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PRODUCED WATER DEMULSIFICATION USING MAGHEMITE NANOPARTICLES

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Dedication:

To my aunt Ana Julia Hernandez, for showing me that education is the most empowering force in the world.

A mi tía Ana Julia Hernandez, por mostrarme que la educación es la fuerza de empoderamiento en el mundo.

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Abstract

Produced water management has become an important topic among oil and gas operators due to recent environmental regulations. Produced water requires treatment for recycling or disposal to the environment. Different methods are developed for reducing the content of residual oil in produced water; however, the existing techniques are usually expensive and/or generate secondary pollutants. Magnetic nanoparticles such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) have been extensively studied for various applications. Maghemite nanoparticles have shown potential in water treatment due to their suitable surface charge, magnetic characteristics, and inexpensiveness. The objectives of this study are to investigate the method of synthesis and residual oil removal efficiency of maghemite nanoparticles.

To achieve these goals, different chemical co-precipitation procedures were considered for the synthesis of maghemite nanoparticles. After synthesis, nanoparticles were used in the treatment process that involves the preparation of nanosuspension, demulsification of produced water using nanosuspension, and separation of oil-containing nanoparticles using a magnet. During the treatment, the nanosuspension was mixed (1:1 volumetric ratio) with produced water samples that were sourced from different oilfields. Then, the mixture was subjected to a magnetic field generated by a permanent magnet, in which a rapid cleaning of water was observed as the magnet quickly attracts the particles.

The removal of oil from produced water was confirmed using an oil content analyzer. The desired oil removal efficiencies were achieved with the implementation of this method. In every

experiment performed, oil removal efficiencies of more than 97% were recorded. After the collection of the used nanoparticles, the oil was removed/extracted by washing particles with ethanol and sodium chloride brine sequentially. Without losing their effectiveness, the nanoparticles were reused up to 11 times in treatment for multiple cycles. The implementation of maghemite nanoparticles constitutes a novel method with great potential for large-scale application in the treatment of produced water in various industries.

Chapter 1. Introduction

1.1 Overview

The importance of fossil fuels in our civilization is indisputable. The processes associated with their production generate large amounts of water (**Fig. 1.1**), which is typically known as produced water. Produced water is a mixture of organic and inorganic materials. Physical and chemical characteristics of produced water are a function of some factors such as the location of the well, the type of geological formation, time that the reservoir has been produced, and type of hydrocarbon product that is being extracted (Fakhru'l-Razi et al., 2009). Often produced water contains a high concentration of solids and pollutants. The disposal of produced water contaminates the soil and groundwater. Based on the United States Environmental Protection Agency (USEPA), the oil disposal limits for offshore produced water are 42 mg/L daily maximum and 29 mg/L monthly average.

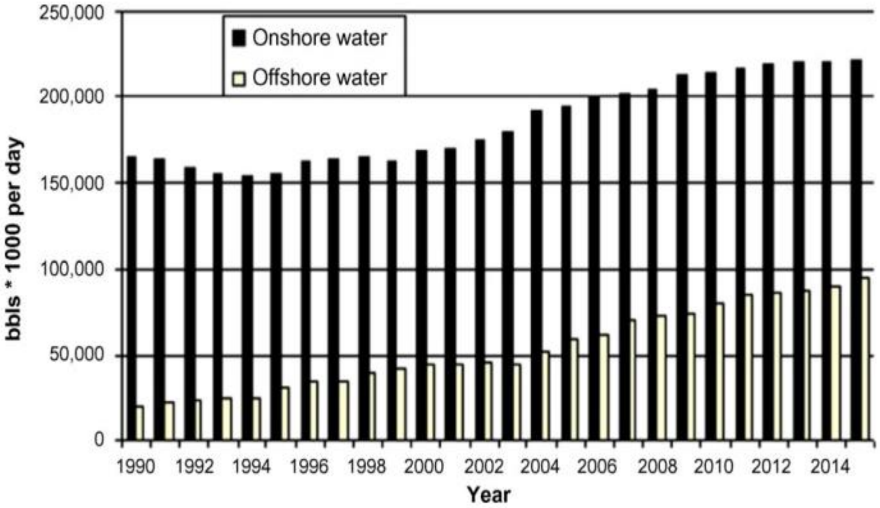
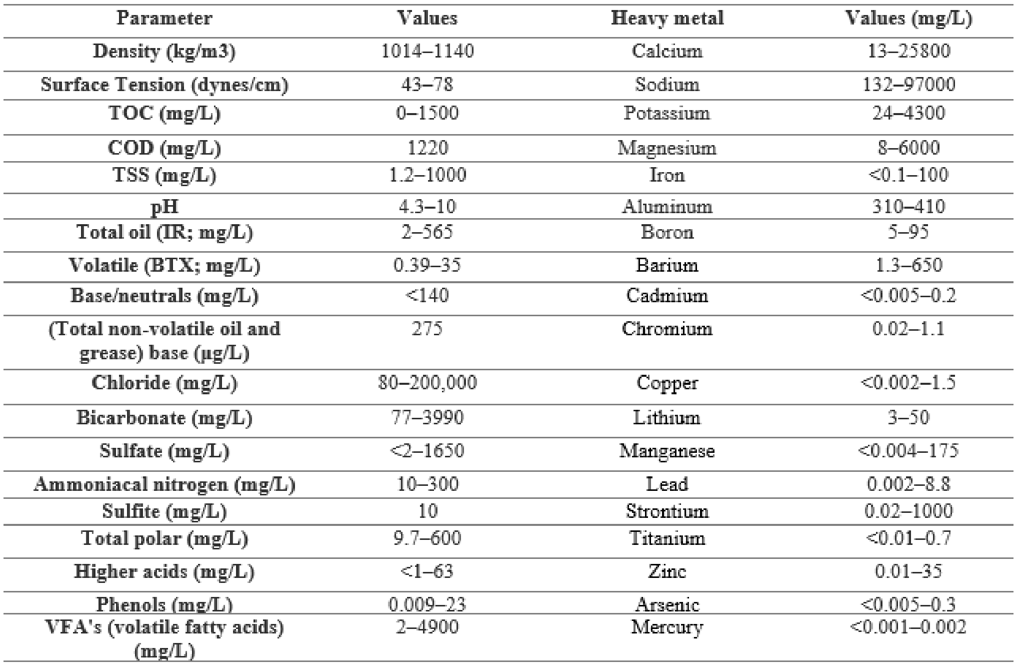


