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Preliminary Considerations for Electrochemical PFOS Detection in Oily Wastewater

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EXECUTIVE SUMMARY

OBJECTIVE

The objective of this effort was the analysis and development of a potential screening tool that could be used to rapidly determine the presence of perfluorooctanesulfonic acid (PFOS) contamination of oily wastewaters at concentrations at or below regulatory limits. Work during this period of performance will address two main project objectives.

1. Evaluate the use of electrocoagulation for oily wastewater treatment
2. Evaluate the use of electrochemical sensing for PFOS detection.

METHODS

A review of published literature and commercial products was performed to determine the state of the art in electrocoagulation treatment of oil wastewater and in the use of electrochemical methods for determining PFOS concentrations. Information from these reviews was used to inform the design and fabrication of prototype electrocoagulation cells for testing with synthetic wastewater containing a known oil and grease concentration.

Samples taken during time course experiments with both sodium dodecyl sulfate (to simulate the presence of a detergent/surfactant) and without. Floc formation and settleability were noted at each time point. Samples were also analyzed for oil and grease content via a modified solvent extraction method utilizing infrared spectrometry as the ultimate detection method.

CONCLUSIONS AND RECOMMENDATIONS

We have shown here that oil and grease content in synthetic wastewaters can be easily be removed through an electrocoagulation process. The presence of a surfactant did not appear to inhibit oil and grease removal. The presence of a surfactant may result in the formation of unwanted foam layers which could be mitigated with proper optimization. Work in future years will focus on the impact of electrocoagulation on PFOS concentrations in treated water and incorporating an electrochemical PFOS sensing technique to determine concentrations in the original wastewater sample.

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ACRONYMS

AFFF	aqueous film forming foam
CONUS	contiguous United States
MIP	molecularly imprinted polymer
NSBM	Navy Standard Bilge Mix
OCONUS	outside the contiguous United States
OWW	oily wastewater
PFOA	Perfluorooctanic acid
PFOS	perfluorooctanesulfonic acid
SDS	sodium dodecyl sulfate
USEPA	United States Environmental Protection Agency

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1. INTRODUCTION

1.1 PURPOSE

During vessel operation, oily wastewater (OWW) often accumulates in the bilge compartment and commingles with a variety of contaminants. Vessels are generally not allowed to discharge OWW to harbors or marinas when near shore or in port and must coordinate disposal with shore-side facilities. The most common disposal method is to send the oily wastewater to a pre-treatment facility to remove the oily fraction prior to disposal at a wastewater treatment plant.

As part of firefighting activities, OWW may contain trace amounts of aqueous film forming foams (AFFF). Historically, AFFF formulations have used long chain fluorocarbon compounds due to their inert nature and ability to form oxygen blocking films on flammable liquid surfaces. Recent reports or their recalcitrance in the environment and potentially harmful health effects have made responsible disposal a primary concern in order to prevent future exposure of even trace amounts of the chemical. In certain foreign ports, detection of a specific fluorocarbon, perfluorooctanesulfonic acid (PFOS), above specified levels (typically in the low ng/L levels) require special disposal and handling.

Testing for PFOS and similar compounds require specialized equipment only maintained in a handful of certified labs in the contiguous United States (CONUS). This limited testing capability and distance from foreign home ports has resulted in delays in confirming the absence of PFOS in OWW collected for disposal at shore facilities outside the CONUS (OCONUS). The purpose of this effort is to streamline the confirmation/testing process by developing an analytical platform that could be deployed OCONUS to aid in confirming the presence or absence of PFOS in oily wastewater.

1.1.1 Objectives

This effort's overall objective is to address a capability gap related to PFOS-impacted OWW originating from surface ships by evaluating emerging electrocoagulation and electrochemical techniques for PFOS control and detection. Impacted water disposal in foreign ports requires special handling that is consuming considerable operational resources, affecting mission readiness of naval assets in strategic locations. The complexity of OWW and potential interference of contaminants in any downstream analysis necessitates a pre-treatment step prior to applying a sensor technology. The application of electrocoagulation techniques provides a pretreatment method that could be developed into a portable application because of the scalability and size of the necessary electrical hardware. Similarly, relying on electrochemical sensing techniques would provide a pathway for rapidly developing a portable sensor for field applications without requiring additional chemicals or other specialized hardware. Applying emerging electrochemical techniques for both oil-water emulsion control and PFOS detection can provide a streamlined solution for rapid waste characterization while vessels are off-loading OWW at shore-side facilities.

To achieve this main objective, the effort focused on the following objectives

1. Evaluate the use of electrocoagulation for OWW treatment
2. Evaluate the use of electrochemical sensing for PFOS detection

1.1.1.1 Objective 1: Evaluate the use of electrocoagulation for OWW treatment

The complex nature of OWW generally complicates analysis of the individual contaminants. The first objective serves to evaluate the use of electrocoagulation as a potential pre-treatment method for samples prior to the determination of possible PFOS contamination.

1.1.1.1.1 Objective 1 Details

The effectiveness of electrocoagulation for the treatment of wastewater impacted by oil and grease has been well documented for the treatment of large volumes. This objective aims to design a prototype to treat small sample volumes suitable for on-site investigation, and not entire waste streams.

The evaluation of electrocoagulation treatment focused on materials for construction, voltage requirements, and ability to remove contaminants from a potential OWW sample. In this effort, construction of a laboratory electrocoagulation setup was performed. Electrochemical activity at various applied voltages was assessed. The effectiveness of oil and grease removal over time was also measured and recorded. Results from these studies will inform potential prototypes that could be taken into field locations for onsite pre-treatment of OWW samples.

1.1.1.2 Objective 2: Evaluate the use of electrochemical sensing for PFOS detection

PFOS analysis has typically required dedicated complex analytical instrumentation that precludes its portability and ease of use. Recent advances in utilizing electrochemical signals to determine PFOS concentration present an opportunity to develop a portable and robust analytical capability. This effort will evaluate reported electrochemical methods and potential alternatives for PFOS detection to inform the development of a PFOS sensing method suitable for rapid field screening of samples.

1.1.1.2.1 Objective 2 Details

Electrochemical PFOS methods that will be tested rely on utilizing electrical signals to determine low-level concentrations. This effort will focus on identification of likely methods that would be suitable for detection at parts per trillion levels. Further down-select of those methods will occur based on ease of implementation in shore facilities.

1.2 BACKGROUND

The following sections provide a brief review of published reports related to electrocoagulation of oily wastewater and electrochemical analytical methods for the detection of PFOS.

1.2.1 Electrocoagulation

The use of coagulation-flocculation for oil and grease removal in wastewater is a well-known and used unit operation in conventional wastewater treatment. This method generally requires the addition of the metal in a chemical form, generally alum or ferric chloride, to a wastewater, followed by mixing to encourage metal hydroxide formation and subsequent precipitation. Precipitates are encouraged to aggregate into flocs that are removed through settling or surface skimming. (Zhao, et al. 2021) (Abuhasel, et al. 2021)

Electrocoagulation, the process of applying an electrical current through electrodes to separate contaminants in a liquid, can be used to separate oil and grease from bilgewater (Rincon and La Motta 2014). The process is described in more detail below alongside and illustrated in Figure 1. The process entails contaminant removal similar to coagulation-flocculation process except that no additional chemicals are required. Metal ions are provided by electrochemical oxidation of an iron or aluminum electrode through an applied voltage or current.

