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REMOVAL OF RESIDUAL OIL FROM PRODUCED WATER USING MAGNETIC
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REMOVAL OF RESIDUAL OIL FROM PRODUCED WATER USING MAGNETIC
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Dedication:

To my wife, children, parents, and grandparents, for demonstrating the value of education and hard work in the pursuit of excellence.

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Abstract

The production of wastewater during hydrocarbon recovery is an unresolvable factor of the oil and gas industry. Oil wells in the US produce on average, nearly 10 barrels of water for every 1 barrel of oil. Most of the produced water is reinjected back into the formation. However, recent studies may have linked increases in localized seismic activity to corresponding rises in wastewater well injection. Consequently, environmental discharge or reuse regulations are becoming more rigorous for produced water. Produced wastewater often originates from areas where water repurposing is an attractive option due to limited water resources in the area. Current water treatment solutions have not been universally successful as practical solutions due to high treatment material costs, long treatments cycles, and the production of additional environmental waste. Therefore, the need for a cost-effective, environmentally safe, and low waste producing water treatment method may change the outcome of millions of barrels of unusable water produced each year. This study explores the recent advancements in nanotechnology to treat oil field wastewaters and demonstrates a newly discovered material's ability to reduce residual oil concentrations below discharge limits.

Iron oxides are commonly found in the environment and display a unique characteristic of superparamagnetism that is desirable for produced water treatment. The inherent magnetism of these particles allows them to be physically manipulated by a magnetic field and can be used to separate trapped oil from oil-in-water emulsions. The principal objective of this study is to examine the abilities of magnetite (Fe_2O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles to reduce residual oil concentrations in produced water samples containing both dispersed and dissolved oil. Amine-coated magnetite

nanoparticles have shown oil removal capabilities in previous studies. The nanoparticles for this study were sourced from a local laboratory and also purchased commercially for comparison. The characteristics of the nanoparticles were measured and analyzed for comparative analysis and particles selection to optimize the water treatment process.

Iron oxide nanoparticles used in water treatment tests relied on carefully designed oil removal experiments, emulsion production, and nanoparticle recovery and recyclability tests. The oil removal tests were conducted with prepared oil-water emulsions at known concentrations and with locally sourced produced water samples. The oil removal tests include the combination of an oil-water emulsion and dispersed nanoparticles in varying concentrations. After mixing the solution, the cloudy oil-water emulsions were made clear almost immediately when an external magnet was applied, indicating good oil-nanoparticle adherence. Oil concentration measurements via non-dispersive infrared spectroscopy confirmed the removal of oil as seen visually in the tests. Initial emulsion oil concentrations were reduced after nanoparticle treatment from 1,000 ppm to less than 10 ppm (>99% oil removal efficiencies). The oil removed from the O/W emulsions was then separated from the nanoparticles to be reused in additional treatment cycles. Maghemite maintained >98% oil removal efficiencies for up to at least ten cycles. These test results confirm iron oxide nanoparticles as a viable treatment solution for produced waters and most importantly, provide an environmentally safe method for removing oil contaminants from oilfield waters without the production of additional waste.

Chapter 1: Introduction

1.1 Overview

The over-abundance of produced waters in the oil field continues to be a challenge for the industry. Current solutions often employed provide additional options for oilfield managers to deal with excessive volumes of produced waters where formation re-injection is not ideal or cost-effective. Produced waters contain contaminants such as high salinity, heavy metals, and even residual oil components (Table 1.1). These contaminants must be removed before disposal or reuse. The primary reduction of these contaminants occurs near the production site where simple gravitational separation techniques begin oil separation. The concentrations of these contaminants are closely monitored and wholly crucial to ensuring disposed or reused oilfield water meets environmental regulations.

Table 1.1 Common produced water components and their concentrations. (Duraismy et al., 2013).

Parameter	Natural Gas Produced Water	Oil field Produced Water
Oil/grease(ppm)	40	560
pH	4.4-7.0	4.3-10
TSS(ppm)	5500	1000
TDS(ppm)	360,000	6554
TOC(ppm)	67-38,000	1500
COD(ppm)	120,000	1220
Density(kg/m ³)	1020	1140
Arsenic(ppm)	0.005-151	0.005-0.3
Lead(ppm)	0.2-10.2	0.008-8.8
Chromium(ppm)	0.03	0.02-1.1
Mercury(ppm)	--	0.001-0.002
Oil droplet size(μm)	2 to 30	--

Gravitational separation is often unable to reduce water contaminant concentrations below the disposal restrictions. Thus, further treatment is required to remove contaminants bound within the water by chemical bonding, emulsification, or other

dissolution phenomena. Produced water may contain natural surfactants that keep oil compounds emulsified. Dissolved oil components such as phenols, polycyclic aromatic hydrocarbons (PAHs), and volatile hydrocarbons exist naturally in produced water and generally cannot be detected without magnification. Free-oil, produced solids, and other suspended contaminants are easily removed, but a more sophisticated and direct approach is required to separate the PAHs, phenols, and volatile hydrocarbons (Duraismy et al., 2013). This study demonstrates the ability of iron oxide nanoparticles to remove the emulsified oil components from water through an environmentally safe and efficient process.

1.2 Problem Statement

Most produced water collected during enhanced oil recovery (EOR) techniques or standard hydrocarbon recovery is injected directly back into the formation. This practice is often used to maintain formation pressures during long-term production and enhanced recovery techniques. This practice is widely accepted because the contaminated produced water does not require treatment before reinjection. While reinjection can help maintain formation pressures throughout production, recent studies have shown that reinjection can produce adverse effects such as aquifer/groundwater contamination and unwanted seismic activities (Peterson et al., 2018). If the produced water could be treated safely and efficiently in the field, it could be utilized by the local agricultural industry or in the fulfillment of local water needs. Many of today's water treatment methods do not meet disposal or reuse regulations and often produce externalities themselves.

Current restrictions of offshore water discharge into the ocean state that oil concentrations in said waters must be below 42 ppm/day and includes a 29-ppm maximum monthly average per the US Environmental Protection Agency regulations. Primary gravitational separation techniques of oil from produced water does not provide an adequate solution for reducing dissolved and emulsified oil concentrations to meet this regulation. More specialized treatment processes must also be applied to target the emulsified oil components. For onshore water disposal/reuse, there is no allowance for residual oil concentrations in the disposed water. The most common specialized treatment solutions for reducing produced water oil concentrations at or below these limits include physical treatments, chemical demulsifiers, ultrafiltration, biological treatments, and specialized thermal solutions. Although, each of these solutions suffers from disadvantages such as extended treatment times, high material cost, and additional waste production. For example, filtration techniques do not offer a reliable solution for the removal of nano-sized dissolved/emulsified oil. Filtration of increasingly small particles also increases filter fouling that prevents flow and slows treatment. Chemical demulsifiers have shown the ability to demulsify the dissolved oil with single-use materials that can be expensive and unsafe for the environment even at low (0.1 ppm) concentrations (Duraismy et al., 2013). Thermal and biological solutions are challenging to use due to energy requirements and expensive machinery.

Therefore, a produced water treatment method that can remove emulsified oil effectively without producing further waste is necessary to the growing challenge of excess produced water production. Oilfield water management teams could benefit from new technologies that provide additional options for produced water reuse and disposal.

Wastewater streams that were previously considered useless could be transformed into an asset, especially in areas where there are limited water resources. However, the acceptance of using the treated effluent for human consumption may be difficult without detailed toxicology and contamination testing.

This study provides a nanoparticle oil removal technique for produced water that is environmentally safe, cost-effective, and efficient in reducing dispersed and dissolved oil concentrations without additional material waste production.

1.3 Objectives

The primary goal of this investigative study aims to demonstrate oil removal and demulsification of produced water samples using superparamagnetic nanoparticles. This study illustrates the demulsification ability of these nanoparticles as an oil and gas wastewater treatment solution. The specific objectives of this study are:

- Develop a produced water treatment method using superparamagnetic nanoparticles to reduce oil concentrations below disposal limits.
- Compare and analyze nanoparticle oil removal efficiencies of synthesized and commercially obtained magnetite and maghemite nanoparticles.
- Seek to understand the characteristics of nanoparticles that aide in demulsification and nanoparticle recyclability.
- Demonstrate sustained oil removal efficiencies of these magnetic nanoparticles over sequential use and reuse trials.

1.4 Methodology

The main objectives of this thesis study were achieved through a systematic experimental investigation and also a thorough literature review of current produced water treatment techniques. The analysis of relevant literature magnified the importance of the proposed nanoparticle produced water treatment process to remove dissolved and emulsified oil components that are often difficult to separate. The experimental investigation of the nanoparticle oil removal process relies on consistent and controlled oil-in-water emulsion preparation. Emulsions were prepared by ultrasonification with real-world oil samples, mimicking the properties of produced water samples collected in the field. The treatment of locally sourced produced water was also tested to ensure the practical application of this oil removal procedure in the field.

The most important objective of this study was the analysis and discrimination of maghemite and magnetite nanoparticles samples. The nanoparticle characteristics, including size and magnetization saturation, were measured and considered throughout the study for data analysis, hypotheses, and conclusion formulation. Dispersion, oil removal, and recyclability tests for each nanoparticle sample were performed, and results analyzed for selecting the best performers. The nanoparticles with the highest oil removal efficiencies were selected for repeat testing and more advanced analysis. The oil removal efficiency was examined by oil concentration measurements before and directly following nanoparticle treatment via non-dispersive infrared spectroscopy. The tests to bolster the efficacy of the nanoparticle treatment was a complete examination of recyclability and reusability of the nanoparticles following successful, sequential oil removal treatments. The experimental data were collected for each trial and analyzed,

along with each of the various testing variables. The efficiency and applicability of the nanoparticle oil removal process were demonstrated visually and by direct experimental result comparisons.

Chapter 2: Literature Review

2.1 Characteristics of Produced Water

Produced water is the water or brine fluid that is carried to the surface along with the hydrocarbons from the subterranean formation. Produced water originates from the pores of the reservoir rock during formation. It becomes trapped in the rock pores along with the other organic materials that will later become hydrocarbons. Due to factors of age, location, temperature, and pressure, the composition and characteristics of produced water are incredibly complex. Many of the phases, the formation waters come in contact with, can dissolve in the water because water itself is an excellent solvent. While the composition of the water is unique from the factors listed, the compositional ranges of these elements can be generalized under the chemical categories listed in Table 1.1. These produced water constituents include dispersed oil, dissolved organic compounds, produced solids, metal, and even treatment chemicals (Duraismy et al., 2013).

Oil and grease found in produced water attract the most significant attention. The presence of oil/ grease in produced water is described as the total amount of dispersed oil and dissolved organic compounds. Dispersed oil droplets are generally present in produced waters in the range of 4-5 microns. However, the droplet size may be greater or smaller depending on the interaction the water has with the other liquids and gases as it moves to the surface. Dispersed oil is considered an especially vital constituent to track as it can be especially toxic to aquatic ecosystems. The majority of dispersed oil droplets are removed by standard gravitational separation techniques at the production site. However, the more challenging trapped oil can remain. Oil droplets smaller than 10 microns in size are generally not removed by primary water processing operations. In

fact, tiny oil droplet can interfere with these processes. (Bansal and Caudle, 1999). The droplets are held dispersed in the aqueous phase often by natural or production treatment surfactants. Factors that can affect produced water oil concentrations include interfacial tensions between the phases, the efficiency of primary separation devices, oil density, and chemical pretreatments. (Ali et al., 1999).

Hydrocarbons existing naturally in produced water that are soluble and become dissolved in the water include phenols, organic acids, volatiles, and polycyclic aromatic hydrocarbons (PAHs). Solubilized hydrocarbons are so challenging to remove that they are often left untreated and disposed of in the ocean (offshore) or reinjected (onshore). (Viel, 2004). Fig 2.1 shows the standard components of oil found in produced water.

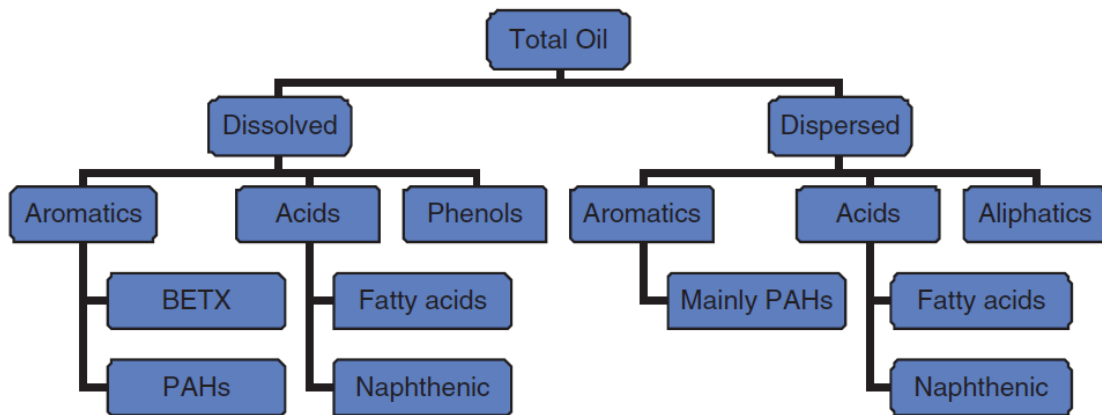


Figure 2.1 Oil components in produced water (Yang, 2006).

The next most concerning produced water constituent is salt concentration. The concentrations are measured as salinity, TDS (total dissolved solids), or conductivity. The salinity of produced water is especially important for onshore water disposal management. However, most produced water has a higher salinity than seawater and therefore, must also be accountable for in offshore production (Cline, 1998). Water salinity can be measured in conductivity. Electrical conductivity is a product of dissolved

ions that conduct electricity in the water. Waste water that contains elevated TDS concentrations are relatively conductive. Conductivity is measured in μ Siemens per centimeter (μ S/cm). TDS is measured in parts per million (mg/L) (Godsey, 2011). Produced waters with high salt concentrations require desalination techniques in preparation for reuse. Produced waters containing residual oil must be pretreated to remove the oil components before desalination. (Drewes et al., 2009). The type of salt found in the produced waters of the oil basins of the western United States as shown in Fig 2.2. Sodium Chloride (NaCl) makes up much of the salt content in many of these basins, including that of the Anadarko basin where the produced water samples for this study were taken. Additionally, oil samples taken from the Anadarko basin show an oil API gravity of 43 degrees (Collins, 1969).

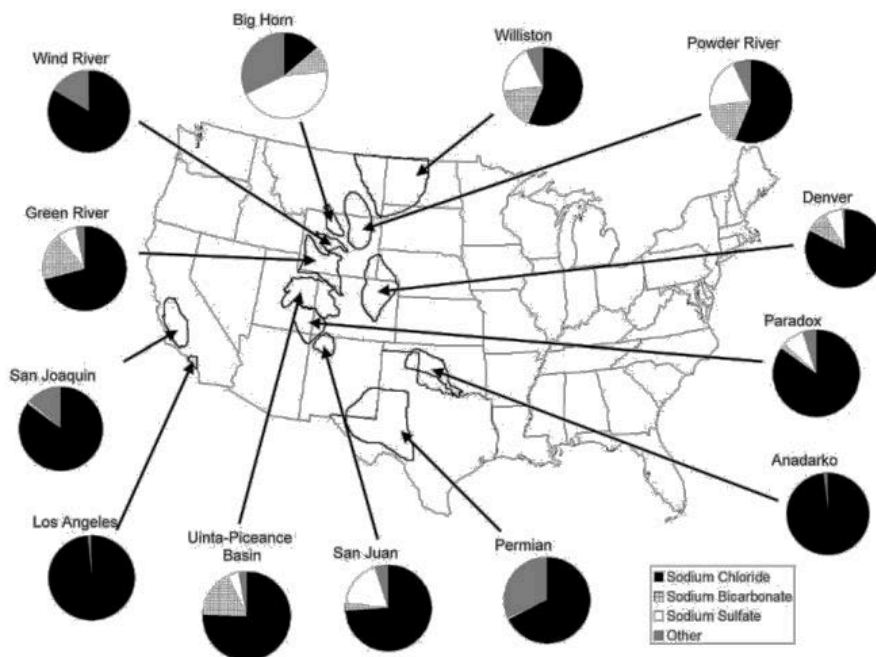


Figure 2.2 Produced water salt composition in the central and western United States (Drewes et al., 2009).