Figure 1.1. Global Summary of produced water production. (Dal Ferro and Smith 2007)

Due to the growing concern for the environment, several oil and gas producing countries have adopted different regulations to mitigate the produced water disposal problem. Normally, produced water is re-injected in oil and gas extraction locations; however, recent studies (Peterson et al., 2018) suggest the link between reinjection and an increase in seismic activities that cause earthquakes. As a result, other methods such as recycling are becoming more feasible than reinjection. To reused produced water in applications such as irrigation, livestock, or industrial process, the contaminants need to be removed. It is for this reason that many countries are investing more and more resources to find efficient and economic recycling methods that guarantee them to comply with the disposal and recycling standards.

There are dissolved and dispersed oil compounds present in produced water (**Table 1.1**). The conventional separation techniques such as settling tanks and oilfield separators are not adequate to bring the oil concentration below the disposal limits established by law. As a result, the residual oil must be removed using other methods.

Table 1.1 Summary of oilfield-produced water parameter in the world (Tibbetts et al., 1992)



Parameter	Values	Heavy metal	Values (mg/L)
Density (kg/m3)	1014–1140	Calcium	13–25800
Surface Tension (dynes/cm)	43–78	Sodium	132–97000
TOC (mg/L)	0–1500	Potassium	24–4300
COD (mg/L)	1220	Magnesium	8–6000
TSS (mg/L)	1.2–1000	Iron	<0.1–100
pH	4.3–10	Aluminum	310–410
Total oil (IR; mg/L)	2–565	Boron	5–95
Volatile (BTX; mg/L)	0.39–35	Barium	1.3–650
Base/neutrals (mg/L)	<140	Cadmium	<0.005–0.2
(Total non-volatile oil and grease) base (μg/L)	275	Chromium	0.02–1.1
Chloride (mg/L)	80–200,000	Copper	<0.002–1.5
Bicarbonate (mg/L)	77–3990	Lithium	3–50
Sulfate (mg/L)	<2–1650	Manganese	<0.004–175
Ammoniacal nitrogen (mg/L)	10–300	Lead	0.002–8.8
Sulfite (mg/L)	10	Strontium	0.02–1000
Total polar (mg/L)	9.7–600	Titanium	<0.01–0.7
Higher acids (mg/L)	<1–63	Zinc	0.01–35
Phenols (mg/L)	0.009–23	Arsenic	<0.005–0.3
VFA's (volatile fatty acids) (mg/L)	2–4900	Mercury	<0.001–0.002

Previous studies (Ko et al., 2017) have shown the benefits of iron oxide nanoparticles in the oil removal process. Iron oxide compounds have been very useful in the history of mankind, the application of iron oxide nanoparticles to various processes of removal of pollutants has been widely practiced. In the last decade, the development of nanotechnology has improved the methods of synthesis, characterization, and application of these materials. Even though many forms of iron oxide nanoparticles exist, maghemite (γ-Fe_2O_3) is selected to conduct this research because of its performance and economic viability. This study shows an oil separation technique using superparamagnetic maghemite nanoparticles that are cost-effective, efficient, and environmentally friendly.

1.2 Problem Statement

Produced water treatment has become a concerning topic among oil and gas companies. It is estimated that around 250 million barrels per day of produced water are extracted globally compared to 80 million barrels per day of extracted oil (Fakhru'l-Razi et al., 2009). Most of this water is considered as a waste in which handling represents a cost. Currently, most of the operators follow one of the available options including injection, discharge, reuse in oil and gas operations, or consumption in other beneficial applications (Arthur et al., 2005). Treatment of produced water has become relevant as it presents the opportunity to recognize produced water as a valuable byproduct rather than a waste.

Conventional separation techniques such as gravity decantation only separate the amount of free oil in produced water. This separation reduces the oil concentration but does not reduce the concentration to the disposal level specified by environmental regulations. In the last decades, specialized treatment methods have been developed whose objective is to reduce the concentration of oil in the water to a disposal level. These treatments include physical methods such as adsorption using activated carbon, filters, cyclones, evaporation, induced air flotation, dissolve air flotation, as well as chemical-based methods such as chemical oxidation and demulsification. Although these methods indeed contribute to the removal of oils, they also have considerable disadvantages such as the high cost of the filters or potential environmental problems caused by the chemicals used in the demulsification.

Considering the large quantity of produced water generated in the industry, it is necessary to develop an effective method that responds to the needs of the entities involved in the problem. The method must be able to remove the emulsified and dissolved oil from produced water effectively, economically, and environmentally friendly manner. This study shows a technique that could be a solution to this problem. The method has the requirements including high removal efficiency, economically viable, and low environmental footprint.