1. Electrical current applied to electrodes
2. Electrodes generate metal ion coagulants due to oxidation of the electrode metal

3. Contaminants destabilize, particulates are suspended, and emulsions break
4. Flocs (aggregation of destabilized particles) form
5. Hydrolysis occurs and bubbles emerge to lift flocs to the surface of the liquid
6. Smaller bubble sizes allow more effective separation of contaminants from water

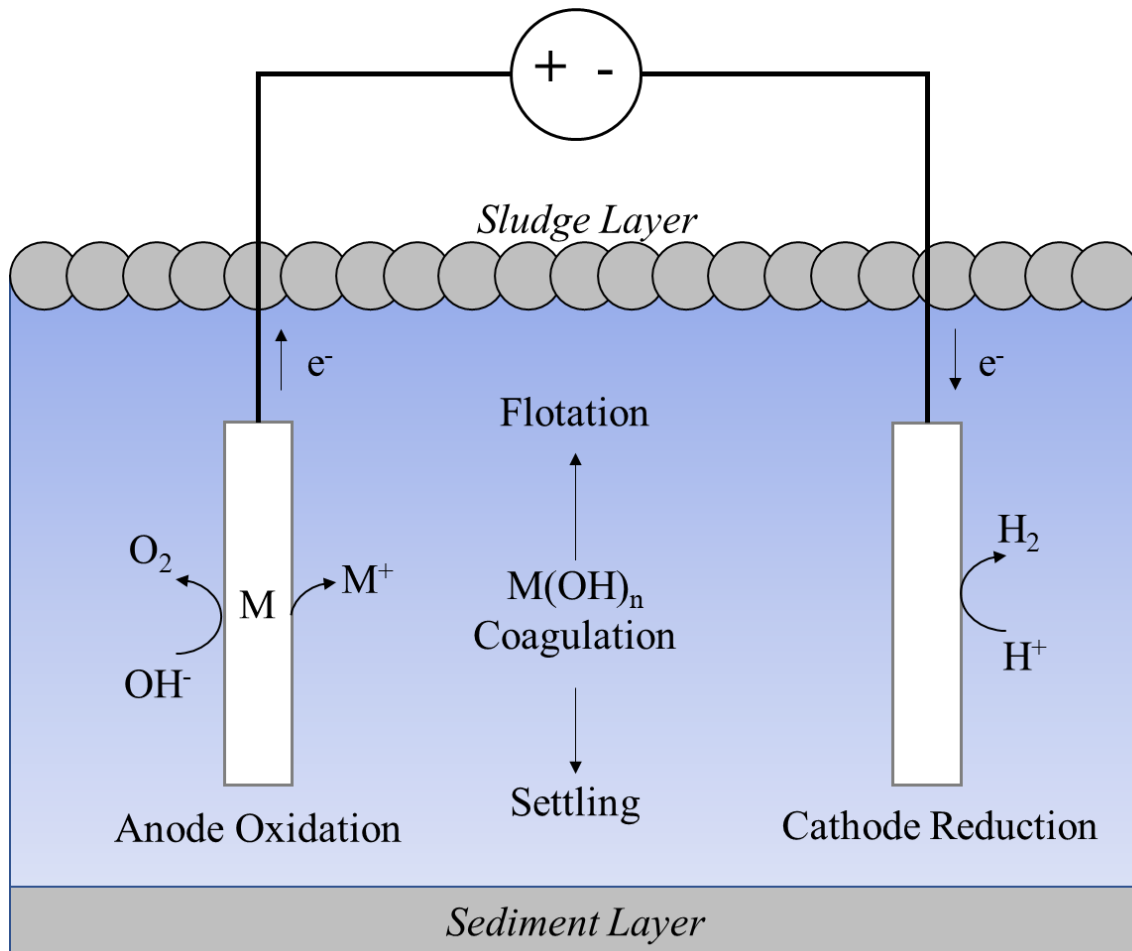


Figure 1. Electrocoagulation schematic where metal electrode (M) is oxidized to form metal hydroxide flocs that are removed via flotation or settling. Oxygen (O_2) and hydrogen (H_2) may also be formed at the electrode surfaces due to hydrolysis.

There are certain variables that can affect the electrocoagulation process and can be chosen depending on the targeted liquid medium. The electrodes typically consist of carbon, steel, aluminum, and/or iron electrodes due to their cost effectiveness. However, other metals such as platinum/iridium, titanium, and stainless steel can also be utilized for the electrode material. The magnitude of electrical current flow between the electrodes is directly related to the amount of floc produced and the ability to separate contaminants from the solution. The electrical current can be altered through changing the applied voltage, electrode geometry, electrode separation distance, and/or solution electroconductivity. Flow rate of the liquid can be controlled with a stirrer, or similar, and improve the amount of contaminant separation during electrocoagulation (El-Shazly and Daous 2013).

Since there are a significant amount of variables associated with the electrocoagulation process, the team analyzed several examples similar to our desired use case—particularly examples that performed electrocoagulation on marine oily wastewater (Han, et al. 2019) (Church, et al. 2019) (Waller, et al. 2019). Table 1 summarizes some of the published reports utilizing aluminum as the electrode material for oxidation.

Table 1. Pollutant Removal Efficiencies of Oily Wastewaters via Aluminum Electrocoagulation

Electrochemical Treatment Method	Oily Wastewater	Result	Reference
Aluminum	Real bilgewater	81.74% Oil-grease Removal	(Ulucan, et al. 2014)
Steel/Aluminum	Synthetic	99.9% Oil-grease Removal	(Rincon and La Motta 2014)
Aluminum	Real wastewater	81% Oil-grease Removal	(Sekman, et al. 2011)
Aluminum	Synthetic wastewater	98.8% diesel removal	(Safari, Aghdam and Kariminia 2015)
Aluminum	Real wastewater	83.91% Total Organic Carbon removal	(AlJaberi 2020)
Aluminum	Synthetic wastewater	94% oil-grease removal (as turbidity)	(Al-Rubaiey and Al-Barazanji 2018)

1.2.2 Oily Wastewater

OWW is a complex matrix that can contain several contaminants that make them a threat to environmental and human health. These include oils, fuels, detergents, heavy metals, other organic pollutants, etc. (Han, et al. 2019) (Church, et al. 2019). As such, OWW is difficult to treat. Multiple contaminants frequently require several different types of treatment and interactions between the contaminants can sharply reduce the effectiveness of these treatment technologies. From a Department of Navy perspective, bilgewater may be the largest source of OWW generated by afloat forces and is the focus of the present project.

There is a present need to easily measure the concentrations of emerging contaminants, such as PFOS and PFOA, in bilgewater as both international and domestic regulatory scrutiny increases for these compounds. Currently, in countries which do not permit the discharge of OWW until PFOS concentrations are verified to be below regulatory values, OWW is containerized and sampled. Samples are then sent to certified commercial laboratories that can perform the specialized analyses needed to measure PFOS and related compounds. The complexity of the bilgewater matrix further complicates the analysis through introduction of potential interferences, resulting in possible data quality issues and long turn-around times for results. This process has resulted slowdown of OWW disposal in affected ports, causing logistical and operational challenges.

One of the most challenging aspects of OWW in terms of chemical analyses is the oil/water emulsions. These form in bilgewater due to mechanical mixing energy from waves (Eskandarloo,

Selig and Abbaspourrad 2018) and from surfactant stabilization due to surfactants commonly found in detergents, cleaning agents, aqueous film forming foams, etc. (Church, et al. 2019). Emulsified oil, defined as oil droplets $<20\ \mu\text{m}$, are difficult to remove as they are neutrally buoyant (e.g. cannot use gravimetric separation) and highly stable. These oil emulsifications can lead to inferences for analytical chemistry, resulting in difficulty to accurately determine PFAS concentrations.

Typically, overtime, these emulsions break down due to thermodynamic instability. As may be expected, methods to separate oil from water in OWW try to take advantage of these processes. These processes are: creaming/sedimentation, flocculation, coalescence, and Oswald ripening (Church, et al. 2019). In the present study, electrocoagulation is used to neutralize repulsive electrostatic forces, allowing for flocculation via attractive van der Waals forces. This flocculation will eventually lead to coalescence of the oil on the surface or bottom of the solution, depending on the oil density.