2.2 Oil-in-Water Emulsions

In an oil-in-water emulsion system, the finely divided particles of dispersed oil are known as the dispersed or discontinuous phase. The non-dispersed or continuous phase is the water that surrounds the dispersed oil droplets. It is common for a third component, the emulsifier or emulsifying agent that is present to aid in emulsion stability through surface interactions. The emulsions used throughout this study are known as oil-in-water (O/W) emulsions designed to mimic the conditions of produced water. However, it should be noted that water-in-oil (W/O) emulsions occur when water droplets are dispersed inside a continuous oil phase.

The first step to produce a two-phase O/W emulsion is size reduction in the discontinuous or dispersed phase. Energy in the form of work must be applied to the system for this process. The amount of work required to produce an O/W emulsion with a given droplet size is described by the equation:

$$W = \gamma_{o/w} \cdot \Delta A$$

where W , is the free energy requirement measured in ergs, γ is the surface tension between the water and oil phases in dynes/cm, and ΔA is the surface area in cm^2 . The use of surface-active agents that can reduce the O/W surface tension is often used in emulsion production to decrease energy input requirements. Two conventional methods for energy input in emulsion preparation are mechanical agitation and ultrasonification. While both ways can be used successfully in emulsion preparation, it has been observed that ultrasonification reduces droplet size and increasing size uniformity of the dispersed

phase better than that of mechanical agitation (Ramisetty and Shyamsunder, 2011). Smaller droplets in the dispersed oil phase correlate with increased emulsion stability.

2.3 Current Produced Water Treatment Methods

Produced water management provides opportunities for discharge, reuse, or consumption in other industries such as irrigation or potable water. Produced water can be turned into an asset if it can be effectively treated. The main objectives for produced water treatment are described as follows (Arthur et al., 2005):

1. De-oiling – Removal of free and dispersed oil/grease.
2. Soluble organics removal.
3. Disinfection – bacteria, microorganisms, algae, etc.
4. Suspended solids (SS) removal.
5. Dissolved gas – removal of hydrocarbon gases, CO₂, hydrogen sulfide, etc.
6. Desalination – dissolved salts.
7. Softening – Removal of excess water hardness.
8. NORM (Naturally occurring radioactive materials) removal.

Current technologies and techniques of produced water treatment are used individually, or they can be combined as physical, biological, and chemical treatment processes depending on the treatment objectives. The chemical contaminant tolerances are stricter for agricultural/irrigation reuse than those of disposal or reinjection. Thus, it is important to select the treatment processes that are best suited to treat produced water with unique compositions and contaminants. Generally, the most crucial factor in determining treatment versus disposal is reliant upon overall treatment cost. It is also desirable that the treatment process can be employed at or near the production site to reduce transportation costs. The advantages and disadvantages of each treatment process must

also be considered, especially those that produce additional waste or excess energy consumption. The economics for each of the reviewed water treatment technologies is shown in Table 2.2. The most common water treatment techniques and processes, including physical, chemical, and biological processes will be examined in the following section.

Table 1.2 Treatment technology cost & efficiency (Adapted from Igunnu & Chen, 2012)

Water Treatment Technology	Overall Cost*	Removal Efficiencies
Ceramic MF/UF membrane	N/A	90-100% water recovered
Polymeric MF/UF membrane	Capital Costs + Operation: \$0.04-0.10/bpd†	85-100% water recovered
NF	Capital Cost: \$35 to \$170/bpd + Operating cost: \$0.03/bbl.	75-90% water recovered
RO	Capital cost: \$35 to \$295/bpd + Operating cost: \$0.03-0.08/bbl.	30-85% water recovered
Thermal (MSF, VCD, MED)	Capital cost: \$140 to \$360/bpd + Operating cost: \$0.08-0.19/bbl.	~75% water recovered
Demulsifiers	Varies greatly by chemicals used	-
Magnetic nanoparticle§	Varies by materials and reusability	~98-100% oil removed, 100% water recovered‡

* Based on best available data

† BPD – capital costs of treatment facility design per barrel treated daily

‡ Recovered water that meets or exceed effluent regulations

§ Still in development and not widely accepted for produced water treatment

2.3.1 Membrane Filtration Technology

Conventional produced water treatment processes can remove particles 5.0 µm and larger. Historically the level of particle size removal from produced waters has been accepted for disposal or reinjection regulation. Improved disposal regulation standards in recent years require new water treatment processes to reduce contamination below the standards of 42 mg/L of oil/water, and less than 10 mg/L of Total Suspended Solids (TSS) (EPA, 2019). Membrane treatment is a newer contaminant separation process that allows water treatment that meet the high standards of regulation (Duraismy et al., 2013).

Membranes are micro or nano-porous films that are used to separate particles according to size and are driven by pressure gradients. Membranes are produced with a specific pore range that set the limit for maximum pore size that can pass through the membrane film. The membranes can also be designed to separate only targeted components. Current membrane filtration processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RS), and specialized material filters such as polymeric or ceramic membranes.

There are two current membrane filtration processes known as cross-flow and dead-end filtration. Either of these systems functions by a pressure gradient or vacuum-driven system. A visual representation of each of these filtration systems is shown in Fig 2.3.

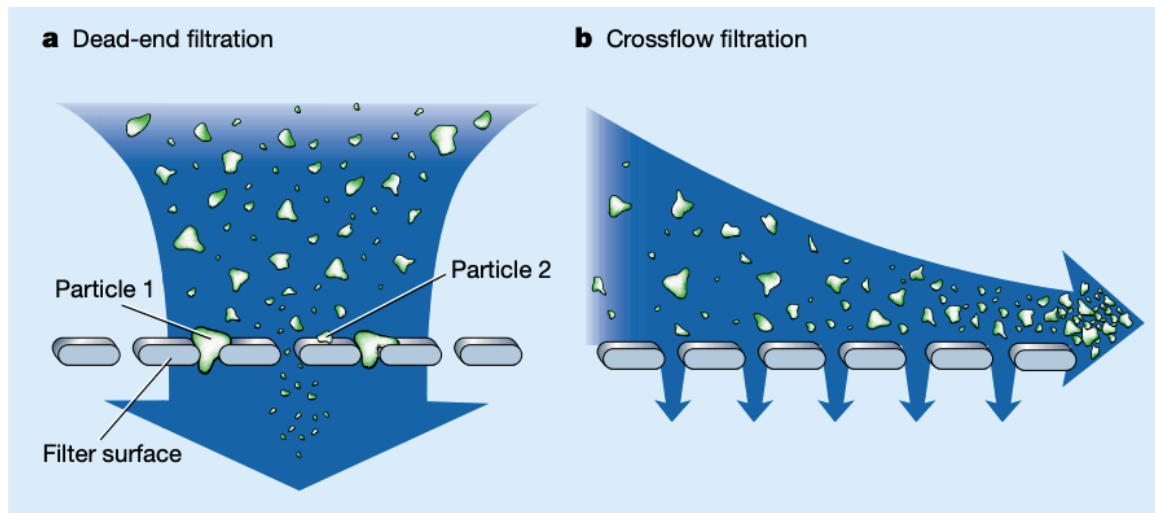


Figure 2.3 Visual comparison of dead-end and cross-flow filtration. (Bilstad and Espedal, 1996)

Membranes can be classified by structure and morphology, or they can be separated by the type of material such as ceramic or composite membranes. Membrane

treatment for produced water is advantageous due to low operation cost, ease of use, few or no chemical requirements, low energy consumption, and the ability to be easily combined with other treatment methods. However, membrane treatments are limited by membrane fouling, low flux, and shortened membrane lifetimes (Duraismy et al., 2013). Membrane processes may also require additional water for flow maintenance and membrane cleaning (Igunnu and Chen, 2012).

2.3.2 Microfiltration (MF) / Ultrafiltration (UF)

The objective of MF and UF filtration is to remove large micellular particles, microorganisms, and suspended solids. The range of MF pore sizes is >50 nm while UF provides separation with pores ranging from 2-50 nm. UF has shown the ability to obtain higher oil removal efficiencies when compared to standard separation techniques (He, 2008). Researchers have also determined that UF is more efficient removal of dissolved components, hydrocarbons, suspended solids, and from oilfield produced water (Bilstad and Espedal, 1996).

Both MF and UF water treatments can be performed via cross-flow or dead-end filtration. The recovery of produced water ranges from 85%-100%, dependent on membrane filtration method selected. It is common for cross-flow filtration to result in higher fluid recoveries than that of dead-end filtration (Duraismy et al., 2013). MF and UF are low pressure (1–30 psi) operating systems and therefore be used prior to desalination. However, they are not able to remove salt from water during filtration (Drewes et al., 2009). Membranes from both processes are typically formed with ceramic or polymeric materials. MF and UF share common disadvantages of required periodic

cleanings of the membrane to reduce fouling. Over time the fouling of the membrane may reach sufficiently high levels that membranes must be discarded and replaced. Fouling introduces additional waste in the water treatment process that must be considered. Additionally, the waste generated during the backwashing and cleaning process creates more waste that must be disposed of/ recycled or further treated (Iggunu and Chen, 2012). Table 2.1 summarizes the parameters and targets of MF and UF treatment processes.

Table 2.1 Membrane water treatment processes (Iggunu and Chen, 2012)

Process	Mechanism of Separation	Material/Type	Objective
Microfiltration (MF)	Separation by sieving through macropores (>50 nm)	Polymeric and inorganic / Porous	Removal of suspended solids, large organic molecules, and large colloidal particles including microorganisms (used for reducing colloidal suspensions and turbidity)
Ultrafiltration (UF)	Separation by sieving through mesopores (2-50 nm)	Polymeric and inorganic / Porous	Removal of large dissolved solute molecules and suspended colloidal particles, including bacteria and macromolecules such as proteins
Nanofiltration (NF)	Separation through the combination of charge rejection, solubility diffusion, and sieving through micropores (<2 nm)	Polymeric / Dense	Removal of multivalent ions and specific charged or polar molecules
Reverse Osmosis (RO)	Separation is based on the difference in solubility and diffusion rates of water and solutes	Polymeric / Dense	Removal of low molecular weight components such as inorganic ions

2.3.3 Polymeric/Ceramic Membranes

Membranes used for MF and UF processes are categorized by material composition, whether they be organic (polymeric) or inorganic (ceramic). Polymeric membranes can be made of polyacrylonitrile (PAN) or polyvinylidene difluoride (PVDF) and can be used to treat feed stream with higher TDS contents. Polymeric membranes

demonstrate high particle removal efficiencies, including dispersed and emulsified oil. They are cheaper than ceramic membranes but are more prone to fouling due to the presence of oil, bacteria, and sulfides in the feed stream (Duraisamy et al., 2013). They may require daily cleaning and low molecular weight, or volatile compounds may be inseparable by membranes.

Ceramic membranes are made from carbides, metal oxides, or nitrides. These membranes are more chemical and thermally stable. Ceramic membranes benefit from tubular modules that increase flux due to high porosity in the membrane. The lifetime of inorganic, ceramic membranes is more significant than polymeric materials due to their ability to withstand higher mechanical, thermal, and chemical stress (Abbasi et al., 2012). Ceramic membranes can be used in water treatment to meet effluent standards without any sort of pretreatment or chemical additives (Ebrahimi et al., 2010). They also can treat feed streams with a higher amount of total dissolved solids (TDS). Ceramic membranes are prone to fouling, especially from feedwater, with a high concentration of ions where irreversible fouling occurs (Duraisamy et al., 2013).

Conversely, cleaning of ceramic membranes is generally more natural due to the material durability. Ceramics have not demonstrated the ability to separated dissolved ions or organics, which limits their use as a single-step treatment. Several studies have concluded that ceramic membranes have better overall performance and durability compared to polymeric membranes.

2.3.4 Reverse Osmosis and Nanofiltration

Reverse osmosis is a well-known technology that has historically been used for seawater desalination and is now used in produced water treatment. It is driven by

hydraulic-assisted osmotic pressure to a dense, non-porous membrane and the clean water (permeate) passes through the membrane. Contaminant particles as small as $0.0001\ \mu\text{m}$ can be removed by RO across a membrane, however, the membrane is prone to fouling and scaling. While few field studies have been successful for RO, laboratory studies have shown the potential of RO membranes to separate oil from produced water. The successful treatment is dependent on a combination of appropriate pre-treatment technologies (Mondal and Wickramasinghe, 2008). RO uses electrical energy for its operation so it can function automatically. It has a high pH tolerance and produced water recovery for RO applications can be as low as 30% or as high as 85%, highly dependent on pre-treatment. Disadvantages of this treatment technique include extensive feedwater pre-treatment, high sensitivity to organic and inorganic materials present, and maximum feed temperatures of 45°C . The operating costs of RO are dependent on energy price and TDS concentrations in the feedwater (Drewes et al., 2009).

Nanofiltration systems are designed to soften water by removing metal contaminants as small as $0.001\ \mu\text{m}$ (Drewes et al., 2009). Produced water with TDS values between 500 – 25,000 ppm can be treated via NF. NF is similar in function to RO. However, lab tests demonstrated an only minor improvement of treating saltwater compared to the effectiveness of RO using the same sample (Mondal and Wickramasinghe, 2008). Therefore, several studies have concluded that NF is an imperfect solution for produced water treatment, especially used exclusively. Similar to RO, NF feedwater is sensitive to high levels of organic and inorganic materials. NF also requires frequent backwash cycles. Water recovery for NF systems ranges between 75% and 90%. RO systems operate at much higher pressures than NF. A NF membranes'

effectiveness is reduced by fouling, which in turn reduces flux and transmembrane pressures increase (Igunnu and Chen, 2012).

2.3.5 Thermal Technologies

Thermal water treatment technologies are desirable where energy costs are lower, and the water is highly contaminated. Thermal treatment options such as vapor compression distillation (VCD), multistage flash (MSF) distillation, and multi-effect distillation (MED) have historically been employed as desalination processes until recent advancements in membrane filtration technology (USBR, 2003). The MSF distillation works through water evaporation that reduces the pressure without raising the temperature. The preheated feedwater is flashed into steam as it is fed into a lower pressure chamber. Expected water recovery for MSF treatment is 20% and may still contain 2–10 mg/L of residual TDS (Drewes et al., 2009). Acids and other descaling chemicals may be required due to the heated feedwater and thus increase chemical costs. A multi-effect distillation MED functions with the application energy sufficient to convert the feed water to steam. The steam is captured via condensation, and the clean water can be recovered. Several evaporator systems are utilized to improve efficiencies and minimize energy consumption. VCD leverages vapor inside alternating evaporation and compression chambers. The chambers can be compressed either thermally or mechanically. The compressed vapor increases in energy, which is then transferred back to the evaporation chamber to be used as a heating source. This heat exchange makes VCD energy consumption significantly lower than MSF or MED systems. Mechanical vapor compression has exhibited advantages in chemical use reduction, reduced overall

cost, and decreased fouling and formation is reduced when VCD is used at temperatures below 70°C (Heins et al., 2005). VCD technology is a mainly a good candidate for seawater desalination, but some enhanced vapor compression technologies have been used in produced water treatment (Drewes et al., 2009). A hybrid VCD-MED treatment system is an example of an enhanced vapor compression technology. Produced water recovery from thermal treatment systems ranges from 20 –67% dependent on equipment, energy use, and single or hybrid systems.

