied (Table 2). These values are higher than those found for UV and UV/H_2O_2, but lower than those reported for ozone (Table 2). Accordingly, although EC is effective in estrogenic compound removal, the energy consumption is high per order of magnitude of compound removed, which indicates that further optimization of the system, or an alternative technology combination, is required. It is important to note that E_{EO} values are highly dependent upon operational parameters used during each experiment and will vary under different conditions.[85]

Table 2. Comparison of Electric Energy per Order (E_{EO}) from studies using advanced oxidation processes (AOPs) for the removal of estrogenic compounds

Author	**Treatment**	**E_{EO} (kWh m^{-1} $order^{-1}$)**			
		E1	**E2**	**E3**	**EE2**
Maher (this study)	EC	82±11.2	67±8.07	70±6.1	37±2.7
Benotti et al., 2009[1]	Photocatalytic reactor membrane	0.18±0.03	0.19±0.37	N.D.	0.23±0.04
Hansen and Andersen, 2012[48]	UV Photolysis	1.2	4.9±0.8	N.D.	6.1±0.7
Hansen and Andersen, 2012[48]	UV/H_2O_2 (60 mg L^{-1})	N.D	2.2±0.2	N.D.	1.8±0.03
Mayer et al., 2019[43]	UV Photolysis	42.9	50.7	41.4	60.7
Mayer et al., 2019[43]	TiO_2 Photocatalysis	38.8	41.3	54.4	45.7
Sarkar et al., 2014[47]	UV (254 nm)	14.2	N.D.	N.D.	N.D.
Sarkar et al., 2014[47]	UV/H_2O_2 (60 mg L^{-1})	8.53	N.D.	N.D.	N.D.
Sarkar et al., 2014[47]	Ozone (0.3 mg L^{-1})	268.32	N.D.	N.D.	N.D.
Sarkar et al., 2014[47]	Ozone (0.65 mg L-1)	246.72	N.D.	N.D.	N.D.

± Indicates plus or minus the standard deviation.

4. Conclusions

EC with iron electrodes demonstrated promise for the removal of estrogenic compounds in water. Greater than 80% removal of E1, E2, and E3 was achieved and nearly complete removal of EE2 was achieved. Higher pH conditions were favorable for estrogenic compound removal using iron EC. This was likely because iron speciation and Fe(II) oxidation is highly pH dependent. Turbidity and DOC had minor impacts on removal. Direct anodic oxidation was the major removal mechanism, with indirect oxidation from ROS (●OH) and higher valence iron species Fe(IV), as well as sorption played a minor role. An experiment using only EE2 revealed that E1 was formed indicating that oxidation was indeed occurring. Overall these findings confirm that EC offers the added advantage over conventional drinking water treatment of removal of organic micropollutants via oxidation. Future work should investigate the estrogenicity of residual oxidation products. An E_{EO} analysis revealed that, while iron EC for the removal of estrogenic compounds was effective at removing estrogenic compounds, it was not energy efficient. These results may be used to inform design of more efficient EC systems, including systems that pair EC with other treatment methods, such as electrooxidation. Because oxidation was the key removal mechanism, EC is likely best used as a pre-treatment system to remove bulk organics via adsorption such as DOC so that advanced oxidation technologies can target organic micropollutants.

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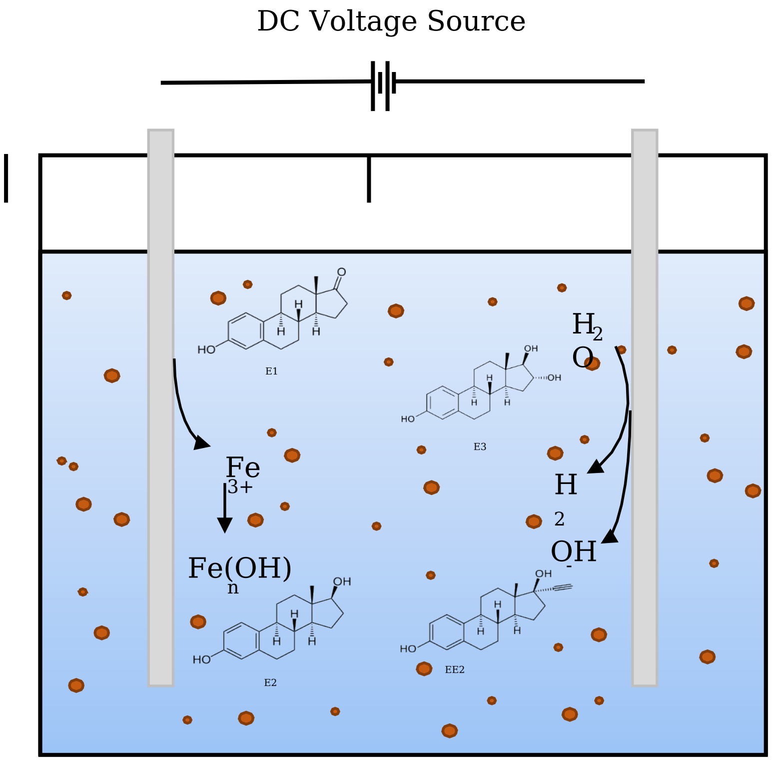

The influence of water quality and elucidation of the removal mechanism of estrogenic compounds removal electrocoagulation.