The process of emulsion destabilization is affected by various physiochemical properties of the OWW and this has been nicely reviewed in (Church, et al. 2019). For the present study, four seem to be particularly relevant. First, in the simplest of emulsions (e.g. DI water and oil), increased temperature results increased oil droplet movement and collision, generally resulting in destabilization. However, in OWW, which has all sorts of other contaminants including surfactants, this increase in molecular collision due to increased temperature may increase the effectiveness of the surfactants in stabilizing the emulsification (Kokal 2005). Types of surfactants and their concentration can also decrease the rate of emulsion destabilization, depending on the specific surfactant and concentration. Destabilization can be complicated by the fact the bilgewater surfactant loads are not well characterized and are highly variable depending on daily shipboard activities, such as cleaning or even fire suppression.

pH can influence the stability of these solutions in complex ways, typically with higher pH resulting in greater destabilization, with typical bilgewater pH reported between 6.8 to 9.0, and likely to frequently change due to chemical composition of the bilgewater. Finally, ionic strength can be especially important in the stability of emulsions. Specifically, increasing ionic strength can shield electrostatic repulsion from the oil droplets, resulting in coalescence and flocculation. In addition, salts can impact surfactant solubility and can increase the density of the aqueous phase. An easy measurement of ionic strength is electrical conductivity and conductivities of bilgewater have been reported in the range of $679\ \mu\text{S}/\text{cm}$ to $8.4\ \text{mS}/\text{cm}$ (Church, et al. 2019).

All of this information regarding OWW characterization indicates that in studies using synthetic OWW, it is critical that the synthetic OWW is representative of OWW. In many studies, synthetic OWW is simply oil mechanically emulsified into DI water, or sometimes with the addition of a surfactant to stabilize. Actual bilgewater, and other OWW, are complex mixtures of salts, surfactants, oils, and many other contaminants. Further, the procedure of OWW is highly variable, which can make it challenging to compare across studies, resulting in some authors calling for a standardization of synthetic OWW (Dardor, et al. 2021). In the present study, we will scale up the complexity of the synthetic OWW used to test our system.

1.2.3 PFOS Detection

Methods of PFOS detection have become an area of interest in recent years due to the chemical's persistence in the environment and impending regulatory actions. The United States Environmental Protection Agency (USEPA) has recently lowered the interim lifetime drinking water health advisory level to 0.02 parts per trillion (United States Environmental Protection Agency 2022), and issued draft aquatic water quality criteria for freshwater and marine water (United States Environmental

Protection Agency 2022). Note that these do not include chronic and wildlife aquatic criteria values for marine systems due to a lack of relevant toxicological data. Currently, only one analytical method (EPA 537) is approved for use with drinking water samples (United States Environmental Protection Agency 2009). A draft validated method (EPA 1633) has been released for use for non-potable water and other matrices as well (United States Environmental Protection Agency 2022). Both of these methods require advanced instrumentation, a liquid chromatograph equipped with tandem mass spectrometers, which is generally only available in analytical laboratories and research institutions. In addition, due to challenging QA/QC requirements, many fewer labs are currently certified for this method. As the Navy is pivoting rapidly to using the Draft 1633 method for non-drinking water matrices, including OWW, the logistics of sampling and analyzing OWW at OCONUS locations is only getting more complicated and delayed.

The cost and availability of testing capabilities is driving the analytical community to research and develop alternative ways that may be cheaper or easier to detect PFOS and related compounds at levels relevant to regulatory limits. Most published methodology not requiring a liquid chromatography instrument generally falls within two categories: (1) chemical/optical detection method and (2) electrochemical analysis (Ryu, et al. 2021).

Chemical/optical approaches to PFOS detection generally rely upon interaction of PFOS with a detection chemical that changes color or fluorescence. Colorimetric methods of detection are advantageous since they are typically easy to use and have a rapid response. Recent studies developing colorimetric sensing methods for PFOS have reported on the use of nanomaterials as the sensing material (Ryu, et al. 2021) (Garg, et al. 2022). Nanomaterial-related sensing methods have been reported with detection levels approaching parts per billion ($\mu\text{g/L}$) (Fang, et al. 2018) (Niu, et al. 2014) (Cong, et al. 2015). Similarly, use of dyes or other color compounds in sensing technology has been reported to yield detection levels at with parts per million (mg/L) or parts per billion levels (Menger, et al. 2022) (He, et al. 2020). These methods may also use a preconcentration step, solid phase extraction, to enhance detection limits. However, these detection limits are still well above the limits set forth for regulatory action.

Fluorescence-based techniques also focus on utilizing nanomaterials to report concentrations based on interaction with PFOS to deactivate or activate the fluorescent phenomena. Strategies to deactivate fluorescence have utilized naturally fluorescent materials such as carbon dots, quantum dots, or dyes. Reports using this “switch off” strategy of detection have been relatively sensitive, with limits of detection reported in the parts per billion and part per trillion levels (Feng, et al. 2014) (Zhang, et al. 2022). Alternatively, a “switch on” approach has also been reported where interaction of PFOS with a reporter appears to enhance fluorescence emissions with similar limits of detection (Cheng, et al. 2019) (Cheng, Du, et al. 2018). Fluorescence-based biosensors for PFOS are not as prevalent as chemical approaches, however one bacterial sensor has been reported to detect PFOS levels down to parts per trillion levels (Sunantha and Vasudevan 2021). These optical methods usually require specialized chemicals which can require special handling requirements and optical measurement capabilities that may be difficult to replicate in for small or portable applications (Shin, et al. 2021).

Electrochemical analyses rely on the interaction of PFOS with an electrode surface during programmed changes in voltage or current. Most of the recent publications have looked into voltammetry or impedance approaches. In voltametric approaches, a current or voltage signal is monitored as electrical signals are used to interrogate an electrode surface. Several different electrochemical tests can be performed. Differential pulse voltammetry has been utilized with a molecularly imprinted polymer (MIP) modified electrode where calibration curves were generated as low as 25 parts per trillion. A similarly MIP-modified electrode was able to perform detection via

impedance spectroscopy at about 1.7 parts per trillion (Clark and Dick 2020). Similar low detection limits have been seen in other studies utilizing MIP-modified electrodes (Kaemi, Potts and Dick 2020) (Lu, et al. 2022), but commercially available services to provide these types of electrodes were not able to be determined and could prove to be problematic for the eventual fielding of a sensor.

Bubble nucleation evaluation has also been a reported electrochemical analysis with low levels of detection. In this method, the potential of the electrode is lowered until hydrogen gas is generated. The interaction of PFOS (as a surfactant) with the stabilization of the gas bubble is detectable as an electrical current shift during the bubble nucleation process. Methods utilizing this phenomenon have been reported to provide limits of detection down to 40 parts per trillion with a preconcentration step (Ranaweera, Ghafari and Luo 2019) (Ranaweera, An, et al. 2022). This bubble nucleation method requires nanoelectrodes (An, Ranaweera and Luo 2020), which may not be commercially available or robust enough for portable systems.

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2. METHODS AND MATERIALS

2.1 METHODS

2.1.1 Oily Wastewater

The protocol for generating a synthetic OWW was a combination of procedures suggested by (Dardor, et al. 2021) and (Church, et al. 2019). First, a 0.1M potassium chloride electrolyte solution was mixed by adding the salt to deionized (dI) water. This electrolyte was used to make the synthetic OWW. For this study, the Navy Standard Bilge Mix (NSBM) #4 was used to bring the oil concentration in the electrolyte to either 200 or 1000 mg/L, depending on the concentration required for the experimental setup.

NSBM #4 was obtained from Naval Surface Warfare Center Carderock and used as received. The density of NSBM #4 was determined to be 0.87 g/mL by taking the average mass of 1 mL aliquots (n=10) using a microbalance scale. The required volume of NSBM #4 was then added to a 2 L glass beaker using a glass syringe. 1.8L of electrolyte was then added to this beaker and sonicated in a heated sonication bath for 30 minutes to emulsify the oil.

For experiments requiring a surfactant, a stock solution of sodium dodecyl sulfate (SDS) was prepared by dissolving 0.05g SDS in 100mL of heated dI water. An aliquot of this stock solution was used to increase the SDS concentration in the electrolyte as required. During preparation of the oil and grease solution, this aliquot was added to the glass beaker prior to sonication.

After sonication, an overhead mixer was used to provide stirring action for 30 minutes at 500 rpm. After stirring, the electrolyte was used in the electrocoagulation experiments.