1.3 Objectives

The main objective of this study is to investigate the removal of oil from produced water through the utilization of superparamagnetic maghemite nanoparticles synthesized in-house specifically for water treatment applications. The specific objectives of this study are to:

- Synthesize effective and inexpensive maghemite nanoparticles for the separation of residual oil from produce water.
- Identify the necessary characteristics of maghemite nanoparticles to remove residual oil from produced water after the hydrocarbon extraction process.
- Create a new water treatment technique to decrease the oil concentration in produced water and meet the disposal concentration.

- Analyze oil removal efficiencies of in-house synthesized maghemite and compare the results against the removal efficiency of maghemite found in the market.
- Investigate the recycling potential of magnetic nanoparticles during oil treatment operation.

1.4 Methodology

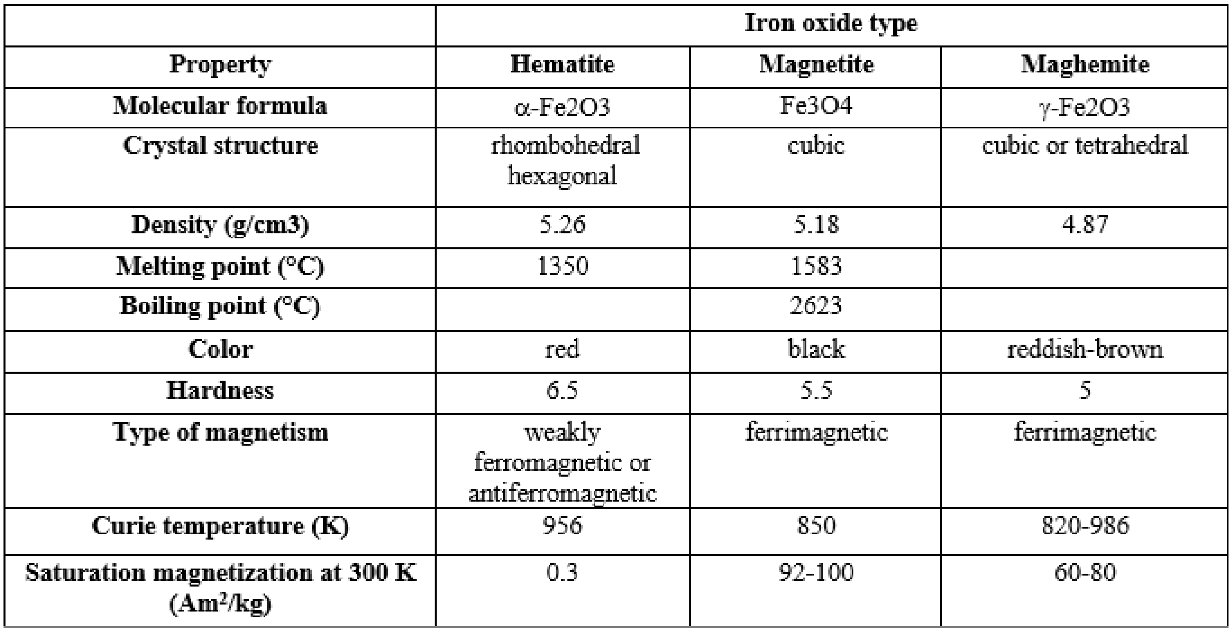
In this study, first, a literature review was conducted on maghemite nanoparticle synthesis to perform an experimental investigation. Various types of co-precipitation methods were used to synthesize the nanoparticles. The oil removal efficiencies of the lab-synthesized and commercial nanoparticles were investigated using produced water samples obtained from different oilfields. Through a detailed literature review, it was possible to determine the required characteristics of nanoparticles for the successful removal of residual oil from produced water. In the first part of the present study, different synthesis methods were used to manufacture nanoparticles. After characterization and analysis for the manufactured samples, locally sourced produced water was tested to ensure the applicability of the procedure in the field. Characterization of the nanoparticles was a vital component of this study because the effectiveness of the maghemite nanoparticles is strongly related to their properties. Oil removal and nanoparticle recycling tests were performed on each sample. To determine oil removal efficiency, initially and final oil concentrations were measured using an oil content analyzer that utilizes the infrared spectroscopy method. Some tests were conducted several times to assess experimental repeatability.

Chapter 2. Literature Review

2.1 Characterization of Maghemite Nanoparticles

Iron oxides are extensively used compounds, which are found in nature and synthesized in the laboratory (Wu et al., 2015). These compounds have been useful to mankind for centuries, for example, there are numerous applications of small iron oxide nanoparticles (Wu et al., 2008). Currently, eight iron oxides are known, among these iron oxides hematite (α-Fe_2O_3), magnetite (Fe_3O_4), and maghemite (γ-Fe_2O_3) have been vastly studied due to their unique characteristics such as surface charge, biochemical, magnetic, catalytic, and other properties that make them suitable for diverse applications (Cornell, 2003, p.517). The iron oxide variant that is used in this study is maghemite. Characteristics of the main types of iron oxides are shown in **Table 2.1**.

Table 2.1: Chemical and physical characteristics of common iron oxides (Lam et al., 2008)



	Iron oxide type		
Property	**Hematite**	**Magnetite**	**Maghemite**
Molecular formula	α-Fe2O3	Fe3O4	γ-Fe2O3
Crystal structure	rhombohedral hexagonal	cubic	cubic or tetrahedral
Density (g/cm3)	5.26	5.18	4.87
Melting point (°C)	1350	1583	
Boiling point (°C)		2623	
Color	red	black	reddish-brown
Hardness	6.5	5.5	5
Type of magnetism	weakly ferromagnetic or antiferromagnetic	ferrimagnetic	ferrimagnetic
Curie temperature (K)	956	850	820-986
Saturation magnetization at 300 K (Am^2/kg)	0.3	92-100	60-80

2.2 Important Concepts in Magnetism

The magnetic moment is the parameter that determines the magnetic force and orientation of an object that produces a magnetic field. There are certain materials that, when applying an external field, their magnetic moments are altered and change their orientation (Cortes, 2018). The magnetism of small ferromagnetic particles (up to 1 μm) is dominated by two main features:

- A size limit below which the particle no longer achieves an energetic configuration favorable by dividing into domains; therefore, it remains in a single domain (Buendia, 2009).
- Thermal energy, which when the size is small enough can decouple the magnetization of the particle to give rise to the phenomenon of superparamagnetism. (Buendia, 2009).