2.3.6 Demulsifiers

Produced waters may contain naturally occurring surfactants that can stabilize oil-in-water emulsions by decreasing the oil-water interfacial tension. The most significant source of surfactants is introduced to formation waters during well production, as a regular part of hydrocarbon recovery. Demulsifiers can disrupt the chemical and physical bonds of surface-active agents (surfactants) that keep oil emulsified in produced water. The presence of certain solids such as silts, iron sulfide, and paraffin in crude oil can affect the process. Demulsifiers must be screened and selected based on the composition of the produced water to ensure compatibility. Past research has found that water-soluble demulsifiers are not effective in reducing oil concentrations of produced water, although oil-soluble demulsifiers can be useful. Previous researchers tested over 200 different emulsifiers, most of which were water-soluble, and discovered that very few were able to reduce the final oil concentration (Deng et al., 2005). Demulsifiers can require long settling times (up to six hours) to reduce oil concentrations in produced water below discharge regulations. The dosage of demulsifiers used is also critical in determining the

overall reduction produced water oil concentration. Fig 2.4 shows the effect of demulsifier dosage on oil concentration in the produced water. It should be noted that a demulsifier dosage of at least 50 mg/L (50 ppm) is required to decrease oil concentrations below 50 mg/L (50 ppm). Residual oil concentrations under 29 mg/L (29 ppm) were observed for demulsifier doses of 100 mg/L (100 ppm) (Deng et al., 2005).

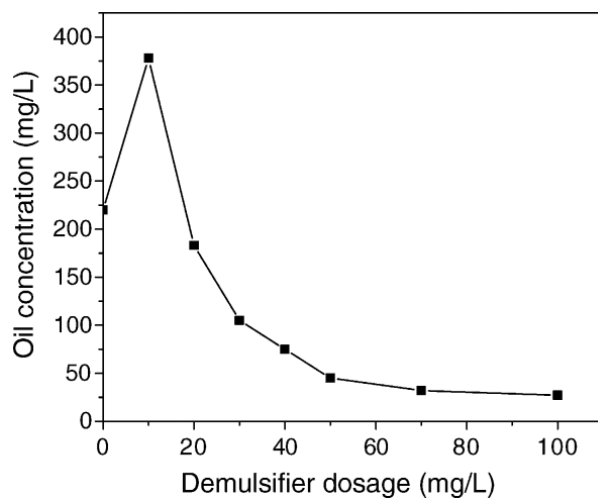


Figure 2.4 Effect of demulsifier dosage on oil concentration for produced water treatment (Deng et al., 2005)

The zeta potential of the oil droplets in produced water also increases in the presence of the demulsifiers. Thus, the net charge on the surface of oil droplets decreases. A decrease in electrostatic repulsion is the driving force for the coalescence of the residual oil droplets. Demulsifiers can be customized for field-specific compatibility, however, this customization can be expensive and the chemical composition of the demulsifiers may also be environmentally hazardous. Demulsifiers are generally single-use products that can remain in the water after oil separation. The demulsifying chemicals can be toxic

to the environment and require further treatment of the produced water before disposal or reuse.

2.4 Characteristics of Iron Oxide Nanoparticles

Iron oxides are found naturally in soils, waterways, rocks, and living organisms. Many processes in the environment rely on the properties of iron oxide nanoparticles. All iron oxides and oxide hydroxides consist of Fe, and with an attached O or OH. Iron oxides differ in composition among the 15 known variations as well as the valence of Fe and in the crystal structure. Due to near universality, the presence of iron oxides is safe under most conditions with the most damaging effect being the corrosion they may cause. Therefore, iron oxide nanoparticles provide an excellent opportunity to use naturally occurring for the treatment of produced water. The two iron oxide variants that are used in this study are magnetite and maghemite. The primary characteristics of these compounds are shown in Table 2.3.

Table 2.2 Characteristics of maghemite and magnetite (Schwertmann and Cornell, 2008).

Mineral name:	Maghemite	Magnetite
Formula	$\gamma\text{-Fe}_2\text{O}_3$	Fe_3O_4
Crystal system	Cubic or tetragonal	Cubic
Cell dimensions (nm)	a=0.834	a=0.839
Formula units, per unit cell, Z	8	8
Density (g m^{-2})	4.87	5.18
Octahedral occupancy	–	–
Maximal Al-for-Fe substitution	+ ²	+ ³
Standard free energy of formation ΔG° (kJ mol^{-1})	-711.14	-1016.1
Solubility product (pFE + 3 pOH)	40.5	n. k.
Type of magnetism	ferrimag.	ferrimag.

2.4.1 Maghemite

Maghemite is the fully oxidized state of magnetite and exists in a cubic crystalline structure. The cubic structure is carried through the increase in positive charge upon oxidation of Fe (II) in magnetite. The oxidation of magnetite to maghemite changes the color from black to red-brown. One of the methods for producing maghemite is oxidizing magnetite. This method also provides well-ordered maghemite with superstructure lines (Schwertmann and Cornell, 2008). Magnetite oxidation can occur naturally over time through direct air exposure or can be accelerated using an oven set to 250°C. The saturation magnetization for maghemite is 60–80 Am²/kg. The solubility of maghemite is still under contestation. References can be found that list maghemite as insoluble, but past research has also demonstrated that maghemite can be soluble in an HNO₃ solution (Taylor and Owen, 1997).

The structure characteristics and surface charge of maghemite nanoparticles are responsible for oil droplet adhesion through electrostatic attraction (Chun et al., 2001). Maghemite retains a cubic structure when derived from magnetite through oxidation. The Oxidation of magnetite creates a void in the cation site. It has been suggested that this cation vacancy is what allows maghemite to exhibit impressive sorption capacities (Dixon and Weed, 1989). This hypothesis was further tested as hydrophobic nanotubes were coated with maghemite to further increase their adsorption capacity. (Fard et al., 2016)

2.4.2 Magnetite

Magnetite contains Fe(II) and Fe(III) elements as the basis of its structure. Magnetite crystals formed synthetically at low temperatures are often very small (<100 nm). Magnetite must be protected from oxidation by storage practice or chemically stabilized to prevent the transformation to maghemite. It is for this reason that many preparation methods of magnetite require reactions to occur in an N₂ gas environment. The two basic ways to produce are (1) by co-precipitation of Fe³⁺/ Fe²⁺ in solution at a ratio between 0.5 or 10, or (2) by partial oxidation of a Fe²⁺ salt in and alkaline environment (Schwertmann and Cornell, 2008).

Magnetite displays ferrimagnetism arising from structurally induced spin moments. These moments occur on the octahedral and tetrahedral locals in magnetite. The existing net magnetic moment is the result of an inequality in valent cations in the octahedral/tetrahedral sites (Faivre, 2016). The saturation magnetization of magnetite is large and reported as 92–100 Am²/kg. In the presence of oxygen, magnetite tends to easily oxidize, losing an O⁻ and becoming maghemite. Under conditions of high temperature (+400°C), the magnetite will oxidize into a secondary structure called hematite.

2.4.3 Functionalized Iron Oxide Nanoparticles

The use of superparamagnetic nanoparticles is becoming prominent among the industries of biotechnology, medicine, oil & gas, and other specialized applications. Some of the well-accepted applications of iron oxide nanoparticles that are used to aid in drug delivery (El-Boubbou, 2018). The biocompatibility of these iron oxide particles has been proven and therefore confirms their use in the water treatments as being safe for humans and most environmental applications (Wu et al., 2008).

Magnetic iron oxide nanoparticles have a large surface-to-volume ratio which correlates with an increased surface energy. The increased surface energies cause the particles to aggregate in order to reduce the energies. Also, uncoated iron oxide nanoparticles such as magnetite are chemically volatile, especially in the presence of oxygen when magnetite oxidizes to form maghemite. Magnetite oxidation generally reduces magnetism and dispersibility as the resulting maghemite aggregates. Therefore, it has become necessary for researchers to provide a proper surface coating to the particles to stabilize the magnetite nanoparticles. Due to the high surface activity of magnetite, the molecule will accept many different forms of chemical coatings such that the nanoparticle and coating can be specialized for unique applications. These coating strategies involve grafting the nanoparticles with organic molecules such as polymers, surfactants, and biomolecules. Surface coating such as inorganic silica, metal, or other nonmetal elementary substances can also be grafted. The protective shell of the grafting not only stabilizes the magnetite nanoparticle but can also allow for additional functionalization and coatings.

Magnetite is the most commonly used iron oxide nanoparticle to coat with a surface-active agent. Magnetite nanoparticles have been favored in recent studies as carriers for chemical demulsifiers due to their desirable zeta potential and magnetization saturation values. Examples of coatings applied to magnetite include propriety demulsifiers, amines, and silicone-based polymers. When magnetite nanoparticles are coated with a surface-active agent, they act as the carrier for the chemical that has the added benefit of being able to be manipulated by an external magnet. This magnetism has been utilized to separate the water from the demulsifying compound during water treatments (Wang et al., 2018). The use of bare or uncoated iron oxide nanoparticle to the oil and gas industry has been limited. Recent studies have shown the ability of maghemite to be used to clean up oil spills by using the particles to adhere to oil films on top of the water (Chun et al., 2001). These studies indicate that uncoated iron oxide nanoparticles do exhibit a natural affinity to oil in an oil and water environment.

2.5 Nanoparticle Oil Removal and Recyclability

Superparamagnetic particles have the unique ability to be manipulated and moved with a magnetic field. Innovations in nanotechnology have improved the value of magnetic nanoparticles due to the vast array of applications in many scientific communities. The use of iron oxide nanoparticles alone or as the carrier for other compounds is becoming more common. The nanoparticles are combined with unique compounds to be translocated to desired areas and then returned using a magnetic field. The specialized chemicals grafted to the nanoparticles can be recovered and reused

rather than lost or simply discarded. Superparamagnetic nanoparticles can decrease costs and improve deliverability.

2.5.1 Techniques

Magnetic iron oxide nanoparticles have a high specific surface area, and the recovery of the particles is attributed to their response to a magnetic field. The structure, surface charge, and nanomaterial develop the unique characteristics of magnetic maghemite nanoparticles, suggesting a high potential of them in the removing of oil from produced water. The removal of oil from produced water using maghemite leverages the electrostatic adsorption and magnetic separation potential of maghemite nanoparticles. The hydrophobicity and positive surface charge of maghemite allow for a favorable interaction with the oil. The zeta potential of maghemite is on average, >35 mV, which is considerably less than magnetite. However, this zeta potential is also dependent on production temperature and the pH during the reaction while synthesizing or oxidizing magnetite. Maghemite has shown to be stable in a water suspension.

The most common technique for nanoparticle introduction to an O/W is first by dispersion of the particles in a solution with water. Ultrasonification has shown the best results for dispersing nanoparticles, especially those that aggregate when stored such as maghemite and magnetite. Following dispersion, the nanoparticles are mixed with the emulsion for one hour or up to 24 hours. The agitation method is not specific and can be carried out any number of ways. After mixing a strong magnet is applied to the solution so that a separated layer is formed. The negatively charged dispersed oil adheres to the surfaces of positively charged maghemite nanoparticles.

Past studies have used dyes to mark the color of the emulsified oil for better clarity; however, the use of marking dyes unnecessary for practical application. The separated oil is then skimmed off the top of the water is decanted depending on the concentration of the nanoparticles. Common nanoparticle concentrations range between 0.4-10 mg/mL. An external magnetic field can be used to separate the nanoparticles from the oil that collects on the water surface. Solvent washing techniques are used to dissolve any hydrocarbon components attached to the magnetic nanoparticles. Current research in produced water treatment using iron oxide nanoparticles have focused mainly on the use of functionalized magnetite nanoparticles although maghemite nanoparticles have been shown to remove asphaltenes from a toluene solution (Peng et al., 2012).

2.5.2 Efficiency and Challenges

The success of magnetic nanoparticle water treatment is dependent upon measurements taken initially and then after treatment to observe the change. Some of the challenges that arise during treatment include nanoparticle dispersion difficulty, emulsion stability, nanoparticle mass loss, and longer than expected mixing times. Due to the high energies of iron oxide nanoparticles, they tend to aggregate over time when stored to reduce this energy. Then when attempts are made to disperse the nanoparticles, more extensive mixing techniques may be required to break up the aggregates. Ultrasonification has shown favorable results in dispersion. Higher sonication amplitudes may be needed for severely aggregated nanoparticles. When low concentrations of nanoparticles are used in treatment (<1 mg/mL), it has been observed that mixing times with the O/W emulsion must conversely increase and may require up to 24 hours of

mixing. Also, during the collection process with the magnet, some of the less magnetic nanoparticles may be left behind with the oil. The magnetization of each nanoparticle varies depending on the size and purity of the sample. Therefore, magnetic nanoparticles will likely need to be washed several times following synthesis to remove the less magnetic or impure iron oxide particles. The need for pre-washing is also dependent on materials and technique used during nanoparticle synthesis. Another important consideration when using functionalized MNPs is the degradation of the coating over time that results in lower removal efficiencies. Fig 2.5 shows the recycle test results of three different studies that utilized functionalized MNPs. The loss of coating was the most common hypothesis for the steep reduction in efficiencies over the cycles.

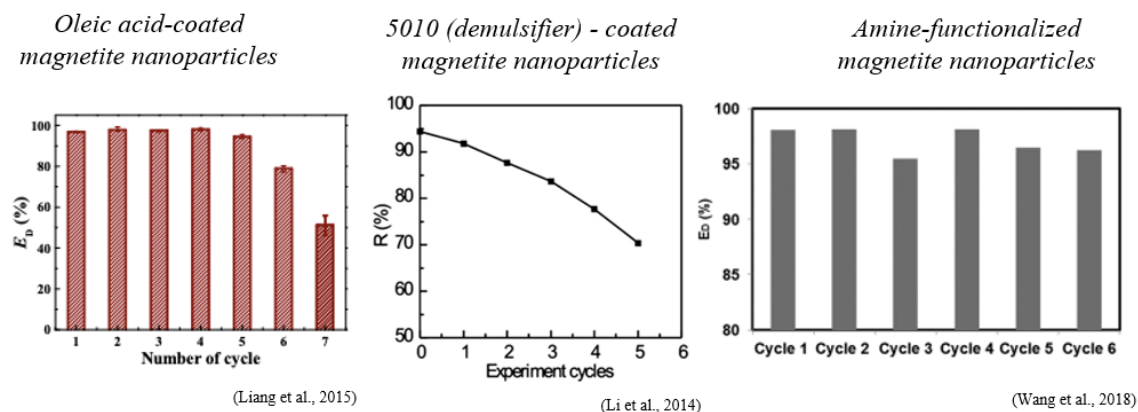


Figure 2.5 Functionalized magnetite nanoparticle recycling test results for three relevant studies. Cycle number (horizontal axis), oil removal efficiency (vertical axis)

Chapter 3: Experimental Studies

3.1 Oil Removal Experiments

Laboratory experiments were conducted for emulsion production, oil removal efficiencies, and nanoparticle recycling. Each experiment was designed with specific materials, measuring parameters, and data collection techniques. The purpose of the tests is to determine the optimal materials and methods required to achieve the highest oil removal efficiencies that could be sustained over multiple reuse cycles of the nanoparticles. Therefore, nanoparticle selection and exclusion were the essential objectives of each experiment. Each of the various tests performed and data collected were driven to optimize the oil removal process while also ensuring low costs, short treatment times, and little environmental impact.

Data was collected throughout the experiments using the instruments discussed in section 3.1.3. Data was measured by reputable instruments that were calibrated correctly and measuring methods given by the instrument manufacturers was followed precisely. Visual data collected also became an essential aspect of all data considered and aided in the determining of the physical processes being observed. Photos and short videos represented the visual data, and the analysis of the relevant data is further shown in the figures of Chapters 3 and 4. The following sections discuss the variables, parameters, and data collected for each of the experiments. The test matrices tables in the following sections denote an “x” for each test that was conducted and noted otherwise with a footnote with further explanation for why these tests were not performed.