2.1.2 Electrocoagulation Cell

Based on the literature review, aluminum plates were chosen as the metal electrodes for electrocoagulation. The team purchased 6"-long, 1/8"-thick aluminum plates. Three different widths (1", 2" and 2.5") were selected to provide different exposed surface areas for the electrochemical reactions. Cells were fashioned by drilling 0.25" mounting holes at the top and bottom of the plates. These mounting holes were centered along the width of the plate and 1" offset from the edge. Plates were mounted to 0.25" threaded nylon rods to create a 6-plate cell. Spacing between the cell was maintained by inserting 0.5" nylon spacers between the plates, on the threaded rod. Aluminum surfaces were then cleaned with Alconox detergent, followed by dI water rinsing, prior to use in oil-electrolyte mixtures.

With these 6-plate configurations, three plates would be used as anodes and three plates would be used as cathodes for a total of three anode-cathode pairs. Anode and cathode designations would alternate so that anodes were only adjacent to cathodes and vice-versa. Electrical connections were made to a laboratory power supply using standard alligator-clip test leads. Voltage and current were monitored through the digital display on the power supply.

Alternate electrical connections were also considered for future iterations of the electrocoagulation cell. Solder connections usually provide robust connections with little resistive loss. However, the aluminum plate material is not amenable to standard electrical soldering techniques and could make fabrication more difficult. Fabrication of screw terminals on the plates using aluminum hardware was identified as the best option to make electrical connections, considering material compatibility and durability.

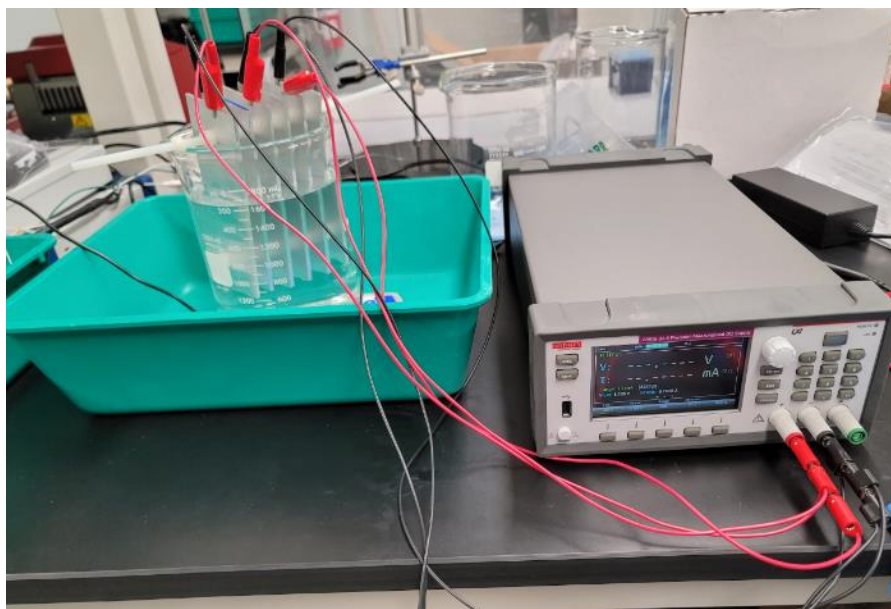


Figure 2. Electrocoagulation Setup.

As shown in Figure 2, the top threaded rod was used to suspend the plates within the beaker to prevent wetting of the alligator clips and connection points. Plates were submerged approximately 3.5" in the oil-electrolyte mixture with this configuration, when using a test volume of 1.8 L. For the tests reported here, the 2.5"-wide plates were utilized, resulting in an electrochemically active surface area of 55.1 in² for both the anode and cathode.

During the tests, a voltage set point was programmed into the power supply and current was monitored at regular intervals. Samples for oil-grease analysis were taken at regular intervals utilizing glass pipettes and stored in glass vials for later analysis.

2.1.3 Oil and Grease Measurement

Oil and grease content was measured utilizing a solvent extraction technique followed by infrared spectroscopy. A Horiba OCMA-550 oil content analyzer was used as the measurement device. Horiba solvent S-316 was used as the extraction solvent. Oil standards (200 mg/L and 100 mg/L) were prepared by adding a known mass of NSBM #4 by glass syringe to a 25 mL volumetric flask followed by the addition of S-316 to reach the final volume. These were used as calibration standards prior to measurement of extracted samples using the Span Calibration mode of the instrument.

Samples were processed for oil and grease content by adding 10 mL of S-316 to 20 mL of sample in glass vials. Samples were then vortexed for 5 minutes at 1800 rpm and allowed to separate. The bottom solvent layer was then extracted from the vial using a disposable glass pipette. Approximately 7 mL of this solvent layer was then placed in a 20 mm quartz cell and measured in the OCMA-550 for oil content. Dilutions were performed with S-316 for samples containing oil content greater than the upper range of the instrument (200 mg/L).

3. RESULTS & DISCUSSION

3.1 OILY WASTEWATER SAMPLING

Samples of oily wastewater were collected from San Diego area Bilge and Oily Wastewater Treatment Systems prior to treatment in order to get some understanding of typical wastewater characteristics at active Navy shore facilities. These samples were collected from two separate systems at Naval Air Station North Island and Naval Base San Diego. Measurements of pH and conductivity were performed at the NIWC facility at Point Loma. Total dissolved solids was estimated from conductivity measurements (Rusydi 2018). Samples were packaged and sent to Weck Laboratories (Compton, CA) to determine chemical oxygen demand, oil and grease content, and total suspended solids. Samples were transported and processed in accordance with prescribed preservation and sample holding times.

Table 2. Characteristics of oily wastewater sampled in the San Diego region.

Location	Conductivity, mS/cm	Total Dissolved Solids (estimated), g/L	pH	Chemical Oxygen Demand, mg/L	Oil & Grease Content (Hexane extractable), mg/L	Total Suspended Solids, mg/L
Naval Base San Diego	10.31	9.18	6.63	570	130	270
Naval Air Station North Island	9.92	8.83	6.63	1900	180	350

The numbers are consistent with the values report in the USEPA's Notice of Discharge reports for submarine and surface bilgewaters (United States Environmental Protection Agency 1999) (United States Environmental Protection Agency 1999). The results show relatively consistent values of conductivity, pH, oil and grease content, and total suspended solids. The chemical oxygen demand loadings in the wastewater were different between the locations by an order of magnitude, which could indicate that the parameter may fluctuate within a wide margin under normal circumstances.

3.2 ELECTROCOAGULATION

Initial experiments with the electrocoagulation cell were performed in order to determine approximate requirements for current and voltage. Two separate experiments were conducted with the different size electrodes and different salt concentrations. These experiments show minimal current and electrochemical activity could be observed with the cell operating in clean dI water with voltages up to 12 V. When the salt concentration was increased to 0.1M (7.45 g/L) potassium chloride, electrochemical activity began to be observed at voltages of 1V and greater was applied to the cell (Figure 3). The average current density was 4.7 mA/in² at an applied voltage of 1V and 54 mA/in² at an applied voltage of 2V. Significant gas generation and precipitate formation was

observed as voltages reached 5V and higher. An applied voltage of 4V was chosen for further experiments based on previously reported studies.