Materials that show ferromagnetism, such as iron, nickel, and cobalt, present atomic magnetic moments of equal magnitude that are aligned in parallel (in the same direction of the external field) because of their crystalline structures. This alignment allows direct coupling of the interactions between the moments. Electrons are exchanged in the case of metals (super exchange in the case of metal oxides since they interact through oxygen atoms), a phenomenon that strongly increases the density of magnetic flux. The strong pairing of the spins continues after removing the magnetic field, resulting in permanent magnetization (Garcia, 2012).

2.2.1 Superparamagnetism

Superparamagnetism is a form of magnetism exhibited by small ferromagnetic or ferrimagnetic nanoparticles, this property is a consequence of the alignment of the magnetic moments. Due to the orientation of all the magnetic moments (in the same direction), a considerable quantity of magnetic energy is generated in some materials. These materials gather the magnetic moments into regions called magnetic domains. A magnetic domain is a portion of ferromagnetic material in which all magnetic moments are aligned in the same direction. Within each domain, the spins are oriented in the same direction but different from that of other magnetic domains. Ferromagnetism and paramagnetism can be distinguished based on the concept of the magnetic domain (Garcia, 2012) When the size of a material decreases to the order of a nanoparticle, the value of the magnetic spins reach a critical value that indicates the transition from ferro to superparamagnetic material. Generally, this characteristic occurs in particles between 10 and 150 nm in diameter, depending on the material (Clemons et al., 2009). Iron oxide when synthesized as nanoparticles of maghemite exhibits superparamagnetic behavior, which is suitable for removing oil from produced water.

2.3 Maghemite and Its Applications

Iron oxide compounds are extensively utilized as aggregates for the steel industry, pigments for paint, as catalysts, and as magnetic pigments. In addition, iron oxides can be used in ferrofluids, jewelry, photochemical, and fertilizers (Cornell, 2003, p.511). Various types of iron oxide have been utilized as coloring agents for a long time in human history; the three main forms mentioned previously are frequently used as a synthetic pigment in paints, ceramics, and porcelain. This is because every form of iron oxide shows a different color, hematite is red, maghemite is brown and magnetite is black. When used as a catalyst, maghemite is present in the Haber process, the Fischer-Tropsch synthesis, water-gas-shift reactions, the dehydrogenation of ethylbenzene to styrene, and the vapor-phase oxidation of alcohols to aldehydes and ketones (Cornell, 2003, p.253)

Maghemite is also regularly utilized in the media-recording industry and biomedical fields, mainly because of its magnetic properties. Maghemite is the main magnetic pigment used in several electronic recording devices. A strong magnetic field is created at the gap of the magnetic head when information is being stored on any kind of recording medium. Maghemite particles on this application have a high coercivity (high-intensity demagnetization field is required to reduce the magnetic polarization to zero from the saturation state). The use of maghemite leads to the long-term stability of the information recorded (Cornell, 2003, p.512). Aside from having convenient magnetic properties, maghemite is broadly used in biomedical applications, due to its biocompatibility and low toxicity in the human body (Alexiou et al., 2006). It has the potential to serve as a drug carrier in magnetic drug targeting (Alexiou et al., 2006), as an agent in magnetic resonance imaging (Nitin et al., 2004), as heating mediators in magnetic hyperthermia (Wust et al., 2006), and the number of its applications continue to increase.

2.3.1 Water Treatment

Nanoparticles are nanomaterials with special physical and chemical characteristics; surface area is one of the main properties exploited from these substances. They have a high surface area and a convenient size (**Fig. 2.1**). In addition, easy modification, separation, and excellent magnetic properties make them the ideal candidate for water treatment applications.

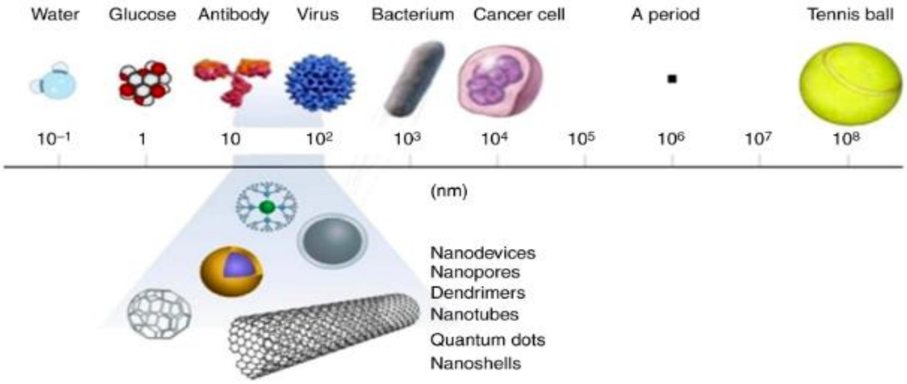


Figure 2.1. Comparison of nanoparticle size (Amin et al., 2014)

Different studies have shown that maghemite nanoparticles have been used in various water treatment applications. For instance, nanocomposite-based maghemite nanoparticles have been synthesized as a membrane for groundwater purification (Al-Hobaib et al., 2015). Also, they are used in the removal of dyes such as methylene blue, methyl orange, Janus Green, and Congo red, as well as contaminant ions in water such as nitrite, nitrate, and cesium (Cheng et al., 2012). Maghemite can perform as a photocatalyst and magnetic nanomaterial, which shows its effectiveness in the degradation and removal of contaminants. Previous studies show that coated maghemite nanoparticles have been used as an adsorbent to remove different contaminants from wastewater with efficiencies of up to 100% for some contaminants (Ashraf et al., 2017).