3.1.1 Test Variables and Matrices

The first tests conducted for this study were focused on gaining basic understanding and experience of the magnetic iron oxide nanoparticles. These nanoparticles are the critical component of the water treatment process and therefore, must be well understood. The nanoparticles were obtained in powdered form that could be manipulated easily by an external magnet while still inside the container or sample vials. It was then necessary to test the dispersibility of the nanoparticles in solution. As mentioned by the literature, iron oxide nanoparticles have an inherent attraction to each other and will aggregate together if left alone, especially in the presence of oxygen. The nanoparticles were placed into a solution to provide protection from this natural aggregation and to evenly disperse the particles for a perfectly homogeneous suspension.

The first solution the nanoparticles were mixed in was sourced from local tap water, and this was done to get an overall sense of the particles ability to disperse into the solution and then be collected and removed from the solution with the application of an external magnet. The complete composition and characteristics of the tap water were not determined as part of this study. Therefore, the plan for future tests was to use DI water so that the composition of the test fluids could be controlled to observe if changes in water source or composition changed the outcome of the tests. Throughout the study, it was determined that some of the iron oxide nanoparticle samples did not respond as quickly or as efficiently to the magnet, depending on the type of water used. Visual data was collected for these tests to inspect the mixed solutions and determine the dispersion compatibility and magnet response while in solution. Table 3.1 shows the eight different

water samples that were used as the mixing fluid for producing the solutions in preparation for water treatment and the corresponding iron oxide nanoparticle samples.

Table 3.1 Test Matrix for Nanoparticle Dispersion in Water Samples

Nanoparticle Source	Dispersion Water Sample							
	DI Water	Distilled Water	Tap Water	1% NaCl Brine	3% NaCl Brine	Produced Water - OK	Produced Water - ARG	Ethanol
Maghemite - WCTC	x	x	x	x	x	x	x	x
Maghemite - WCTC	x	x	x	x	x	x	x	x
Magnetite - WCTC	x	x	x	x	x	x	x	x
Magnetite - Commercial	x	x	x	x	x	x	x	x
Amine - Coated Magnetite	x	x	x	x	x	x	x	x

The next sets of tests were used to determine the optimal emulsion preparation procedure. Emulsion preparation was designed with two goals including, (1) an emulsion using real-world oil samples than can mimic the residual oil found naturally, (2) and emulsion with consistent and known compositions to exclude other molecular interactions apart from the iron oxide nanoparticles and the oil. Two different oil samples were used to ensure that the results from subsequent tests could not be explained solely by fortuitous oil sample selection with perfect test compatibility. The other dependent variables used were brine salinity (%), salt type, and oil concentration (ppm). The salts chosen are common to the locale and the oil concentrations were congruent with standard oil-field produced water concentrations.

The data for these emulsion preparation tests were to be collected visually and verified through subsequent instrumentation measurements. The prepared emulsions were observed over time for demonstrating stability and homogeneity and were to be

tested for oil content using infrared spectroscopy to verify composition. The tests conducted for oil samples used, oil concentration, and brine salinities are shown in Table 3.2.

Table 3.2 Test Matrix for Emulsion Preparation and Stability

Emulsion Oil Source & Concentration (ppm)		NaCl Brine Concentration		CaCl ₂ Brine Concentration		PW-ARG
		1%	3%	1%	3%	
Medium Oil Sample	10,000	x	x	*	*	†
	1,000	x	x	x	x	x
	500	x	x	*	*	†
	100	x	x	*	*	†
Heavy Oil Sample	1,000	x	x	x	x	†

*Untested due to poor results from initial CaCl₂ brine emulsion tests

† Untested. A single emulsion prepared with produced water was tested to ensure water components (other than oil) do not affect emulsion production or nanoparticle water treatment.

The main tests conducted in this experiment designed to determine which nanoparticle sample produced the highest oil removal efficiencies, and what water treatment preparation methods reduced treatment time. The goal of these test parameters as described in Tables 3.3 and 3.4 is to select the iron oxide nanoparticle that removes the most amount of oil in the shortest amount of time.

The introduction of the prepared iron oxide nanoparticle solutions to the emulsion samples required agitation or mixing so that the nanoparticles would directly contact the oil droplet that was dissolved and dispersed in the emulsion. All mixing/agitation methods selected were elementary and required minimal equipment or materials and are shown in Table 3.3, with their corresponding nanoparticle samples. The first mixing method was a standard shaking plate mixer and the second was a lab vortex instrument. The data for these tests were only recorded as what test was used for mixing so the data could be later

referenced and compared to oil removal efficiency data for determining the effects of each mixing type and selecting an optimized mixing approach.

Table 3.3 Test Matrix for MNP Treatment Mixing Methods

Nanoparticle Source		Emulsion + MNP Dispersion Mixing		
		Shaker Plate 10 min/180 rpm	Shaker Plate >10 min/180 rpm	Vortex 30 sec/3200 rpm
Maghemite	Commercial	x	x	x
	WCTC	x	x	x
Magnetite	Commercial	x	*	x
	WCTC	x	*	x
Amine - Coated Magnetite	WCTC	x	x	x

*Untested due to poor cleaning results of previous tests with uncoated magnetite nanoparticles.

The next variable that was tested was to show how the nanoparticle concentration would affect oil removal efficiencies. The results of these tests were crucial for optimizing oil removal procedures. The iron oxide nanoparticles are relatively inexpensive; however, the associated costs of purchase or production contribute a more significant percentage of materials costs than any other chemical used in this study. Determining the lowest concentration of nanoparticles allowable to maintain oil removal efficiencies provides substantial evidence and purpose to the practical use of these nanoparticles on a larger scale. Primary nanoparticle concentrations were selected from the literature (Wang, 2018) and were later reduced by one-half for the tests later used to determine critical nanoparticle concentrations for the treatment process. Table 3.4 summarizes each nanoparticle sample the corresponding concentrations (mg/mL) tests that were conducted. The data from these tests was also referenced to compare to oil concentrations of treated water to select the highest oil removing nanoparticles and optimized nanoparticle concentrations.

Table 3.4 Test Matrix for Demulsification Experiments

Nanoparticle Source		Nanoparticle Concentration (mg/mL)				
		5	2.5	1.25	0.625	0.313
Maghemite	Commercial	x	x	x	x	x
	WCTC	x	x	x	x	x
Magnetite	Commercial	x	*	*	*	*
	WCTC	x	x	x	x	x
Amine - Coated Magnetite	WCTC	x	x	x	x	x

*Untested due to poor cleaning results of previous tests with uncoated magnetite nanoparticles.

3.1.2 Materials Used

Laboratory produced magnetite and maghemite nanoparticles were obtained through cooperation with a research project in the same facility. The amine-functionalized magnetite nanoparticles were also obtained on location shortly after the amine coating process was complete. Locally synthesized magnetite nanoparticles were labeled “WCTC-T__” with an accompanying batch number, and locally manufactured maghemite nanoparticles were labeled “WCTC-Jh__” with an accompanying batch number. Each of these nanoparticles will be referenced similarly in this study. WCTC magnetite and maghemite nanoparticles samples were dark brown or black. Commercially produced maghemite nanoparticles (Iron (III) oxide nanopowder, <50 nm particle size) were purchased from Sigma-Aldrich and are reddish-brown. Commercially produced magnetite nanoparticles (Iron (II, III) oxide nanopowder, 50-100 nm particle size) were also obtained from Sigma-Aldrich and are black in color. Commercial iron oxide nanoparticle samples are labeled as “Commercial” or “S.A.”

Deionized water (DI-H₂O) (0.23 MΩ resistivity) was obtained through LabChem (ASTM Type II). Sodium chloride (NaCl, ≥99.0 %) was purchased from Fisher BioReagents and a calcium chloride (CaCl₂) salt sample was used from the current lab

inventory. The first produced water sample of this study (PW-OK) was obtained from a random well in Oklahoma and was orange in color, had visible suspended particles, and contained measured residual oil of 80-120 ppm. This oil/grease components were not removed during standard gravitational separation techniques at the well site. The second produced water sample was obtained from Argentina (PW-ARG), and it is estimated that the sample was pretreated to remove contaminants before shipment. This hypothesis is based on its transparent appearance and low measured residual oil content of 20-40 ppm. Other water samples used for testing include local tap water and distilled water purchased from a local grocery store. The medium crude oil sample used in this study was sourced from a random well in Oklahoma and had the following characteristics: density of 0.814 g/cm³, API gravity of 41.7 degrees, and a viscosity of 2.60 cP. Oil samples of similar API gravity (43 degrees) have been recorded previously in the same basin (Collins, 1969). The heavy oil sample was found on location and had an API gravity of 21 and a density of 0.925 g/cm³. Both oil samples were chosen for their availability and convenience rather than for their unique characteristics and composition. Ethanol (Histoprep, 100% alcohol) was used for solvent washing.

3.1.3 Equipment Used

The most important data collected in this study were the initial and final oil content measurements to determine the oil removal efficiency of the nanoparticle treatment process. Therefore, the instrumentation and methodology for measuring oil content in water samples were extensively researched for proper instrument selection. The chosen instrument (Fig 3.1) for these measurements was the oil content analyzer

(Horiba OCMA-550). This oil content analyzer was selected for its fast measurement times, simple sample extraction procedure, ability to measure volatile hydrocarbons, and its compliance with the ASTM D7066-004 (2004) standard. The measurement principle of this instrument, as stated by the manufacturer, is “solvent extraction non-dispersive infrared absorption analysis.” Non-dispersive infrared absorption an often-used method in the field for analyzing oil in water. The infrared absorption is measured by passing an infrared beam through the sample cell (containing the extracted oil), and the amount of infrared absorbed by the sample is measured at the necessary wavelength. ASTM D7066-04 method uses a single wavelength reference, usually around (2930 cm^{-1}), corresponding to the CH_2 stretch vibration frequency (Yang 2011). This method can determine all the CH_2 that is contained in a sample. Therefore, this method can measure the volumetric concentrations of oil extracted from the sample. The analyzer has a stated measurement range of oil concentration between 0 and 200 ppm. The precision and accuracy of the instrument are summarized below:

Oil Content Analyzer

Measurement range (actual): 0 mg/L – 220 mg/L

Resolution: 0.1 mg/L (for measurements 0 to 99.9 mg/L)

1.0 mg/L (for measurements 100 to 200 mg/L)

Repeatability: $\pm 0.4\text{ mg/L} \pm 1\text{ digit}$ (for measurements 0 to 9.9 mg/L)

$\pm 2\text{ mg/L} \pm 1\text{ digit}$ (for measurements 10.0 to 99.9 mg/L)

$\pm 4\text{ mg/L} \pm 1\text{ digit}$ (for measurements 100 to 200 mg/L)



Figure 3.1 Non-dispersive Infrared Spectrometer (Horiba OCMA-550).

As stated in the measurement principle, the oil content analyzer utilizes solvent extraction for oily water samples to separate the fluids in preparation for oil concentration measurements. The only solvent suitable for this instrument is a proprietary solvent named S-316 that is composed of polychlorotrifluoroethylene (65-75%) and chlorotrifluoroethylene trimer or tetramer (25-35%). S-316 is one of two chlorofluorocarbons (CFC) solvents that are still available for use to extract residual oil in water samples for measuring oil concentrations.

The S-316 solvent demonstrates excellent ability to extract residual oil from water, soil, and metals parts. Remaining oil components in the water samples are extracted by the S-316 with equal parts water and solvent. The mixture is agitated for one minute and the formation of separated solvent and water layers are shown for successful oil extraction. The extraction fails if the layers do not separate within 40 seconds or a cloudy layer forms between the two layers. 6.5 mL of solvent is required for the measurement cell. Calibrations of the oil content analyzer are comprised of a two-point calibration including a zero (S-316 solvent blank) and a span calibration of a known,

prepared calibration solution. A heavy-oil sample is included with the instrument and can be used for making the span calibration solution. The span calibration can be prepared for any value within the measurement range of the instrument. The calibrations must be performed daily to ensure accuracy as humidity and changes in room temperature can affect measurement results. Measurements of oil concentration are taken over a specified time wherein the sample measurement is left to stabilize to a singular 10-sec moving average value. Sample dilution is required for samples with oil concentrations higher than the instrument's measurement range. Sample dilution is accomplished by increasing the solvent to water sample ratio until the oil concentration measurement can stabilize within the measurement range. The S-316 solvent can be recycled and reused using a reclaimer (Horiba SR305), which is a filtration system used to recover used solvent (Fig 3.2).



Figure 3.2 Solvent Reclaimer (left) and S-316 Extraction Solvent (right) (Horiba)

A sonifier (Branson SFX550) was used to conduct nanoparticle dispersion and emulsion preparation testing. The sonifier is marketed as a cell disruptor and homogenizer by producing ultrasonic energy waves inside the central control unit. The ultrasonic energy is transferred to the sample via a 1/2" diameter Tapped Bio disruptor horn. The output power of the sonifier is 550 watts at 20 kHz. It is capable of homogenizing samples from 0.2 to 1,000 mL in volume. The sonifier (Fig 3.3) was chosen for its demonstrated ability to disperse nanoparticles within a solution and for the large homogenization capacity for large test samples. The programs created on the main control unit detail the parameters of sample sonication for a set amount of time or a prescribed amount of energy, measured in joules. The instrument can also homogenize a sample until reaching a specified temperature with the use of an accompanying temperature sensor. The sonifier can deliver the energy continuously or as energy pulses. For this study, sample sonication occurred continuously during the homogenization for a period of 2 to 7 minutes. The amplitude of the sonication can also be adjusted between 20-100%. The instrument can store up to 20 preset sonication programs specified as a continuous or pulse program according to the desired input variable (time, energy, temperature). The sound level produced by the Sonifier while in use is high enough to cause hearing discomfort and possible impairment. Therefore, proper ear protection is required while using the instrument, especially for amplitudes higher than 50%.

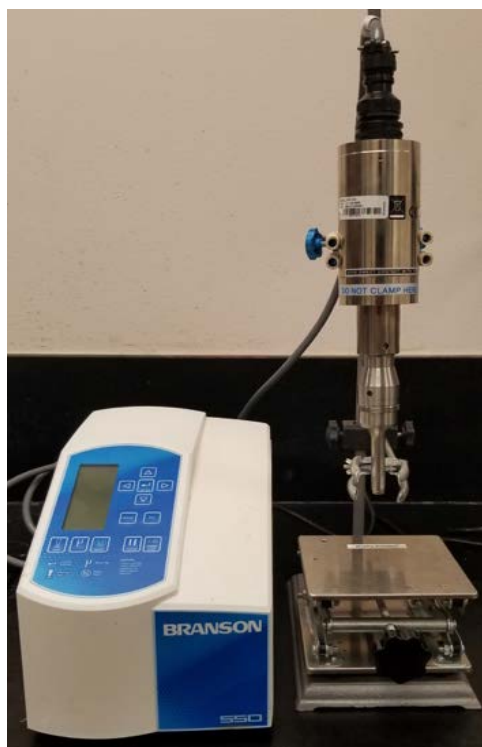


Figure 3.3 Sonifier and Homogenizer (Branson SFX550)

For sample mixing in this study, three different methods and instruments were used and shown in Fig 3.4. A standard lab magnetic stirring plate was used for brine preparation and for heating oil samples for instrument calibration. The stir plate was selected for its low cost and versatility of capabilities including stirring and heating of samples. The temperature range of the stir plate was 200°C and the stirring range was between 200-1500 rpms. A magnetic stir bar was used in conjunction with the plate to mix 1-3% brine solutions. The stirring took place for 10 minutes to ensure salt dissolution. The heating element of the plate was used to heat oil samples to 70°C for viscosity reduction. This was necessary for proper mass measurements of the oil samples when calibrating the oil content analyzer.