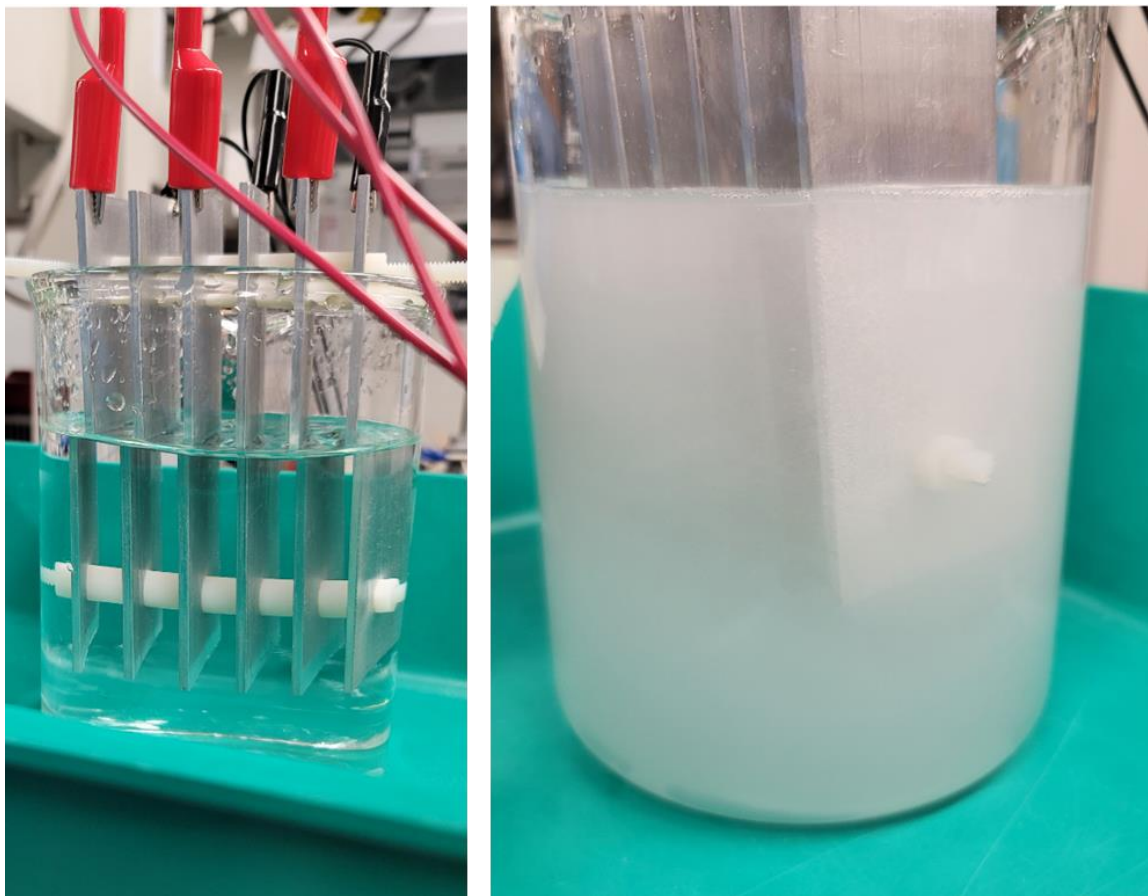


Figure 3. Electrocoagulation cell before (left) and during (right) during voltage application.

Time course experiments were performed with oil and grease concentrations of 200 mg/L and 1000 mg/L. In these experiments an applied voltage of 4V was used to perform the electrocoagulation action. An initial scoping experiment was performed with a starting oil-grease concentration of 200 mg/L. Electrical current density was observed to increase from 16.5 mA/in² initially to 24.5 mA/in² after one hour. White precipitate and vigorous gas bubble formation was observed from the start of voltage application and continued through the full hour, with the precipitate becoming darker towards the end. Samples taken over the course of 1 hour indicated that oil-grease was not detectable in samples recovered from the electrochemical cell. Floc formation was allowed to occur overnight and observed to settle to the bottom of the samples after formation (Figure 4). It appeared that increases in floc volume did not continue after 20 minutes and suggests that shorter time course experiments would be sufficient.



Figure 4. Images showing precipitate formation immediately after the conclusion of an experiment (top) and after allowing for floc development (bottom).

Replicate experiments were performed with a 1000 mg/L oil and grease concentration were allowed to react over 15 minutes with an applied voltage of 4V. During these experiments, similar current densities were observed starting at a mean current density of 18.2 mA/in^2 and increasing steadily to an average of 20.5 mA/in^2 after 15 minutes. A fluffy floc was formed after 30 seconds of voltage, but did not settle into a well defined layer (Figure 5). Good separation of the floc from the overlying liquid was not observed until at least 1 minute of voltage applications. While the settled floc layer did appear to steadily increase in volume in proportion to the time of applied voltage, floc formation in both the 10 minute and 15 minutes samples were observed to be approximately equal.

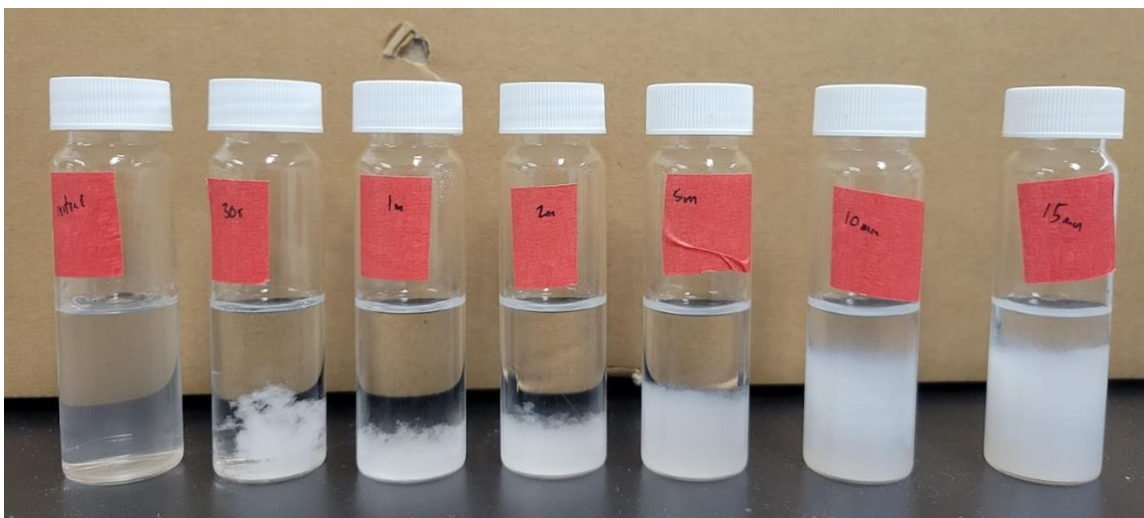


Figure 5. Floc formation during electrocoagulation experiments on synthetic wastewater without surfactant.

Oil and grease content were observed sharply decrease through about 2 minutes (Figure 6). After this, the detected concentrations appeared to fluctuate, reaching a minimum value followed by a slight rebound in concentration. Removal of up to 96.6% and 93.1% of the oil and grease content were seen with the 1st and 2nd experimental replicates respectively. The observed trends appear to indicate that an optimal amount of electrocoagulation may need to be determined as the concentrations of oil and grease did not continue to decrease with increased time. Furthermore, the quality of the floc and settability also appeared to be impacted with additional electrocoagulation time.