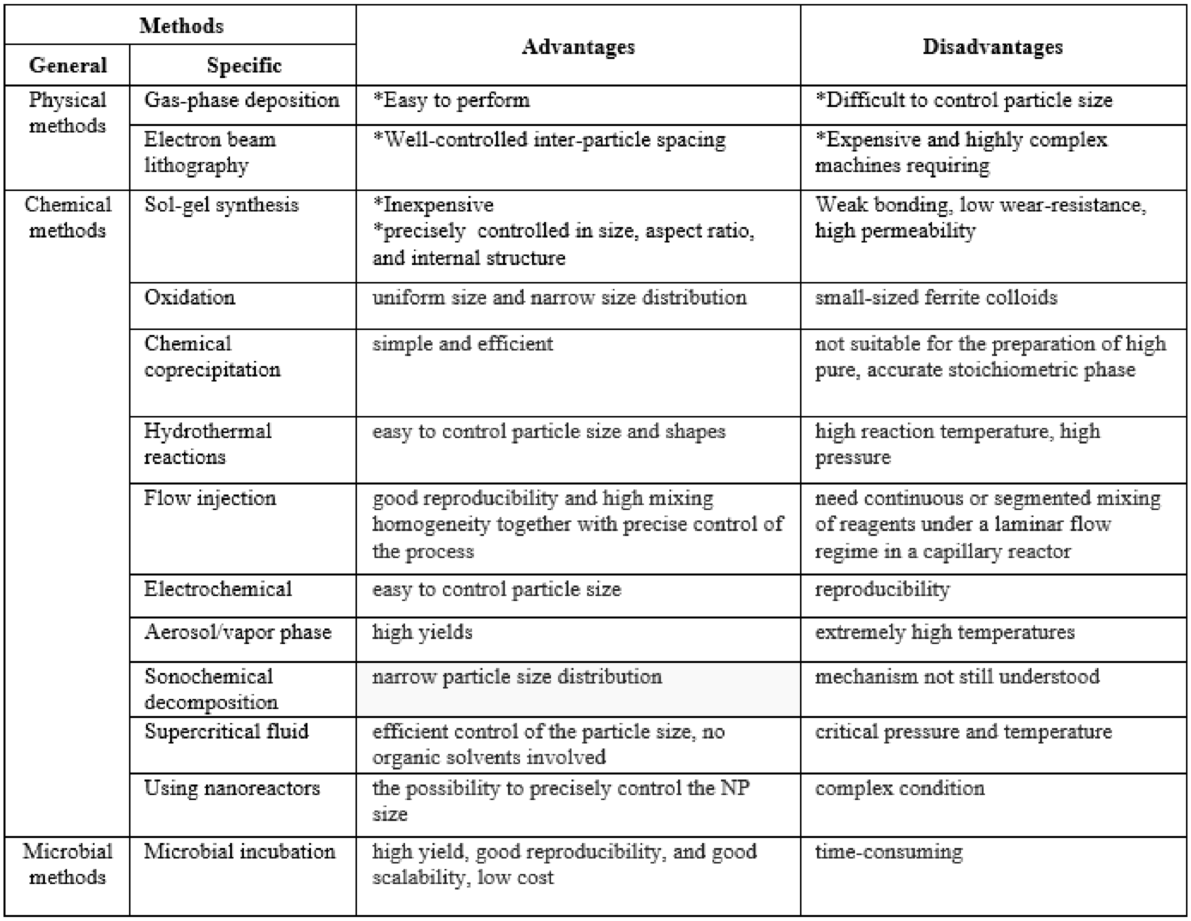
Maghemite nanoparticles intercalated into an alumino-silicate matrix was used as a photocatalyst for the catalytic reduction and removal of chromium from aqueous solutions. In such applications, maghemite showed huge potential for the removal of dyes from wastewater. After several tests and analysis, recently, it was found that maghemite has an outstanding performance when it is used in water treatment, with oil removal efficiencies higher than 98%. (Obeid et al., 2013).

2.4 Magnetic Nanoparticles Synthesis Techniques

The characteristics of magnetic nanoparticles strongly depend on the way they are synthesized, and the modifications made to the surface of these materials. In recent years, great development and progress have been made in the production methods of magnetic nanoparticles. These methods are classified into three main techniques: physical, chemical, and biological (Xu et al., 2014). Methods such as gas-phase deposition and electron beam lithography are part of the physical methods. Usually, these methods are relatively simple and inexpensive. However, making use of physical methods it is difficult to control properties of nanoparticles such as size, and some types of nanoparticles cannot be produced by these methods (Ashraf et al., 2017). Chemical methods are the most widely used due to their versatility in addition to their high yield of nanoparticles.

The disadvantage of chemical methods is that in some cases they require drastic conditions such as high temperature or pressure. However, with these methods, greater control over the properties of the nanoparticles can be achieved by adjusting the reaction parameters. The microbial approach includes the use of different organisms such as bacteria, yeast, fungi, plant and plant extracts, and algae to synthesize nanoparticles. These methods have several merits including high yield, low cost, and good reproducibility. However, biological methods involve a fermentation step, which is a time-consuming process (Pawar et al., 2013).