Figure 3.4 Mixing/Agitation Instruments; (a) magnetic heat/stir plate, (b) shaker plate, and (c) lab vortex

The next instrument used for mechanical agitation was a standard orbital shaker plate. This instrument was selected for availability, price, and its ability to mix multiple samples concurrently. The orbital shaker plate was capable of sample agitation in the range of 0-220 rpms. Generally, the mechanical agitation of the test samples was 10 mins or less. The shaker plater could be used to mix indefinitely, or a timed mix could be set for 0 to 15 mins.

A third mixing instrument was used in this study after successful oil removal tests using the orbital shaker plater. To reduce mixing times and increase the success of the oil removal process in the field, it was required that mixing times be minimized. The lab vortex mixer was chosen to reduce mixing times by providing greater agitation rpms, up to 3,200 rpms. The use of the vortex was able to reduce sample mixing times by 95%. The lab vortex used was capable of mixing samples up to 50 mL. The vortex was used to mix samples at the highest speed (3,200) rpms for 30 seconds for the oil removal tests.

The properties of the water samples used in this study were measured using a portable conductivity meter (Apera Instruments EC400S) that can measure TDS, salinity, and resistivity (Fig 3.5). The handheld instrument included a data logger with a removable sensor probe. The unit required a 2-point calibration before sample measurements using the provided calibration fluids. The sensor probe measures the sample properties with appropriate units (results shown in Table 4.2): conductivity (mS/cm), TDS (mg/L), salinity (ppt), and resistivity (Ω). Conductivity measurements sometimes required 10-15 seconds to stabilize, which was expected from the instrument documentation. This instrument was selected due to its on-site availability and its capabilities of near-instant measuring of the four parameters as previously discussed. The probe was cleaned with DI water between sample measurements. The accuracy, range, and resolution of the portable meter measurements are summarized below:

<u>Portable Conductivity Meter</u>
<i>Conductivity</i> Range: 0 to 200 mS/cm [(0.00 to 1999) μ S/cm; (2.00 to 199.9) mS/cm] Resolution: 0.01-1 μ S/cm, 0.01/0.1 mS/cm Accuracy: $\pm 1.0\%$ F.S ± 1 digit
<i>TDS</i> : (0 to 100) g/L;
<i>Salinity</i> : (0 to 100) ppt;
<i>Resistivity</i> : (0 to 100) M Ω
<i>Temperature</i> Range: -10~110°C (32 to 230°F) Resolution: 0.1°C Accuracy: $\pm 0.5^\circ\text{C} \pm 1$ digit



Figure 3.5. Handheld conductivity, resistivity, TDS, and salinity meter (Apera Instruments EC400S)

N52 grade magnets were used for oil removal, nanoparticles treatment, and recycling. The magnets were square or cylindrical with dimensions of 40 x 20 mm. The strength of the magnets measured in residual flux density, Br, was about 15,000 Gauss. An example of a magnet in use is shown in Fig 3.6.



Figure 3.6 Cylindrical rare earth magnet used for MNP collection

Nanoparticle magnetization characterization tests were performed using a test stand (Mark-10 ALX-S) configured with a digital force gauge (Mark-10 Series 2, model M2-5) (Fig 3.7), a custom-built sample vial holder, digital caliper, and a rectangular rare earth magnet (40 x 40 x 20 mm, 15,000 Gauss).

Digital Force Gauge

Force Measurement:
Capacity: 20 N (5 lbF)
Resolution: 0.02 N (0.005 lbF)
Accuracy: $\pm 0.5\%$
Overload: 200% capacity

Sampling:
Rate: 500 Hz
Type: Continuous, Peak Tension/Compression

Environmental Conditions:
Temperature Range: 40-100°C
Max Humidity -96%



Figure 3.7 Digital force gauge (Mark-10 Series 2, model M2-5)

3.1.4 Nanoparticle Magnetization – Pull Force Test

The magnetic characteristics of the nanoparticles were measured using a force gauge configured on a test stand. A prescribed mass of nanoparticles (1.92 g) was added to a small glass sample vial. The sample vial was attached to the bottom of the force gauge using a custom-built securement. A rare earth magnet was secured to the bottom of the test stand and the built-in digital caliper on the test stand was used to measure the distance between the sample and the magnet. The sample was lowered towards the magnet and the force gauge measured the tensile force exerted from the downward pull of the magnetic iron oxide nanoparticles towards the magnet. The force measurements were recorded as N/g, however, the force was standardized for analysis. The peak force measurement was taken at two distances between the magnet and the nanoparticles samples. The two distances separating the sample from the magnet were 0.25” and 0.00.” The 0.25” measurement results were used for batch comparison and the 0.00” separation test was used to describe peak magnetization of the sample. Fig 3.8 shows the instrument used to measure the magnetic pull force.



Figure 3.8 Instrument set-up for magnetic force measurement – 0.00” sample spacing (left); 0.25” sample spacing (right)

3.1.5 Oil Removal Test Procedure

Oil-in-water emulsions of varying concentrations (100-1,000 ppm) were synthesized using a prepared brine solution of salinities ranging from 1,000-3,000 ppm. Brine solutions were mixed on a magnetic stir plate with DI water and powdered NaCl (Sigma Aldrich, $\geq 99.0\%$) or CaCl_2 . The most commonly used salinity of the prepared brine was 1180 ppm (1.18 g/L) as referenced by a previous study (Wang et al., 2018). The standard preparation concentration of crude oil to brine for emulsion production was 1,000 ppm (1% vol wt). Emulsions were homogenized using a probe sonicator (Branson SFX 550) at 70% amplitude for 7 mins. The visual stability of the emulsions was observed over time. Emulsions with visible loss of stability were mixed via sonication daily or as needed before demulsification testing. Oil stability was observed visually for 1 hour to

ensure homogeneity among test emulsions. The concentrations of the produced oil-in-water emulsions were confirmed using oil content analyzer. 10 mL of the produced emulsion was transferred to a clean 20 mL glass sample vial. 10 mL of the S-316 solvent was added to the vial and was mixed by hand for 1 minute to separate any residual oil. The separation of the solvent and water layers was observed before extracting 6.5 mL of the solvent layer into the oil content analyzer measurement cell for analysis.

3.1.6 Demulsification Test

Synthesized and commercial (Sigma Aldrich, nanopowder) maghemite nanoparticles were prepared for demulsification treatment by dispersion in various water sources including DI water, tap water, distilled water, and produced water samples. The standard concentrations of nanoparticles dispersed was 5.0 mg/mL. Concentrations as low as 0.313 mg/mL were also prepared to determine critical concentrations. The nanoparticles were dispersed in each water samples via probe sonication for 2 mins at 20% amplitude. Dispersed nanoparticles were used immediately to reduce settling time and prevent aggregation. An external magnetic field was applied to the nanoparticles after dispersion to observe homogeneity and ensure proper magnetic response for complete nanoparticle recovery. An example of dispersed nanoparticles in solution is shown in of Fig 3.9b.



Figure 3.9 Commercial maghemite treatment test visualization, a) 1,000 ppm emulsion, b) 5 mg/mL MNPs, c) separated water and oil+MNPs, d) Treated water

The demulsification capability of the synthesized and commercial maghemite nanoparticles was tested by mixing 10 mL of a prepared emulsion with 10 mL of a prepared nanoparticle dispersion in a 20 mL sample vials (1:1 ratio). The samples were mixed by an orbital shaker plate for 10 mins at 180 rpm or on a lab vortex for 30 seconds at 3200 rpm. The mixing instruments are shown in Fig 3.4. The effect of mixing was observed in the solution before an external magnet was applied. An external magnet was applied to the bottom or side of the sample vial, and the magnetic response of the nanoparticles was observed. The samples remained on the magnet until no further visual response was observed (10 sec - 1 min). Examples of successful demulsification in the sample vials including the treated water are shown in Figs. 3.9c and 3.9d. Fig 3.10 shows a diagram for oil removal demulsification test using the nanoparticles.

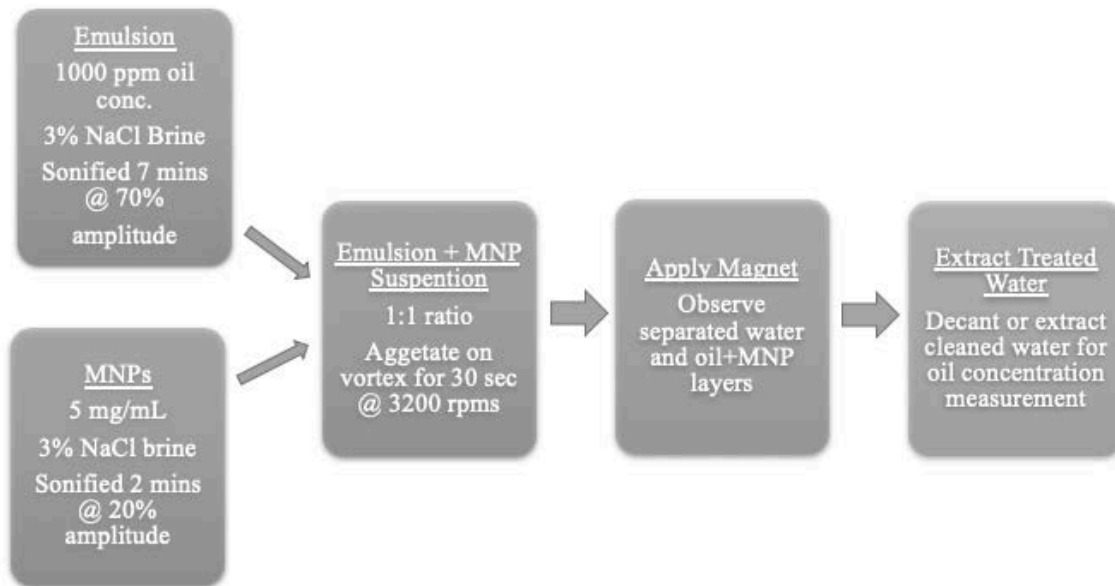


Figure 3.10 Step diagram of the nanoparticle demulsification test

The samples also remained on the magnet during treated water extraction to prevent nanoparticles from also being removed. A syringe was used to extract and transfer 10 mL of the treated water to a clean 20 mL glass vial. The treated water was mixed with 10 mL of the S-316 solvent and shaken by hand for 1 minute. The separated solvent and water layers were observed. The lower solvent layer was extracted, and 6.5 mL was transferred to the measurement cell for oil content analysis. An example of the separated layers in the water/solvent sample is shown in Fig 3.9e. The sample measurement was observed by the instrument for 60 secs, after which it was recorded when the 10 sec moving average measurement stabilized. All tests and procedure for these demulsification tests were conducted at standard conditions. The oil removal efficiencies (η_R) were calculated from initial emulsion concentrations (C_i) and residual oil concentrations in the treated water (C_r) following that: $\eta_R = [(C_i - C_r) / C_i] \times 100$.

3.1.7 Accuracy and Repeatability

An essential part of conducting and recording a successful study is being able to demonstrate consistency in the results of the tests as well as being able to repeat the tests and obtain similar data. For this study, many of the same tests were conducted over several months which led to a sufficient sample size to provide a basic statistical analysis of the results of the oil removal efficiency tests for the various types of iron oxide nanoparticles. The data were collected throughout the study and then the statistical analysis is performed on the test measurements. Table 3.5 shows the raw data for the repeated tests including relevant parameters.

Table 3.5 Oil Removal test results for maghemite

Batch #	NP Source	Dispersion Concentration (mg/mL)	Emulsion Oil Concentration (ppm)	Oil Conc. (mg/L)	Removal Efficiency
B004 J	Commercial	5	1,000	20.8	97.92%
B009 J	Commercial	5	1,000	6.8	99.32%
B026 J	Commercial	5	1,000	9.4	99.06%
B032 J	Commercial	5	1,000	2.4	99.76%
B033 J	WCTC (B005 Jh)	5	1,000	0	100.00%
B046 J	Commercial	5	1,000	2.6	99.74%
B050 J	WCTC (B005 Jh)	5	1,000	4	99.60%
B067 J	WCTC (B005 Jh)	5	1,000	12.9	98.71%
B070 J	Commercial	5	1,000	7.5	99.25%
B071 J	WCTC (B005 Jh)	5	1,000	2	99.80%
B072 J	Commercial	5	1,000	7.9	99.21%
B073 J	WCTC (B005 Jh)	5	1,000	4.3	99.57%
B077 J	WCTC (B005 Jh)	5	1,000	10.1	98.99%
B078 J	WCTC (B005 Jh)	5	1,000	10.1	98.99%

Matched nanoparticles batch results were considered unified and the measurement values were used to calculate the basic test statistics of mean, range, standard deviation, and sample size. Table 3.6 contains a summary of all the statistical

parameters calculated for the maghemite samples that had sufficient repeated tests. Standard tests for both the synthesized (WCTC) and commercial maghemite nanoparticles were conducted that allows a direct comparison.

Table 3.6 Oil Concentrations and Removal Efficiencies after MNP treatment

Maghemite Sample	n	μ - Oil Conc. (mg/mL)	μ (η R)	σ Oil Conc. (mg/mL)	σ (η R)	Min Oil Conc. (mg/mL)	Max Oil Conc. (mg/mL)	Min (η R)	Max (η R)
WCTC (B005 Jh)	7	6.2	99.38%	4.83	0.48%	0	12.9	98.71%	100.00%
Commercial	7	8.2	99.18%	6.16	0.62%	2.4	20.8	97.92%	99.76%

n – sample size; μ – mean; σ – standard deviation; η R – removal efficiency

3.2 Nanoparticle Recovery Test

The second primary objective of this study was to demonstrate a water treatment technique that allowed for material recovery and reuse. Many of the most commonly used water treatment technologies rely on single-use chemicals and other materials that are not candidates for reuse. As has been shown in previous studies, iron oxide nanoparticles are a promising candidate for reuse as the molecules can be easily manipulated with a simple magnet. Their inherent superparamagnetism allows the nanoparticles to be manipulated without disrupting any other part of the water treatment test. Therefore, the following tests were designed to show the durability and maximum reusability of the iron oxide nanoparticles.

Magnetite reuse was not within the scope of these recovery tests due to poor performance in the past and the unreliability of the coating to remain fixed to the iron oxide nanoparticles after repeated solvent washings. Also, the instruments available for this study did not allow for the coating of the nanoparticle to be observed before, during,

and after treatment cycles. Therefore, the tests for measuring the recyclability of magnetite were excluded. This decision to exclude the magnetite from the nanoparticle reuse treatment cycles was also made considering the effect that the water sample had on the nanoparticles and is explained in Chapter 4 with the data collected in (Table 4.2).

3.2.1 Test Variable and Matrices

The physical mechanisms that allow the iron oxide nanoparticles to adhere and collect the oil from the prepared emulsions must be counter-acted in the nanoparticles washing process. The tests conducted to remove the residual oil for the nanoparticles in preparation for reuse is summarized in Tables 3.7 and 3.8. The most effective method for oil extraction from water samples is solvent washing. The type and concentration of the solvent used for washing could have an impact on the volume of solvent required, and the washing time. Two widely-available and inexpensive solvents including lab-grade ethanol and consumer-grade isopropyl alcohol were used in the tests. The use of the 100% ethanol solvent was only tried after less-than-satisfactory results with the cheaper, consumer-grade isopropyl alcohol. However, both solvents are inexpensive and only small volumes are required to wash the nanoparticles. The use of a 3% brine to complete the solvent wash by removing any residual alcohols was selected to due to the excellent compatibility of the nanoparticles that were seen in the nanoparticle's dispersibility in the water samples tests (See Table 4.2)

Table 3.7. Test Matrix for MNP Solvent Washing

Nanoparticle Source		Nanoparticle Washing		
		Isopropyl (91%)	Ethanol (100%)	3% Brine
Maghemite	Commercial	x	x	x
	WCTC	x	x	x
Magnetite	Commercial	*	*	*
	WCTC	*	*	*

*Untested due to observed mass loss during solvent washing in previous tests.