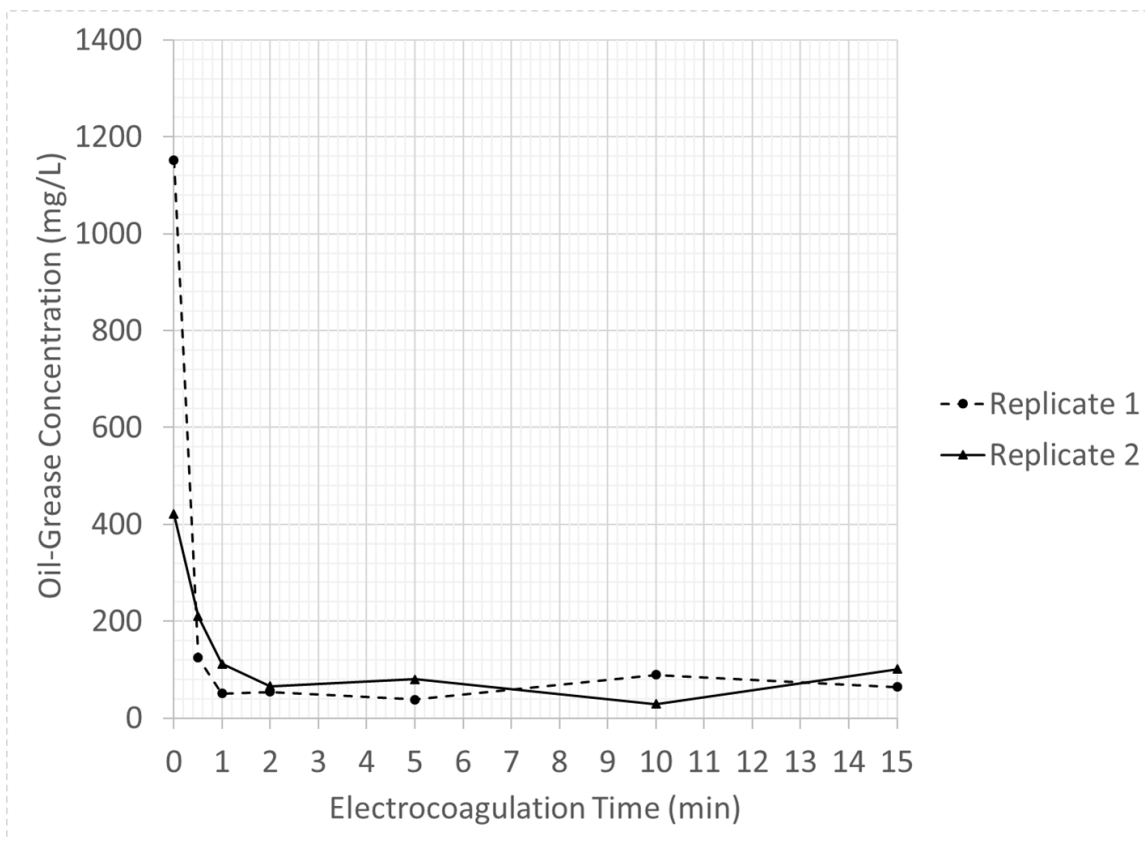


Figure 6. Oil removal over time for syntetic wastewater without surfactant.

Another set of replicate experiments were performed with a 1000 mg/L oil and grease concentration again, but with an additional SDS concentration of 100 mg/L. With a 4 V applied voltage, current densities started at an average of 21.5 mA/in², similar to the instance without SDS. However, current densities decreased as the experiment progressed to an average of 16.2 mA/in². A significant amount of stable foam, mixed with aluminum precipitate, was formed at the top of the beaker holding the electrocoagulation cell (Figure 7).

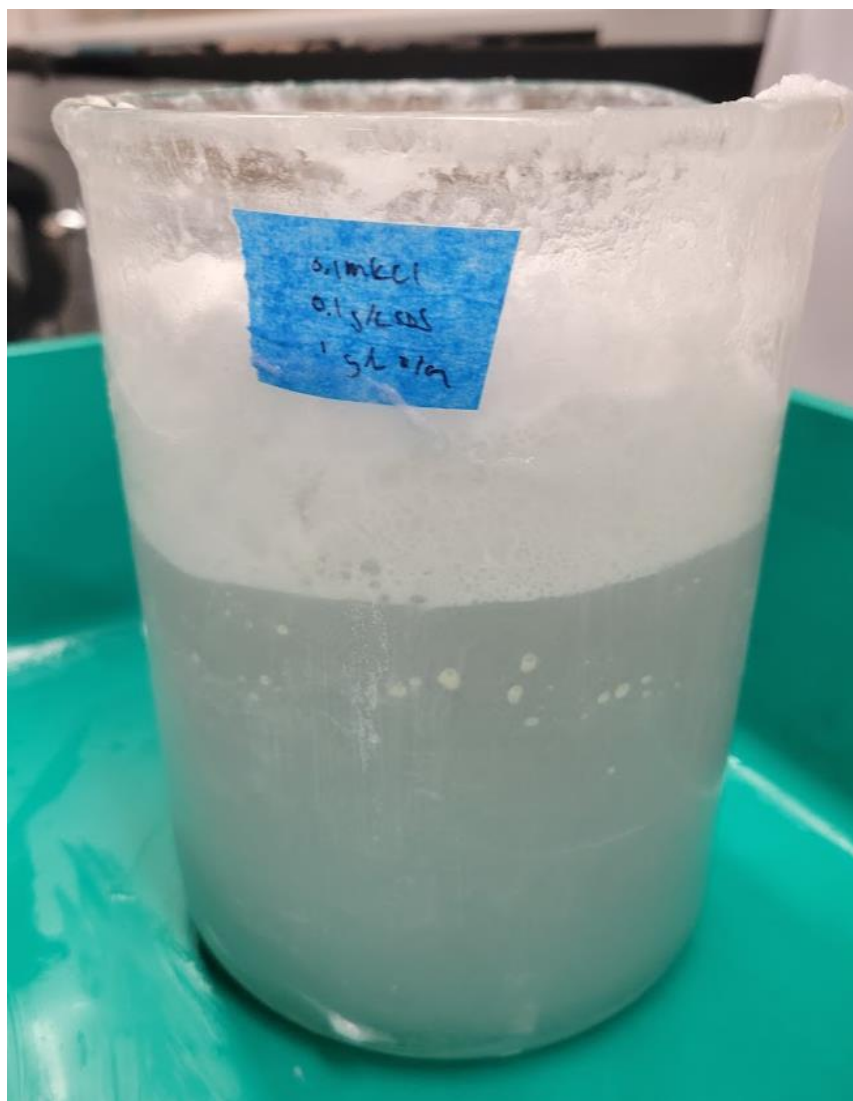


Figure 7. Metal precipitate and foam formation from electrocoagulation of oily wastewater with SDS as surfactant.

The formation of this foam likely began to interfere with the available surface area at the top of the beaker, which would be consistent with the steady decrease in observed current density. The amount of floc that settled to the bottom of the beaker was also substantially less than that seen with the previous experiment (Figure 8), possibly influenced by the stability of the floating foam layer.



Figure 8. Floc formation from oily wastewater with surfactant as seen in samples taken over 15 minute.

The same rapid decline in oil and grease content was observed while the rebound in concentration was not observed (Figure 9). Oil and grease was at or near non-detect levels by the 5 minute time point. Removal of close to 100% was seen in both replicates. While the SDS did appear to stabilize the formation of gas bubbles and foam, the presence of a surfactant may also help in the stabilization of the oil and grease removal by the aluminum hydroxide precipitates.