Table 2.2 Summary of manufacturing methods of magnetic nanoparticles (Xu et al., 2014)



Methods		Advantages	Disadvantages
General	Specific		
Physical methods	Gas-phase deposition	*Easy to perform	*Difficult to control particle size
	Electron beam lithography	*Well-controlled inter-particle spacing	*Expensive and highly complex machines requiring
Chemical methods	Sol-gel synthesis	*Inexpensive *precisely controlled in size, aspect ratio, and internal structure	Weak bonding, low wear-resistance, high permeability
	Oxidation	uniform size and narrow size distribution	small-sized ferrite colloids
	Chemical coprecipitation	simple and efficient	not suitable for the preparation of high pure, accurate stoichiometric phase
	Hydrothermal reactions	easy to control particle size and shapes	high reaction temperature, high pressure
	Flow injection	good reproducibility and high mixing homogeneity together with precise control of the process	need continuous or segmented mixing of reagents under a laminar flow regime in a capillary reactor
	Electrochemical	easy to control particle size	reproducibility
	Aerosol/vapor phase	high yields	extremely high temperatures
	Sonochemical decomposition	narrow particle size distribution	mechanism not still understood
	Supercritical fluid	efficient control of the particle size, no organic solvents involved	critical pressure and temperature
	Using nanoreactors	the possibility to precisely control the NP size	complex condition
Microbial methods	Microbial incubation	high yield, good reproducibility, and good scalability, low cost	time-consuming

2.4.1 Chemical Co-precipitation

The co-precipitation technique (**Fig. 2.2**) is the simplest and most efficient method to obtain magnetic nanoparticles chemically. Iron oxides (Fe_3O_4 or γ-Fe_3O_4) are generally prepared by maintaining the stoichiometric ratio between ferrous and ferric salts in an aqueous solution. The chemical reaction that occurs during the formation of Fe_3O_4 is shown in Equation (2.1) (Laurent et al., 2008).

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \longrightarrow Fe_3O_4 + 4H_2O \quad (2.1)$$

As stated by the thermodynamics of the chemical reaction for the synthesis of maghemite, the complete deposition of Fe_3O_4 is reached when the pH of the solution is raging between 8 -14. Also, a molar ratio of 2:1 (Fe^{3+} / Fe^{2+}) and an oxygen-free environment are necessary to avoid iron oxidation. Iron oxide in its magnetite form is not stable and it can be oxidized easily. Therefore, when the reaction occurs in the presence of oxygen, maghemite (γ-Fe_2O_3) is formed, according to Equation (2.2).

$$Fe_3O_4 + 2H^{+} \longrightarrow \gamma\text{–}Fe_2O_3 + Fe^{2+} + H_2O \quad (2.2)$$

According to Equation (2.2), oxidation with air not only causes the transformation of magnetite into maghemite but also transfers various electrons or ions depending on the pH. . Under acidic and anaerobic conditions, the surface of Fe^{2+} ions will form Hexa-aqua complexes in solution, whereas, under basic conditions, the oxidation of magnetite will produce reactions redox on the surface of it (Laurent et al., 2008). The main advantage of this method is that a large amount of nanoparticles can be synthesized. Nonetheless, particle size control is limited because kinetic factors influence crystal growth. The size and shape of the nanoparticles can be controlled with relative success by adjusting solution pH, ionic strength, temperature, nature of salts, or the ratio

Fe^{2+} / Fe^{3+} concentration. The addition of chelating organic anions (carboxylates such as oleic acid, etc.) or polymers surface areas that act as complexing agents (dextran, polyvinyl alcohol, etc.) during magnetite formation can help control the size of the nanoparticle (Laurent et al., 2008).

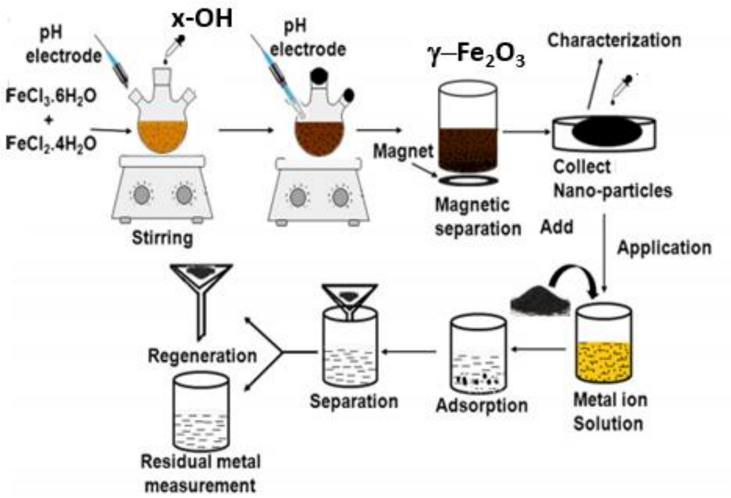


Figure 2.2. Chemical co-precipitation of nanoparticles with iron chlorides

2.4.2 Hydrothermal Synthesis Method

These reactions are carried out in aqueous media in reactors or autoclaves, where the pressure can reach up to 2000 psi and temperature can reach 200ºC. By utilizing this type of synthesis method, hydrates or dehydrates metal salts can form in extreme conditions. Metal oxide solubility can be controlled by maintaining favorable conditions of supersaturation. It is important to determine the proper concentration, temperature, and residence time of the particle precursors to control the size and morphology of the nanoparticles obtained using this method (Fakhru’l-Razi et al., 2009). The size of the particles increases depending on the iron precursor concentration used. However, the residence time is a factor used in controlling the size of the nanoparticles. After the synthesis, nanoparticles are obtained monodisperse when the residence time is low.