After the nanoparticles were successfully washed of any oil following an initial oil removal test, additional tests of the exact sample parameters were implemented again with the nanoparticles. The process for the nanoparticles water treatment and reuse cycles is shown in Fig 3.11.

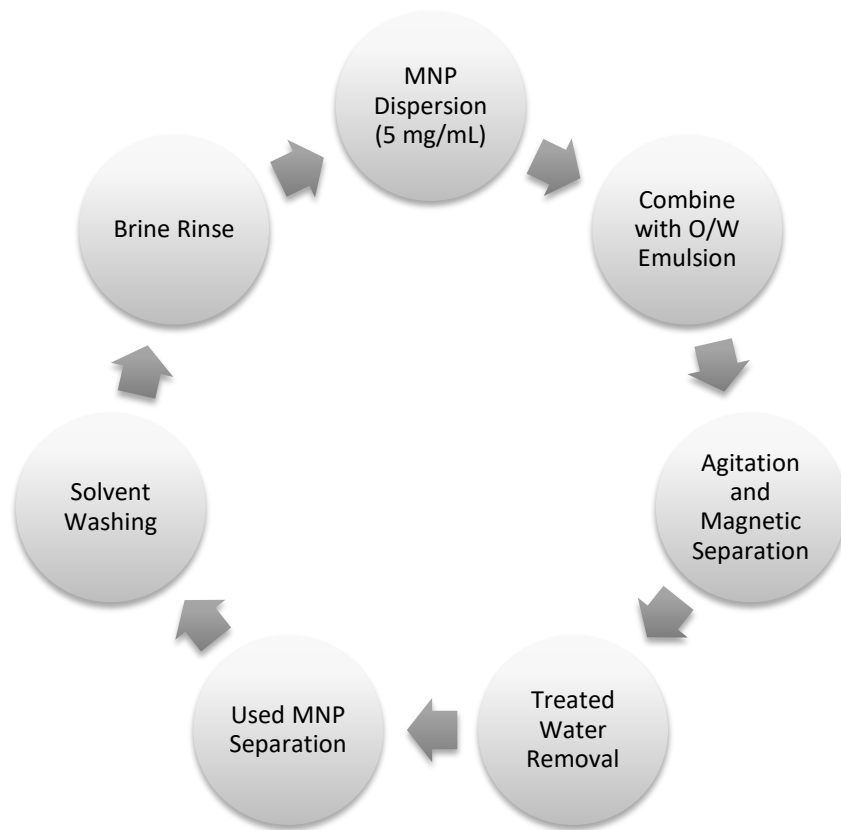


Figure 3.11 Schematic of the nanoparticle recycle test procedure

The total number of water treatment cycles tested are summarized in Table 3.8. The maximum number of tests was selected to be higher than previous studies but within reasonable time constraints. The washing process proved to be quite tricky and a single mistake would disrupt the entire washing process or subsequent reuse attempts. An individual water treatment test, including data collection, took about 20 minutes, followed by a 15-minute solvent washing. The entire recycle process up to 10 hours is therefore in the time range of 5-6 hours of continuous testing.

Table 3.8. Test Matrix for MNP Recovery and Recycling

Nanoparticle Source	Nanoparticle Recycling and Recovery								
	Recycle #1	Recycle #2	Recycle #3	Recycle #4	Recycle #5	Recycle #6	Recycle #7	Recycle #8	Recycle #9
Maghemite - WCTC	x	x	x	x	x	x	x	x	x
Maghemite - WCTC	x	x	x	x	x	x	x	x	x
Magnetite - WCTC	*	*	*	*	*	*	*	*	*
Magnetite - Commercial	*	*	*	*	*	*	*	*	*
Amine - Coated Magnetite	*	*	*	*	*	*	*	*	*

*Untested due to observed mass loss during solvent washing in prior tests and poor oil removal efficiencies

3.2.2 Materials Used

Magnetite and maghemite nanoparticles that were collected from previous treatment cycles through solvent washing and magnet collection. The nanoparticles were labeled according to the number of times they were reused, i.e. R1, R2, and R3. Deionized water (LabChem), distilled water was purchased from a local grocery store, and tap water sourced on site. The solvents used for removing the oil from the nanoparticles following

water treatment were ethanol (Histoprep, 100% alcohol), and isopropyl alcohol (Equate, 91%).

3.2.3 Equipment Used

A standard overhead lab mixer with a steel paddle was used to mix in the solvent washing process. The mixer was found on-site and used for its convenience and size. The mixing speed was not measured due to the small volumes and low mixing speeds. A rough estimate of the mixing rates used is 150 rpms. The other equipment and instruments used for nanoparticle recovery tests are described in section 3.1.2 including the sonifier, magnets, and oil content analyzer.

3.2.4 Nanoparticle Recovery Test Procedure

The recovery and recyclability of the maghemite nanoparticles were tested following successful demulsification tests. A solvent washing procedure was used to extract the oil collected by the maghemite nanoparticles in preparation for reuse. Remaining nanoparticles in the sample vial were collected with a magnet and washed with ethanol twice in a standing mixer (T-Line Laboratory Stirrer, Model 104). Residual ethanol was removed from the nanoparticles by washing with a 3% NaCl brine solution two times. A magnet was used to collect and recover the nanoparticles throughout the cleaning process as excess liquids were easily decanted. The cleaned nanoparticles were re-dispersed in a corresponding volume of 3% NaCl brine to ensure a consistent nanoparticle concentration of 5 mg/mL. The recycled nanoparticles were again used to demulsify another 10 mL of prepared emulsion for a total of nine times. The recycling

tests plus initial demulsification tests were used to demonstrate the capability of the maghemite nanoparticles to be reused up to ten treatment cycles.

Chapter 4: Results and Discussion

4.1 Nanoparticle Characteristics

Preliminary testing included all four types of MNPs including a commercial and synthesized version of both magnetite and maghemite. All MNPs responded well to a magnet and dispersed completely in the 1-3% NaCl brines used in this study. However, after some poor results with the magnetite samples, the testing was expanded to include other types of water for MNP dispersion and emulsion production. As the tests continued, some of the magnetite tests were not performed due to poor results of previous trials that relied on a successful outcome. The characteristics of the nanoparticles should be discussed to explain the differences and possible explanations for some of the test results.



Figure 4.1 MNP samples used for demulsification testing.

4.1.1 Maghemite vs. Magnetite

The saturation magnetization for the magnetite particles used in this study was higher than those of the maghemite samples. The magnetization data for the MNP samples are shown in Table 4.1. The differences in saturation magnetization were

expected from previous studies and explains why most researchers have selected to use magnetite nanoparticles as carriers for a grafted surface agent. However, the increases in magnetization saturation did not correlate with the success of the oil removal experiments in this test.

The crystalline structure of magnetite is cubic and that of maghemite can be cubic or tetragonal. Magnetite does not possess a surface charge, so a coating is necessary to keep it from oxidizing into maghemite. The differences in molecular structure, especially those of surface charge and contribute to the differences in saturation magnetization values but do not explain why maghemite outperformed magnetite in the tests of this study. Therefore, the data collected from this study suggest that saturation magnetization may not be the best indicator of MNPS performance for produced water treatment.

The solubility of the MNPs may also have been observed in this study. Magnetite is known to be water-soluble due to its high surface activity, but maghemite is generally considered to be insoluble. However, some researchers have discovered that maghemite can become more soluble in a nitric acid solution with calculated pH values between 1-2. This result may explain why maghemite was able to perform well in the oil removal tests while being dispersed into water samples that contain at least a 1% NaCl concentration. Further details of the possible solubility conflict with specific water samples is later described.

Table 4.1 Magnetization measurements for magnetite and maghemite samples

Sample	Mag(H)emite or Mag(N)etite	Magnetic Portion (%)	Saturation Polarization (Guass [^] cm [^] 3/g)	Magnetic Dipole Moment (10 ^{^-} 7*Vsm)
WCTC B002	N	38.62%	61.77	0.3912
WCTC B003	N	32.70%	52.31	0.6212
WCTC B004	N	31.76%	50.81	0.5733
WCTC B005	H	26.90%	43.03	0.4374
WCTC B006	N	41.35%	66.14	0.6591
WCTC B007	H	36.63%	58.59	0.4771
WCTC B009	H	24.97%	39.95	0.4322
WCTC B010	H	38.13%	61.06	0.706
Sigma Aldrich (N)	N	55.28%	88.42	1.027
Sigma Aldrich (H)	H	49.60%	79.33	0.2163

The magnetic pull force data collected for each of the nanoparticle sample as described in section 3.1.4. The measurements considered for nanoparticle comparison and analysis were measure with a 0.25” separation between the magnet and the sample. The pull force data was compared with the saturation magnetization data to determine the relationship of the two magnetization tests. Fig 4.2 shows a positive correlation between the two magnetism measurements. An increase in saturation magnetization was consistent with an increase in magnetic pull force. The correlation of the magnetization measurements was near linear with an R² value of 0.9171. The saturation magnetization measurement requires expensive instruments and training. The strong correlation in the magnetization data suggest that the pull force measurements tests could be performed to estimate magnetization saturation with a certain degree of accuracy quickly and with minimal equipment. This discovered relationship can save time and money in future comparative analysis of magnetic nanoparticle samples.

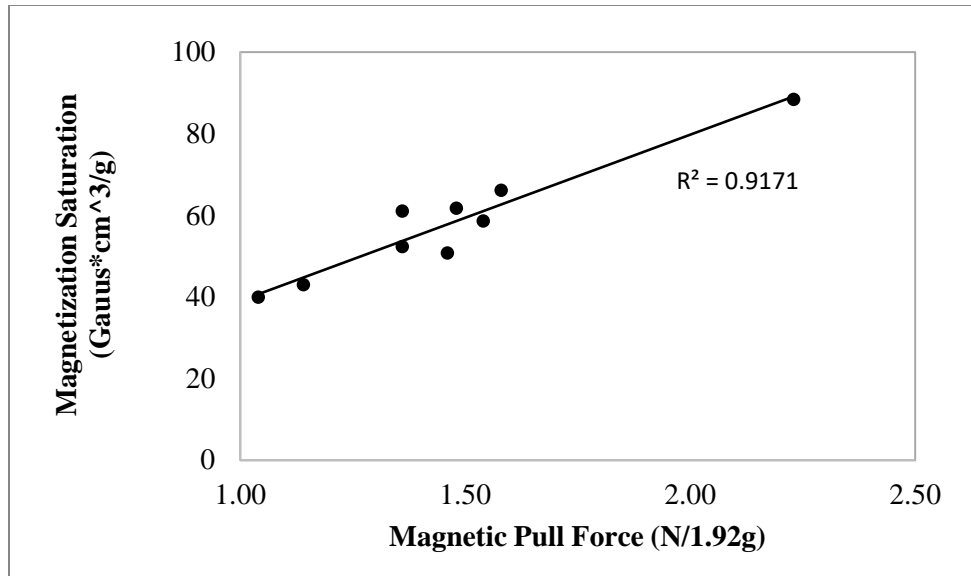


Figure 4.2 Magnetic Pull Force vs Magnetization Saturation

4.2 Oil Removal Efficiency Testing

The purpose of this study is to test the ability of iron oxide nanoparticles to remove dissolved and dispersed oil in contaminated water. Reducing the oil concentrations below the discharge limit of 42 ppm, or below 10 ppm fulfills the same effect that current treatment options provide. However, using MNPs takes only minutes to demulsify the oil and separate the treated water and the other current treatment methods can take days and multiple pre-treatment and treatment methods to reduce oil concentrations below these limits. Data from these tests that show oil removal efficiencies >97% provide sufficient evidence for the practical use of these MNPs for produced water treatment

4.2.1 Demulsification Test

Prepared emulsions demonstrated a consistent homogeneity after sonication, as shown in Fig 4.3. The oil was emulsified completely when mixed with 1-3% NaCl brines.

Emulsions prepared with a CaCl_2 brine were also observed to be homogenous; however, within 30 minutes after sonication, a slight oil layer formed at the surface indicating emulsion instability. For the emulsion prepared with NaCl brine, the 3% brine was observed to remain stable up to two hours after sonication before an oil layer began to develop on the surface. NaCl is the ideal choice for emulsion production in this test because it accurately represents the salt type of the produced water sourced for this study as represented in Fig 2.2. The 1.18% NaCl brine demonstrated excellent stability for the applications of further tests and remained stable for more than eight hours and was therefore selected as the preferential salinity for all emulsion produced for demulsification testing. The stability of the emulsions could be further improved with the addition of a stabilizing surfactant, as noted in the literature (Lin et al. 2012). Due to the use of non-dispersive infrared spectroscopy for oil content analysis in this study, a surfactant was not used according to potential incompatibilities with the S-316 measuring solvent.

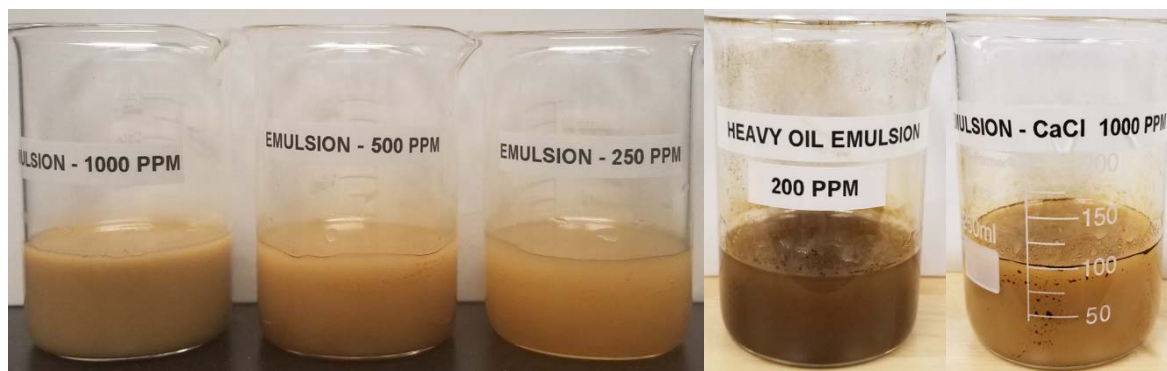


Figure 4.3 Prepared emulsions: a) NaCl , medium oil, 1,000-250 ppm oil conc. b) NaCl , heavy oil, 200 ppm oil conc. c) CaCl_2 , medium oil, 1,000 ppm oil conc.

Oil content analysis by infrared spectroscopy was performed for prepared emulsions, produced water samples, and treated watered from successful demulsification

tests. Appropriate calibration of the content analyzer was confirmed using known concentrations of prepared emulsions (100-ppm lab-synthesized and manufacturer-provided oil emulsions). The oil content measurements for both emulsions following calibration were 96 ppm and 102 ppm, respectively. These measurements are consistent with the manufacturer's referenced repeatability range of ± 5 ppm (mg/L). A two-point calibration method was performed with a zero and span (200 mg/L) calibration sample. The residual oil concentrations of the two produced water samples used in this study, PW-OK and PW-ARG, were measured to be 42.8-107 mg/L and 54 mg/L. The oil concentrations of the PW-OK produced water varied due to natural separation of oil in water over the course of a few months. Examples of the sourced produced water samples used throughout this study are shown in Fig 4.4

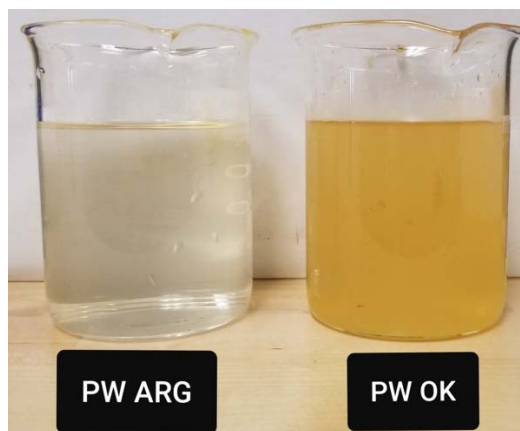


Figure 4.4 Produced water samples sourced locally (PW OK) and from Argentina (PW-ARG)

The dispersibility and magnetic response of the nanoparticle before emulsion treatment was dependent on the characteristics of the water used for dispersion. The measurements of water properties analyzed in this study are shown in Table 4.2.