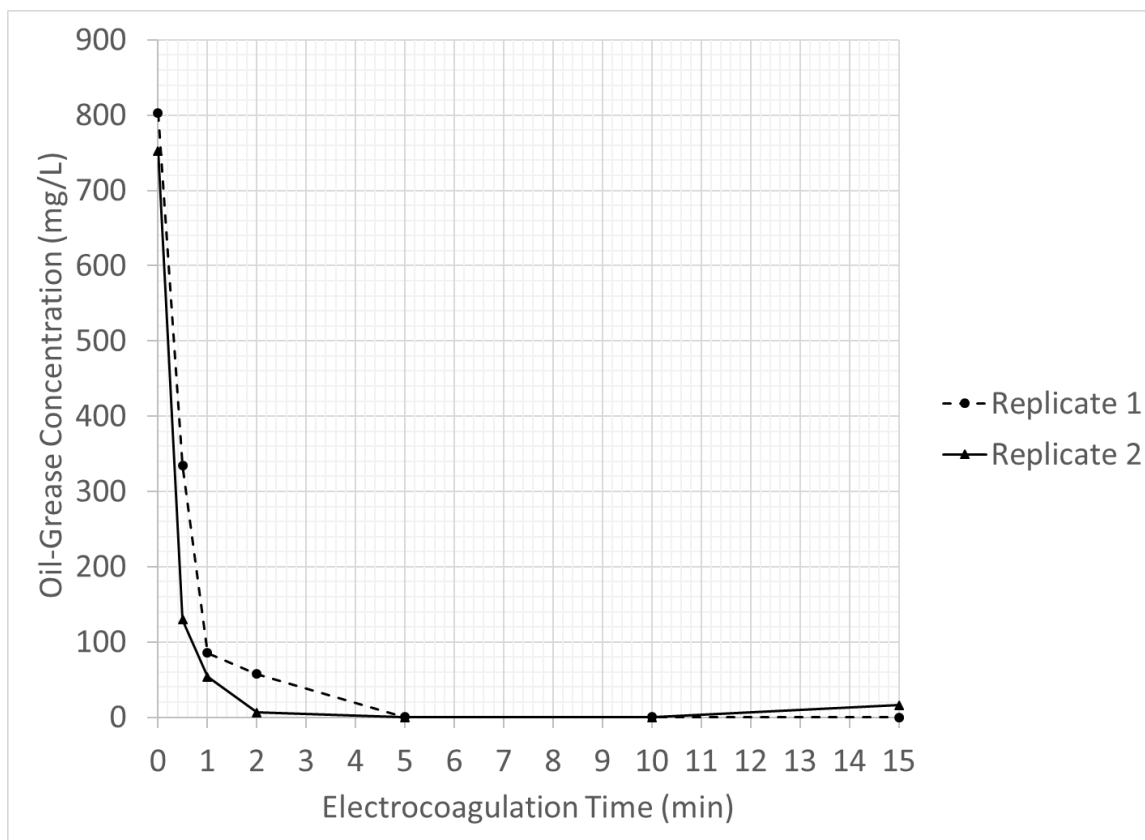


Figure 9. Oil removal over time for syntetic wastewater with surfactant.

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4. CONCLUSIONS AND FUTURE WORK

We have shown here that oil and grease content in synthetic wastewaters can be easily be removed through an electrocoagulation process. In the cases tested here, oil and grease removal could be considered complete within a few minutes of treatment followed by floc separation. The impacts of surfactant did not appear to be a significant factor in ultimate oil and grease removal. Instead, the main impact of surfactant, if present in a wastewater, may be the unintentional formation of a foam precipitate layer.

Future work in this area will examine the ability to optimize the electrocoagulation process and design a semi-portable system for use in conjunction with a PFOS sensor. Some reports of PFOS removal via electrocoagulation have been reported recently (Leung, et al. 2022). Therefore, the impacts of electrocoagulation on PFOS content will also need to be determined and the electrocoagulation process should be optimized to minimize loss of PFOS from the treated water fraction so that accurate measurements can be performed.

Additional work will need to be performed to refine PFOS sensing techniques for such a system. The effort in the next fiscal year will evaluate both anodic stripping voltammetry and bubble nucleation as possible analytical methods with the most promise to be successfully integrated into a PFOS detection system.

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REFERENCES

- Abuhasel, Khaled, Mohamed Kchaou, Mohammed Alquraish, Yamuna Munusamy, and Yong Tzyy Jeng. 2021. "Oily Wastewater Treatment: Overview of Conventional and Modern Methods, Challenges, and Future Opportunities." *Water* 13: 980. doi:https://doi.org/10.3390/w13070980.
- AlJaberi, Forat Yasir. 2020. "Removal of TOC from oily wastewater by electrocoagulation technology." *IOP Conf. Series: Materials Science and Engineering* 928. doi:10.1088/1757-899X/928/2/022024.
- Al-Rubaiey, Najem , and Mohammed Al-Barazanji. 2018. "Electrocoagulation Treatment of Oily Wastewater in the Oil Industry." *Journal of Petroleum Research and Studies* 8 (3): 274-289. doi:10.52716/jprs.v8i3.285.
- An, Shizhong, Ruchiranga Ranaweera, and Long Luo. 2020. "Harnessing bubble behaviors for developing new analytical strategies." *Analyst* 145: 7782-7795. doi:10.1039/D0AN01497D.
- Cheng, Zhen, Hongcen Dong, Jiaman Liang, Fang Zhang, Xianping Chen, Lingling Du, and Kejun Tan. 2019. "Highly selective fluorescent visual detection of perfluorooctane sulfonate via blue fluorescent carbon dots and berberine chloride hydrate." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 207: 262-269. doi:10.1016/j.saa.2018.09.028Get rights and content.
- Cheng, Zhen, Lingling Du, Panpan Zhu, Qian Chen, and Kejun Tan. 2018. "An erythrosin B-based "turn on" fluorescent sensor for detecting perfluorooctane sulfonate and perfluorooctanoic acid in environmental water samples." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 201: 281-287. doi:10.1016/j.saa.2018.05.013.
- Church, Jared, Jeffrey Lundin, Daniela Diaz, Dianne Mercado, Marjorie Wilner, Woo Hyoun Lee, and Danielle Paynter. 2019. "Identification and characterization of bilgewater emulsions." *Science of The Total Environment* 691: 981-995. doi:10.1016/j.scitotenv.2019.06.510.
- Clark, Rebecca, and Jeffrey Dick. 2020. "Electrochemical Sensing of Perfluorooctanesulfonate (PFOS) Using Ambient Oxygen in River Water." *ACS Sensors* 5: 3591-3598. doi:10.1021/acssensors.0c01894.
- Cong, Yan-bin, Yong-hong Zheng, Li Zheng, Fei Wu, and Ke-jun Tan. 2015. "Colorimetric Assay of Perfluorooctanesulfonate Based on Gold Nanoparticles." *Spectroscopy and Spectral Analysis* 35 (1): 189-192. doi:10.3964/j.issn.1000-0593(2015)01-0189-04.
- Dardor, Dareen, Mashaal Al-Mass, Joel Minier-Matar, Arnold Jason, Ramesh Sharma, Mohammad K Hassan, Mariam Al Ali Al-Maadeed, and Adham Samer. 2021. "Protocol for Preparing Synthetic Solutions Mimicking Produced Water from Oil and Gas Operations." *ACS Omega* 6881-6892.
- El-Shazly, Ahmed, and Mohammad Daous. 2013. "Investigations and Kinetics Study for the Effect of Solution Flow Rate on the Performance of Electrocoagulation Unit Used for Nutrients Removal." *International Journal of Electrochemical Science* 8: 12509-12518.
- Eskandarloo, Hamed, Michael J Selig, and Alireza Abbaspourrad. 2018. "In situ H₂O₂ generation for de-emulsification of fine stable bilge water emulsions." *Chemical Engineering Journal* 434-442.