2.5 Characteristics of Produced Water

Produced water is a fluid mixture that is brought to the surface when hydrocarbons are produced. The chemical composition of produced water varies with the type of hydrocarbon that is being produced. Commonly, produced water not only contains oil or grease from the hydrocarbons but also dissolved or suspended solids. Also, produced water may contain solids such as sand, and other chemical components present in the rock formation (Veil et al., 2004).

Residual oil is one of the most relevant components of produced water onshore and offshore locations. However, in-ground operation, salt content (expressed as salinity, conductivity, or TDS) plays a major role and increases concerns. Furthermore, produced water contains many organic and inorganic compounds (Duraisamy et al., 2013). These vary greatly from place to place, over time, and even in the same well. The organic and inorganic constituents of produced water from offshore locations can be found in diverse physical conditions including solution, suspension, emulsion, adsorbed particles, and particulates.

Along with the natural components previously mentioned, produced water also contains groundwater or seawater (also known as "source" water) that is injected to maintain depleted pressure into the formation. Solids and bacteria can also be part of its components. The salinity of produced water is higher than the salinity of seawater. Sometimes, chemical additives used in drilling and production operations are also found in this fluid. Treatment chemicals are typically complex mixtures of various molecular compounds. The mixtures contain corrosion inhibitors and oxygen scavengers to reduce equipment corrosion, scale inhibitors to limit mineral scale deposits; biocides to mitigate bacterial accumulation, emulsion switches, and clarifiers to break water-in-oil emulsions and reverse switches to break oil-in-water emulsions, coagulants, flocculants, and clarifiers to remove solids, and solvents to reduce paraffin deposits. These chemicals can affect the oil-water partition coefficient of produced water, and its toxicity, bioavailability, and biodegradability.

Produced water from gas production has high molecular weight contents such as BTEX compounds (benzene, toluene, ethylbenzene, and xylene). The toxicity of these compounds tends to be higher than the ones obtained during oil extraction. Often, produced water from gas condensate is about 10 times more toxic than that generated from oil production. However, offshore gas production is much lower than oil; therefore, the total impact may be less. Also, chemicals used for gas processing typically include dehydration, hydrogen, sulfide removal, and chemicals to inhibit hydrates. These chemicals can be found in produced water from gas operations. Hence, the produced water from these sources can have acidic minerals, dense brines, and additives (Jacobs et al., 1992).

2.6 Current Produce Water Treatment Methods

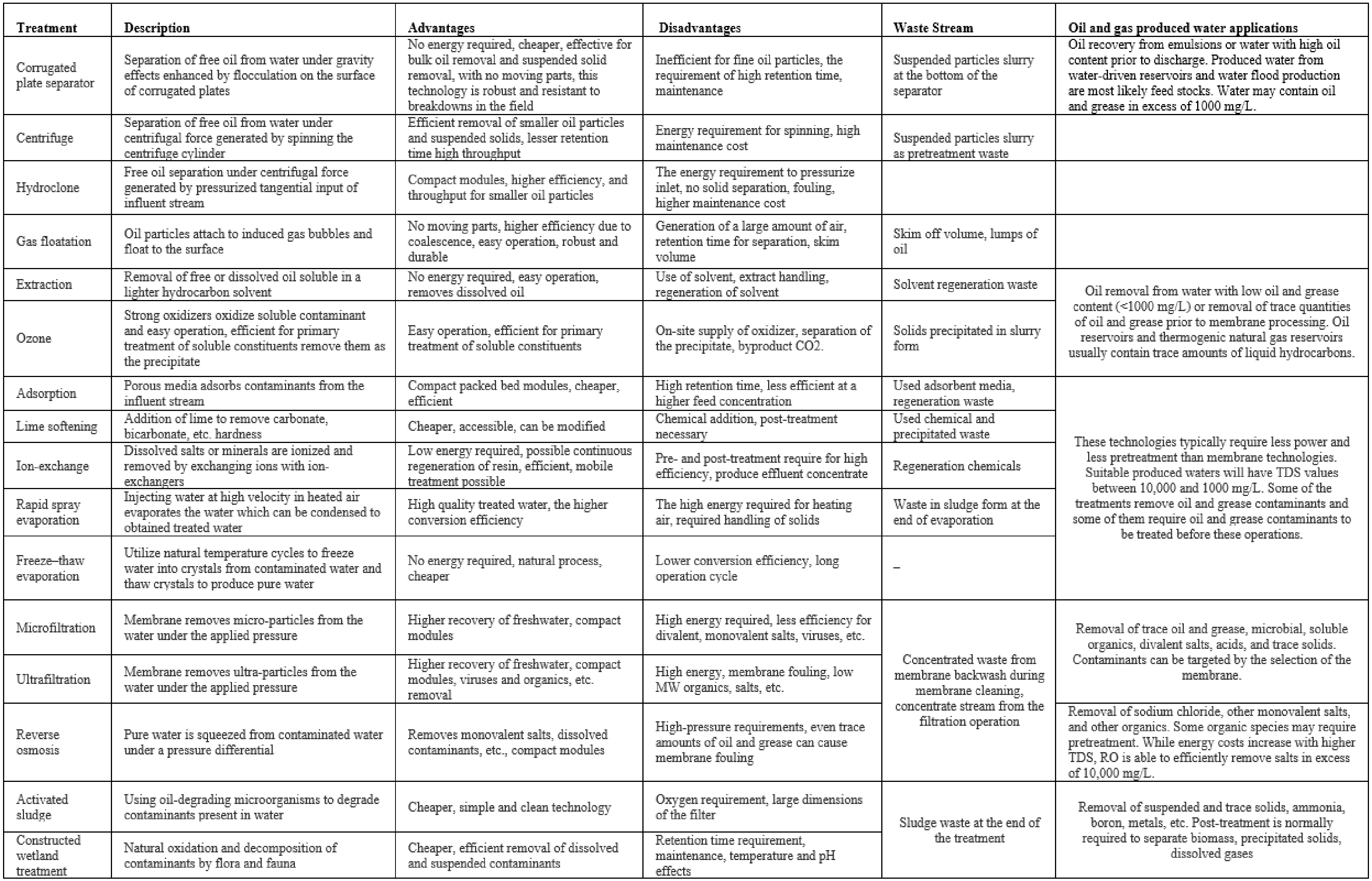
Produced water can be treated using various methods; most of the techniques have been tested in different oilfields. In general, existing produced water treatment methods follow the following steps (Arthur et al., 2005): i) De-oiling: Removal of residual free oil/grease, ii) Soluble organics removal, iii) Disinfection: removal of biological components, iv) Suspended solids (SS) removal, v) Dissolved gas removal, vi) Desalination vii) Softening: Removal of excess water hardness, and viii) NORM (Naturally occurring radioactive materials) removal. Companies dealing with produced water need to minimize pollution by treating, reusing, or disposing of this fluid if all other options are impossible. In either case, these operations introduce a cost that needs to be optimized.