Table 4.2 Properties of Experimental Water Samples.

Water Sample	Conductivity (mS/cm)	TDS (mg/L)	Salinity (ppt)	Salinity (ppm)	Resistivity (Ω)
Tap Water	0.306	217	0.15	150	3270
DI Water	0.00439	3.07	0	0	230,000
NaCl Brine (1180 ppm)	2.34	1660	1.17	1170	428
DI Water (CT)	0.0714	50	0.04	40	14,000
Produced Water (OK)	179.7	100,000	89.8	89,800	5.6
Produced Water (ARG)	55	39,000	27.5	27,500	18
NaCl Brine (3000 ppm)	5.84	4100	2.91	2910	172
Distilled Water	0.00777	6	0	0	129,000

The water samples with a salinity concentration of at least 150 ppm were successful in dispersion and recovery tests among the majority of MNP samples. Water salinities at or above this threshold demonstrated an ability to stabilize the dispersed nanoparticles. Water samples with low or zero salinity caused dispersion instability and also allowed for some of the dispersed nanoparticles to remain suspended in solution even after a magnetic field was applied as shown in Fig 4.5. The preferred water selected for demulsification tests in this study is a 3% NaCl brine (3 g/L) to maintain consistency and repeatability across all trials. This salinity was used for all nanoparticles dispersion and washings as it allowed for an excellent magnetic response during the tests.

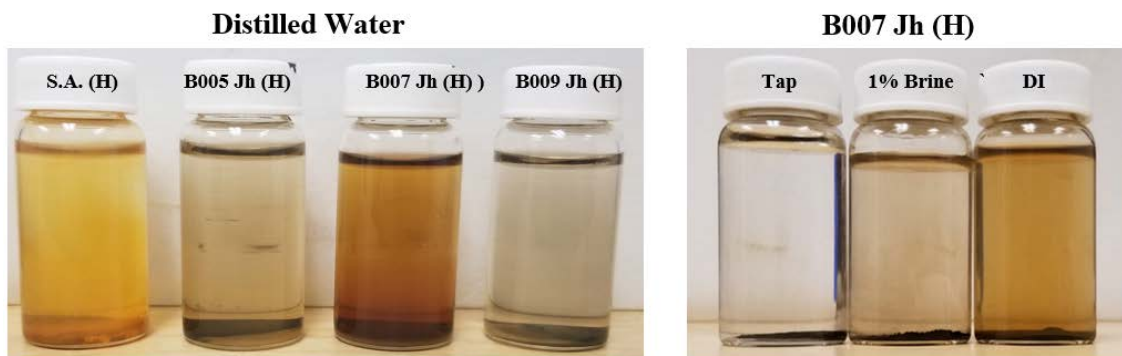


Figure 4.5 Water dispersion and recovery tests for distiller water – low salinity using various MNP samples (left), and for a maghemite sample (right) dispersed and recovered in three different water samples.

The demulsification ability of the maghemite nanoparticles is shown in Fig 3.9. Synthesized and commercial maghemite/magnetite nanoparticles all demonstrated an ability to demulsify and separate oil in the emulsions with the application of an external magnetic field. The most consistent tests results were observed using a nanoparticles concentration of 5 mg/mL, a 1,000-ppm medium oil emulsion, and a 3% NaCl brine concentration. The highest oil removal efficiency results for each of the separate batches tested is shown in Fig 4.6.

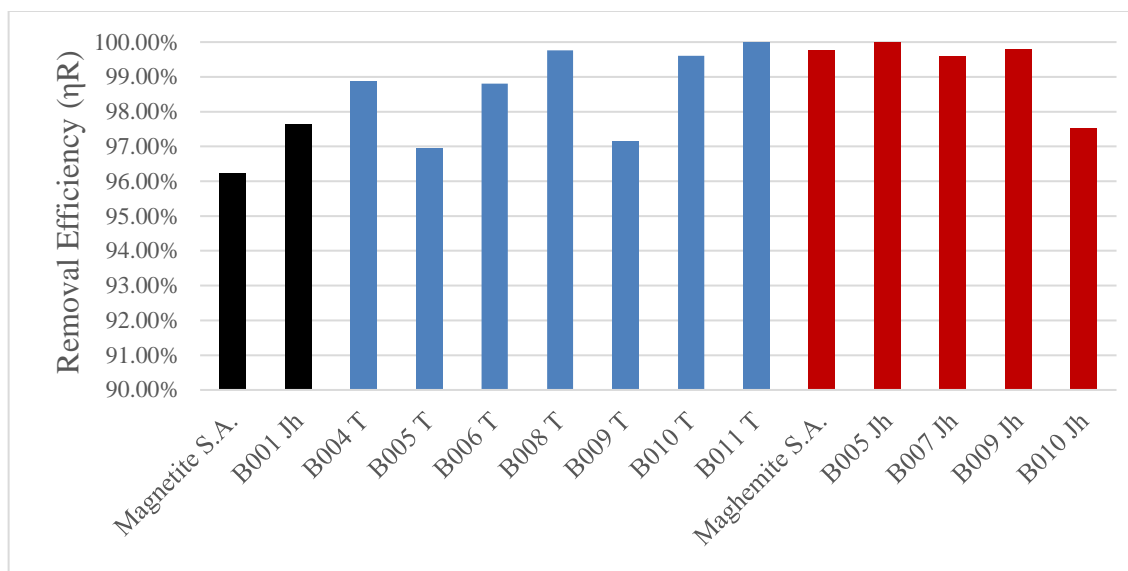


Figure 4.6 Highest oil removal efficiencies for each batch of nanoparticles tested - Bare magnetite (black); amine-functionalized magnetite (blue); maghemite (red)

At least one amine-functionalized magnetite (B011 T) and one maghemite sample (B005 Jh) were capable of reducing oil concentrations below detectable limits by the oil content analyzer, corresponding to an oil removal efficiency (η_R) of 100%. Although both types of nanoparticles showed success in the demulsification tests, the availability, short synthesization times, and readiness of the maghemite samples provide a clear advantage over the use of the amine-functionalized magnetite. The cost of the reagents, long synthesizing times, and degradation over repeated use are known disadvantages of the amine-functionalized particles. The results of this study indicate that similar (or in some cases better) oil removal efficiencies can be achieved using less expensive and more durable maghemite nanoparticles compared to the amine-functionalized magnetite. The bare magnetite samples were the least effective in reducing the oil concentrations as expected from past studies.

Complete demulsification occurred as the maghemite nanoparticles adhered to the emulsified oil (oil+MNPs) and separation from the water was observed between 10 and 30 seconds after the magnet was applied. The completion of demulsification for the synthesized nanoparticles was at or near 10 seconds after the magnet was applied. For the commercial nanoparticle demulsification, complete water and oil+MNPs separation was observed near 30 seconds after the magnet was applied. The commercial maghemite nanopowder size distribution was defined by the manufacturer as <50 nm and it was found that the smaller or weaker ferromagnetic nanoparticles were slower to respond to the applied magnetic field.

Nanoparticle concentrations were varied from 0.313 mg/mL to 5.0 mg/mL. Higher concentrations of dispersed nanoparticles that were used in demulsification testing allowed for shorter mixing times and greater oil removal efficiencies (η_R). A 5.0 mg/mL nanoparticle concentration demonstrated consistent and repeatable results, as also reported by past researchers (Lin 2012, Wang 2018). The critical concentration of nanoparticles is defined in this study as the concentration in which significant loss in oil removal efficiencies was observed with the subsequent reduction in nanoparticle concentration. The critical concentration was determined by a series of tests while reducing the concentration of nanoparticles by half-step increments from 5.0 mg/mL, to 2.5 mg/mL, to 1.25 mg/mL, and so on. The removal efficiency curves for the synthesized and commercial maghemite nanoparticles are shown in Fig 4.7.

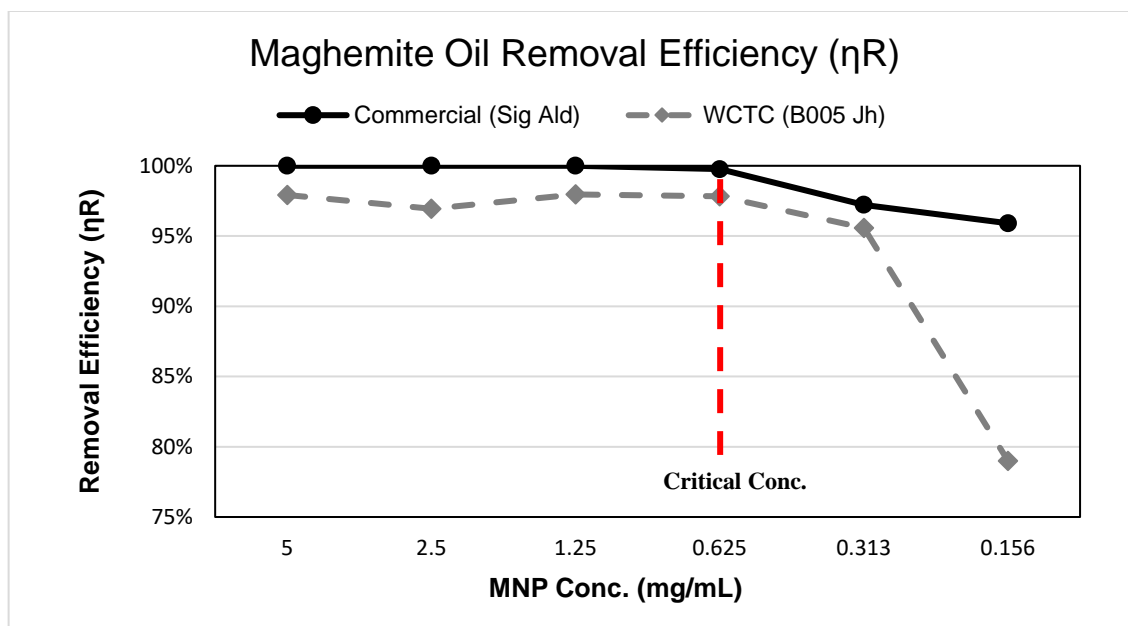


Figure 4.7 Removal efficiency vs. MNP Conc. for synthesized and commercial maghemite nanoparticles

The critical concentration was determined to be 0.625 mg/mL. Observed critical concentration in this study was dependent on mixing times and methods of the nanoparticles and emulsion solution. The critical concentrations of iron oxide nanoparticles of other studies were determined without mixing time limits and included solution mixing up to 24 hours (Wang et al., 2018). For oil concentrations <0.313 mg/mL, longer mixing times @ 180 rpms on the shaker plate were required to achieve acceptable oil removal efficiencies. Fig 4.8 shows the effect that longer mixing times had on the very low MNP concentrations tested as part of determining mixing optimization.

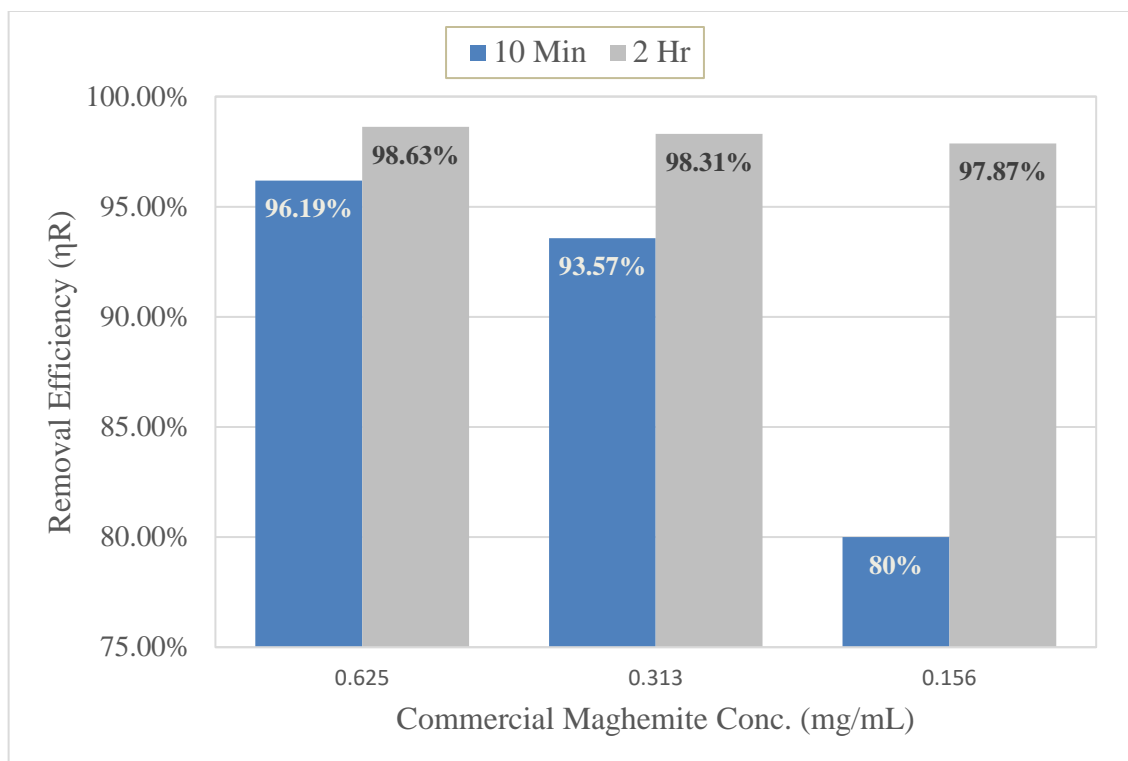


Figure 4.8 Effect of mixing time (@180 rpms) on oil removal efficiency for low concentrations of commercial maghemite

It was confirmed that oil removal efficiencies for lower nanoparticle concentration tests could be improved by increasing the mixing times to allow more time for the nanoparticles to contact the emulsified oil. For the feasibility of this study and its application in an oil field, the solution mixing times were subsequently limited to 30 secs and 10 mins. The two types of mixing employed in this study were performed with a 10-minute mechanical shaker plate at 180 rpm and a laboratory vortex mixer for 30 seconds at 3200 rpm. The mixing instruments were shown previously in Fig 3.4.

For all tested nanoparticle concentrations, the nanoparticles and demulsified oil were collected at the bottom or on the side of sample vials when the external magnet was applied. At high nanoparticle concentrations, it was observed that the nanoparticles

remained in the bottom of the sample vial even after the removal of the magnetic field indicating that the collection of oil+MNPs at the bottom is governed by gravitational force. For lower concentrations, including those below the critical concentration, the oil+MNPs were collected at the top of the sample vial after the removal of the magnetic field. This result indicates that at low nanoparticle concentrations, the aggregation of the particles governs buoyancy force of the oil+MNPs. These observations were expected as reported by previous studies (Li et al., 2014).

After successful demulsification, the treated water was easily removed with a syringe and prepared for oil content analysis. The prepared 1,000 ppm emulsions that were used in this study to simulate a controlled example of a produced water was reduced by the maghemite nanoparticles to oil concentrations below <10 ppm.

For lower MNP concentrations, it was observed that the buoyancy of the oil and MNP aggregate was the dominant force and the residual oil floated to the top of the sample (Fig 4.9) after the magnet was applied to the vial to collect the oil+MNPs.