- Fang, Cheng, Xian Zhang, Zhaomin Dong, Liang Wang, Mallavarapu Megharaj, and Ravi Naidu. 2018. "Smartphone app-based/portable sensor for the detection of fluoro-surfactant PFOA." *Chemosphere* 191: 381-88. doi:10.1016/j.chemosphere.2017.10.057.
- Feng, Hui, Niya Wang, ThanhThuy Tran, Lijuan Yuan, Jiezhen Li, and Qingyun Cai. 2014. "Surface molecular imprinting on dye-(NH₂)-SiO₂ NPs for specific recognition and direct fluorescent quantification of perfluorooctane sulfonate." *Sensors and Actuators B: Chemical* 195: 266-273. doi:10.1016/j.snb.2014.01.036.
- Garg, Shafali, Pankaj Kumar, George Greene, Vandana Mishra, Dror Avisar, Radhey Sharma, and Ludovic Dumeé. 2022. "Nano-enabled sensing of per-/poly-fluoroalkyl substances (PFAS) from aqueous systems – A review." *Journal of Environmental Management* 308: 114655. doi:10.1016/j.jenvman.2022.114655.
- Han, Meiling, Jin Zhang, Wen Chu, Jiahao Chen, and Gongfu Zhou. 2019. "Research Progress and Prospects of Marine Oily Wastewater Treatment: A Review." *Water* 11 (12): 2517. doi:10.3390/w11122517.
- He, Jincon, Peipei Qiu, Jiayi Song, Shiyun Zhang, and Yan Bai. 2020. "A resonance Rayleigh scattering and colorimetric dual-channel sensor for sensitive detection of perfluorooctane sulfonate based on toluidine blue." *Analytical and Bioanalytical Chemistry* 412: 5329-5339. doi:10.1007/s00216-020-02748-9.
- Kaemi, Rezvan, Emili Potts, and Jeffrey Dick. 2020. "Quantifying Interferent Effects on Molecularly Imprinted Polymer Sensors for Per- and Polyfluoroalkyl Substances (PFAS)." *Analytical Chemistry* 92: 10597-10605. doi:10.1021/acs.analchem.0c01565.
- Kokal, Sunil. 2005. "Crude-Oil Emulsions: A State-Of-The-Art Review." *SPE Production & Facilities* 5-13.
- Leung, Shui, Pradeep Shukla, Dechao Chen, Ehsan Eftekhari, Hongjie An, Firuz Zare, Negareh Ghasemi, Dongke Zhang, Nam-Trung Nguyen, and Qin Li. 2022. "Emerging technologies for PFOS/PFOA degradation and removal: A review." *Science of the Total Environment* 827: 153669. doi:10.1016/j.scitotenv.2022.153669.
- Lu, Dingnan, David Zhu, Huihui Gan, Zhiyuan Yao, Jiayue Luo, Shiran Yu, Pradeep Kurup, and . 2022. "An ultra-sensitive molecularly imprinted polymer (MIP) and gold nanostars (AuNS) modified voltammetric sensor for facile detection of perfluorooctane sulfonate (PFOS) in drinking water." *Sensors and Actuators B: Chemical* 352: 131055. doi:10.1016/j.snb.2021.131055.
- Menger, Ruth, Josianne Beck, Thomas Borch, and Charles Henry. 2022. "Colorimetric Paper-Based Analytical Device for Perfluorooctanesulfonate Detection." *ACS EST Water* 4: 565-572. doi:10.1021/acsestwater.1c00356.
- Niu, Hongyun, Saihua Wang, Zhen Zhou, Yurong Ma, Xunfeng Ma, and Yaqi Cai. 2014. "Sensitive Colorimetric Visualization of Perfluorinated Compounds Using Poly(ethylene glycol) and Perfluorinated Thiols Modified Gold Nanoparticles." *Analytical Chemistry* 86 (9): 4170-4177. doi:10.1021/ac403406d.
- Ranaweera, Ruchiranga, Carina Ghafari, and Long Luo. 2019. "Bubble-Nucleation-Based Method for the Selective and Sensitive Electrochemical Detection of Surfactants." *Analytical Chemistry* 91: 7744-7748. doi:10.1021/acs.analchem.9b01060.

- Ranaweera, Ruchiranga, Shizhong An, Yue Cao, and Long Luo. 2022. "Highly efficient preconcentration using anodically generated shrinking gas bubbles for per- and polyfluoroalkyl substances (PFAS) detection." *Analytical and Bioanalytical Chemistry*. doi:10.1007/s00216-022-04175-4.
- Rincon, Guillermo J, and Enrique J La Motta. 2014. "Simultaneous removal of oil and grease, and heavy metals from artificial bilge water using electro-coagulation/flotation." *Journal of Environmental Management* 144: 42-50. doi:10.1016/j.jenvman.2014.05.004.
- Rusydi, Anna. 2018. "Correlation between conductivity and total dissolved solid in various type of water: a review." *IOP Conference Series: Earth and Environmental Science* 118: 012019. doi:10.1088/1755-1315/118/1/012019.
- Ryu, Heejeong, Baikum Li, Sylvain De Guise, Jeffrey McCutcheon, Yu Lei, and . 2021. "Recent progress in the detection of emerging contaminants PFASs." *Journal of Hazardous Materials* 408: 124437. doi:10.1016/j.jhazmat.2020.124437.
- Safari, Sania, Mojtaba Azadi Aghdam, and Hamid-Reza Kariminia. 2015. "Electrocoagulation for COD and diesel removal from oily wastewater." *International journal of Environmental Science and Technology* 13: 231-242. doi:10.1007/s13762-015-0863-5.
- Sekman, Elif, Gamze Varank, Selin Top, Mehmet Sinan Bilgili, and E Uslu. 2011. "Treatment of Oily Wastewater From Port Waste Reception Facilities by Electrocoagulation." *International Journal of Environmental Research* 5 (4): 1079-1086. https://www.researchgate.net/publication/288108705_Treatment_of_Oily_Wastewater_From_Port_Waste_Reception_Facilities_by_Electrocoagulation.
- Shin, Young-Ho, M.Teresa Gutierrez-Wing, Jin-Woo Choi, and . 2021. "Recent Progress in Portable Fluorescence Sensors." *Journal of The Electrochemical Society* 168: 017502. doi:10.1149/1945-7111/abd494.
- Sunantha, Ganesan, and Namasivayam Vasudevan. 2021. "A method for detecting perfluorooctanoic acid and perfluorooctane sulfonate in water samples using genetically engineered bacterial biosensor." *Science of The Total Environment* 759: 143544. doi:10.1016/j.scitotenv.2020.143544.
- Ulucan, Kubra, Harun Akif Kabuk, Fatih Ilhan, and Ugur Kurt. 2014. "Electrocoagulation Process Application in Bilge Water Treatment Using Response Surface Methodology." *International Journal of Electrochemical Science* 9: 2316-2326. <http://www.electrochemsci.org/list14.htm#issue10>.
- United States Environmental Protection Agency. 2022. "2nd Draft Method 1633. Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS." Washington, DC, June. <https://www.epa.gov/system/files/documents/2022-07/2nd%20Draft%20of%20Method%201633%20June%202022%20508-compliant.pdf>.
- . 2022. "Draft Recommended Aquatic Life Ambient Water Quality Criteria for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonic Acid (PFOS)." *Federal Registrar*, May 3: 26199-26201. <https://www.govinfo.gov/content/pkg/FR-2022-05-03/pdf/2022-09441.pdf>.
- . 2022. "Lifetime Drinking Water Health Advisories for Four Perfluoroalkyl Substances." *Federal Registrar*, June 21: 36848-36849. <https://www.govinfo.gov/content/pkg/FR-2022-06-21/pdf/2022-13158.pdf>.

- . 2009. "Method 537. Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) v1.1." Washington, DC: United States Environmental Protection Agency.
- United States Environmental Protection Agency. 1999. "Phase I Final Rule and Technical Development Document of Uniform National Discharge Standards (UNDS): Submarine Bilgewater: Nature of Discharge."
- United States Environmental Protection Agency. 1999. "Phase I Final Rule and Technical Development Document of Uniform National Discharge Standards (UNDS): Surface Vessel Bilgewater/Oil Water Separator: Nature of Discharge."
- Waller, Gordon, Curtis Martin, Nicholas Jones, and Danielle Paynter. 2019. "Treatment of oil-in-saltwater emulsions by in-situ production of magnetic FeOx nanoparticles." *Journal of Water Process Engineering* 31: 100851. doi:10.1016/j.jwpe.2019.100851.
- Zhang, Qiaojuan, Mengyu Liao, Keren Xiao, Kangyuan Zhuang, Weilian Zheng, and Zhiyi Yao. 2022. "A water-soluble fluorescence probe based on perylene diimide for rapid and selective detection of perfluorooctane sulfonate in 100% aqueous media." *Sensors and Actuators B: Chemical* 350: 130851. doi:10.1016/j.snb.2021.130851.
- Zhao, Chuanliang, Junyuan Zhou, Yi Yan, Liwei Yang, Guohua Xing, Huanyu Li, Pei Wu, Mingyuan Wang, and Huaili Zheng. 2021. "Application of coagulation/flocculation in oily wastewater treatment: A review." *Science of the Total Environment* 765: 142795. doi:10.1016/j.scitotenv.2020.142795.

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The potential presence of perfluorooctanoic acid (PFOS) in oily wastewaters presents disposal challenges since the chemical is becoming highly regulated. Current methods for PFOS analysis are not conducive to field measurements and cannot be completed in a timely manner. Thus, environmental managers at shore facilities face difficulties in managing the growing volume of potentially impacted oily wastewaters. We present here an approach to pretreat a sample with electrocoagulation in order to provide for electrochemical concentration determination of PFOS. A review of the state of the art in oily wastewater treatment by electrocoagulation and electrochemical PFOS determination is presented here along with results from initial electrocoagulation experiments.						
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