Figure 4.9 WCTC B005Jh maghemite gravity dominated vs. buoyancy dominated MNP conc. (left), commercial maghemite gravity dominated vs. buoyancy dominated (right) MNP conc.

When concentrations of MNPS was increased, the gravity force dominated and the oil droplet-MNP aggregates sunk to the bottom of the sample vial. A visual representation of the forces is shown in Fig 4.10 where F_b represents the buoyancy force, F_{drag} is the drag force, F_g is the gravitational force, and nF_m is the magnetic force applied on the side bottom of a nanoparticle. The oil droplet is shown as the black circle with the magnetic nanoparticles are surrounding the droplet. Higher concentrations of MNP demonstrated a thicker MNP coating around the oil droplet.

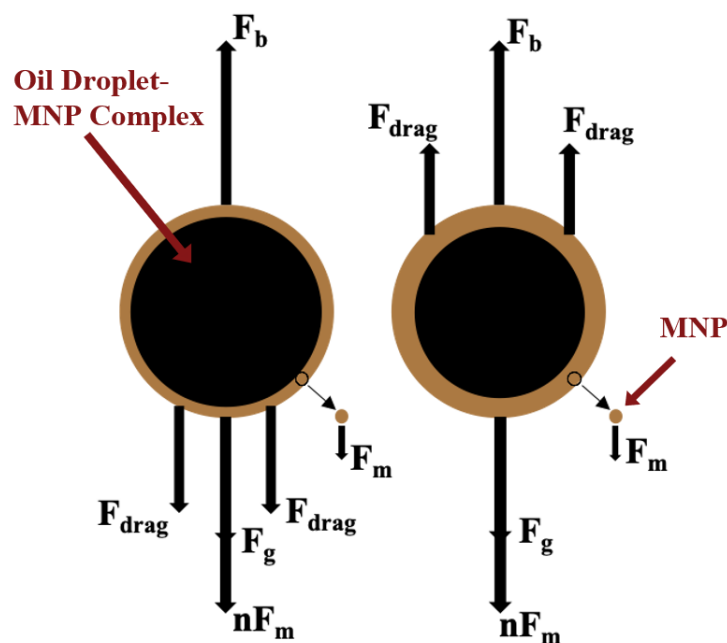


Figure 4.10 Forces acting on the nanoparticles and oil colloid for a buoyancy force dominated system (left) and gravity force dominated system (right) (adapted from Wang et al., 2018)

4.3 Nanoparticle Recyclability

To demonstrate and increase the efficacy of the nanoparticle water treatment test, and a series of reuse treatment cycle experiments were performed to evaluate nanoparticle recyclability. First, the used nanoparticles need to be washed to remove the oil that is coating the particle. After the oil is removed and a final water rinse to remove residual solvent, the nanoparticles can be reused, thus increasing their practical application by reducing material costs. The use of the same nanoparticles at a constant concentration for ten treatment cycles shows the material durability and little to none environmental impact.

4.3.1 Nanoparticle Recovery

The recyclability and reusability of the maghemite nanoparticles were observed successfully over a series of consecutive test cycles. The nanoparticle samples used in this study demonstrated adequate oil removal efficiencies above 97% for all test samples used for ten cycles (Fig. 4.11). This study confirmed the ability of a 5 mg/mL solution concentration of suspended maghemite nanoparticles to effectively reduce residual oil concentrations of 1,000 ppm (mg/L) oil-in-water emulsions below the disposal limit for offshore applications. In some cases, infrared spectroscopy was unable to detect any residual oil after successful demulsification and treated water separation tests.

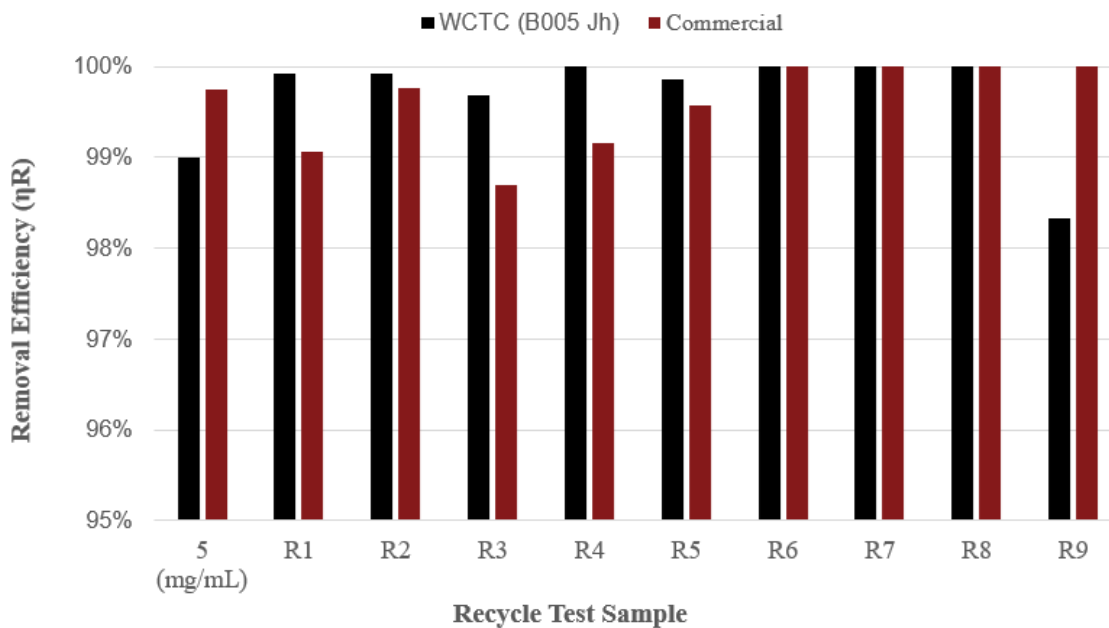


Figure 4.11 Commercial vs. synthesized maghemite recycling test results

The process of solvent washing and magnetic recovery demonstrated an adequate ability to prepare the maghemite nanoparticles for resuspension and reuse. Two ethanol solvent washes and two 3% NaCl brine washings were used to remove any remaining oil components from the nanoparticles.

The consistency of oil removal efficiencies exhibited by both types of maghemite nanoparticles suggests excellent reusability and high efficiencies over many repeated uses. This study examined maghemite oil removal up to ten cycles, and it is probable that the number of cycles could be much higher if the washing and recovery process is performed carefully as not to lose any nanoparticles that would later affect the concentrations of future demulsification cycles. It should also be noted that the maghemite nanoparticles showed no degradation in terms of their inherent ability to demulsify trapped oil or to be recovered by a magnetic field. The results of ten successful treatment cycles for WCTC B005Jh maghemite nanoparticles is shown in Fig 4.12. It was

observed that some of the treatment cycles resulted in separated water that was partially clouded. However, this cloudiness did not correlate to an increase in oil concentration because there was no significant reduction in oil removal efficiencies throughout the ten treatment cycles.

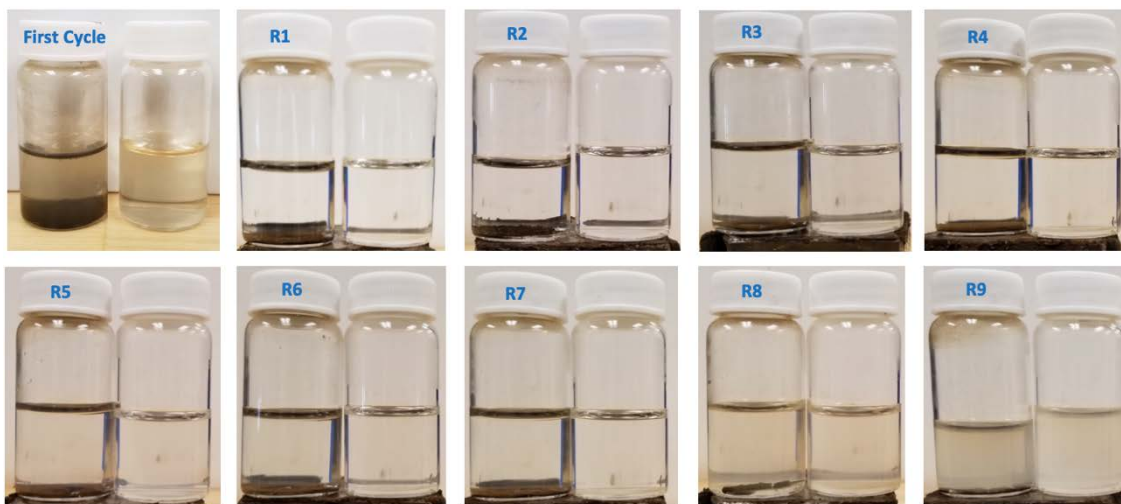


Figure 4.12 Maghemite recycling from the first cycle through nine recycling tests (WCTC B005Jh)

In this study, it was observed in the later cycles that the mass of nanoparticles appeared to be decreasing due to nanoparticle loss in the washing process. This loss could be avoided with more considerable attention given to the washing process including reducing the number of times the nanoparticles are transferred from one sample vial or beaker to the next. Deionized water was used for initial recycling tests; however, significant mass loss was observed in some of the later treatment cycles. The hypothesized reason for the mass loss is that the solubility of the maghemite nanoparticles into the deionized water sample attributed to the loss over repeated cycles. Past studies have demonstrated the solubility of maghemite, even though maghemite is generally considered insoluble by chemical standards. Fig 4.13 shows the solubilities of a few iron

oxide nanoparticles in a nitric acid solution at 25°C and calculated pH values between 1-2. The solubility products are shown as apparent values for each of the referenced iron oxide nanoparticles, compared to the relative ionic strength of the particles (Taylor and Owen, 1997). There was an observed residual dependence of pK_{sp} on ionic strength of the solvent. Therefore, the loss in mass in the initial recycling tests using deionized water may be attributed to the maghemite solubilizing in the water and lost when the water was removed, even in the presence of a strong magnet. The mass loss for subsequent recycling tests was not observed in later tests when a NaCl brine solution was used for washing. The brine was chosen for the test due to favorable results from the dispersion tests as previously described in Chapter 3.

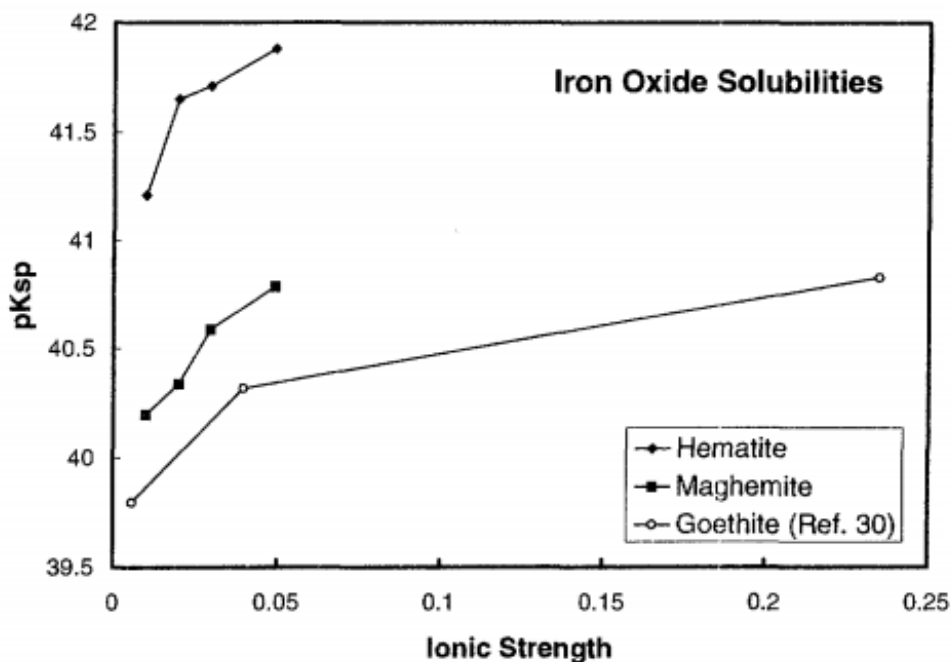


Figure 4.13 Apparent K_{sp} values for maghemite, hematite, and goethite as a function of ionic strength, I (Taylor and Owen, 1997).

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

The use of iron oxide nanoparticles in the oil and gas industry can provide an effective produced water treatment option. The natural abilities of the nanoparticles to separate oil-in-water emulsions makes them superior to many other current treatment options that require expensive materials, have long treatment cycles, or produce additional waste to the environment. From this study of the use of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite nanoparticles to separate residual oil in produced water, it can be concluded that:

- Maghemite nanoparticles demonstrate an inherent ability to demulsify O/W emulsions and separate residual oil. Magnetite nanoparticles require a surface-active coating to achieve acceptable O/W demulsification.
- Both synthesized and commercial iron oxide nanoparticles exhibit sufficient magnetization characteristics and oil-adherence capabilities that allowed for effective oil removal efficiencies of emulsions containing up to 1,000 ppm of oil.
- Oil removal efficiencies up to 99% were consistently observed using both commercial and synthesized maghemite nanoparticles. In some cases, the oil content analysis instrument used was unable to detect any residual oil after treatment.
- Nanoparticle concentrations as low as 0.313 mg/mL can remove oil at a 97% efficiency.
- The used nanoparticles can be collected, cleaned, and recycled immediately with some nanoparticles maintaining oil removal efficiencies up to at least ten

treatment cycles. Maghemite nanoparticles showed no degradation or loss in oil removal efficiency over the reuse cycles.

- Due to the low cost of iron oxide nanoparticles, environmental compatibility, and repeated recyclability, maghemite nanoparticle have been determined to be a practical option for produced water treatment.

5.2 Recommendations

Based on the previously discussed conclusions, the following recommendations are given for future work in the study of produced water treatment with iron oxide nanoparticles:

- Expanding the research to more trials per nanoparticle sample and additional produced water samples from actively producing oil wells.
- Increasing the number of reuse cycles beyond 10 to observe whether or not the particles lose their oil removal abilities after many reuse cycles.
- Additional imaging techniques such as DLS and SEM could be used to further characterize the nanoparticles to understand and compare the various forms of iron oxide nanoparticles that could be used.
- Further studies should seek to provide greater clarification of the physical mechanisms that drive the nanoparticle-oil interaction.
- An investigation of the scalability of this water treatment process to confirm its application in the oil and gas industry.
- Develop a method for customizing iron-oxide nanoparticles for water treatment plans based on compatibility and composition of the sourced produced water.

This will include determining critical concentrations required to maintain high oil removal and compatibility with the other components found in the produced water.

- Future studies may also investigate the complete composition of the produced water before and after nanoparticle treatment to observe whether the nanoparticles can affect other water contaminants.

Nomenclature

MNP(s) – Magnetic nanoparticle(s)

O/W – Oil-in-water

TDS – Total dissolved solids (mg/L or ppm)

W – Free energy requirement (ergs)

ΔA – Surface area (cm^2)

$\gamma_{o/w}$ – Surface tension (dynes/cm)

SS – Suspended solids

TSS – Total suspended solids (mg/L or ppm)

NORM – Naturally-occurring radioactive material

MF – Microfiltration

NF – Nanofiltration

UF – Ultrafiltration

RO – Reverse osmosis

MSF – Multistage flash (distillation)

VCD – Vapor compression distillation

MED – Multi-effect distillation

BBL – Barrels

BPD – Barrels per day

PPM – Parts per million (ppm or mg/mL)

PPT – Parts per trillion (ppt)

Ω – Resistivity (ohms)

Br – residual flux density (Gauss)

η_R – Removal efficiency (%)

F_b – Buoyancy force

F_{drag} – Drag force

F_g – Gravitational force

nF_m – Normal force applied as a magnetic force

I – Ionic strength

pK_{sp} – Apparent solubility product

n – sample size

μ – mean

σ – standard deviation

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