Table 2.3 Treatment technology cost & efficiency (modified from Igunuu & Chen, 2012)

Water Treatment Technology	Overall Cost*	Removal Efficiencies
Ceramic Microfiltration/ Ultrafiltration membrane	N/A	90-100% water recovered
Polymeric Microfiltration/ Ultrafiltration membrane	Capital Costs + Operation: \$0.04-0.10/bpd†	85-100% water recovered
Nanofiltration	Capital Cost: \$35 to \$170/bpd + Operating cost: \$0.03/bbl.	75-90% water recovered
Reverse Osmosis	Capital cost: \$35 to \$295/bpd + Operating cost: \$0.03-0.08/bbl.	30-85% water recovered
Thermal (Multistage Flash, Multi-effect distillation)	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‡

The produced water treatment method must be selected depending on the application and the intended destination for the fluid. There are physical, chemical, and biological methods that are implemented according to the properties of compounds dissolved in produced water. Some requirements must be met during produced water treatment. The rules always aim to minimize soil and water contamination to avoid irreversible damage in the short, medium, and long term. A summary with the most relevant aspects of the most recently used methods, including advantages and disadvantages of various methods analyzed in previous studies is presented in **Table 2.4**.

Table 2.4 Summary of water treatment methods (Arthur et al., 2005)

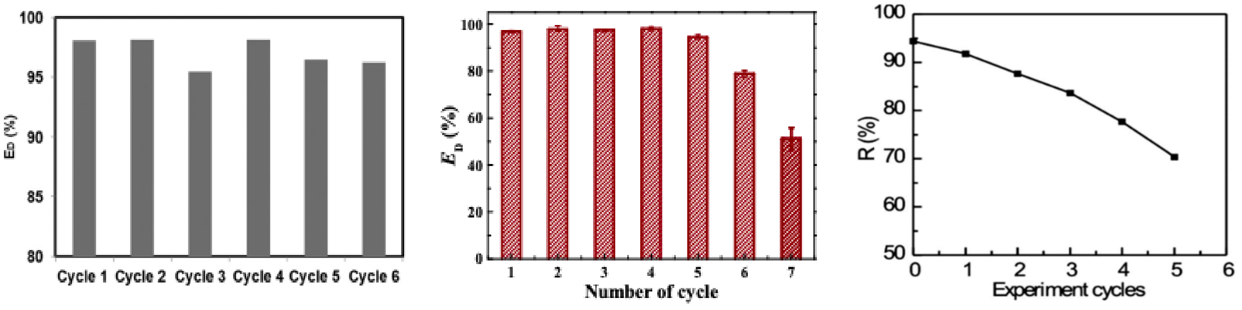


Treatment	Description	Advantages	Disadvantages	Waste Stream	Oil and gas produced water applications
Corrugated plate separator	Separation of free oil from water under gravity effects enhanced by flocculation on the surface of corrugated plates	No energy required, cheaper, effective for bulk oil removal and suspended solid removal, with no moving parts, this technology is robust and resistant to breakdowns in the field	Inefficient for fine oil particles, the requirement of high retention time, maintenance	Suspended particles slurry at the bottom of the separator	Oil recovery from emulsions or water with high oil content prior to discharge. Produced water from water-driven reservoirs and water flood production are most likely feed stocks. Water may contain oil and grease in excess of 1000 mg/L.
Centrifuge	Separation of free oil from water under centrifugal force generated by spinning the centrifuge cylinder	Efficient removal of smaller oil particles and suspended solids, lesser retention time high throughput	Energy requirement for spinning, high maintenance cost	Suspended particles slurry as pretreatment waste	
Hydroclone	Free oil separation under centrifugal force generated by pressurized tangential input of influent stream	Compact modules, higher efficiency, and throughput for smaller oil particles	The energy requirement to pressurize inlet, no solid separation, fouling, higher maintenance cost		
Gas floatation	Oil particles attach to induced gas bubbles and float to the surface	No moving parts, higher efficiency due to coalescence, easy operation, robust and durable	Generation of a large amount of air, retention time for separation, skim volume	Skim off volume, lumps of oil	
Extraction	Removal of free or dissolved oil soluble in a lighter hydrocarbon solvent	No energy required, easy operation, removes dissolved oil	Use of solvent, extract handling, regeneration of solvent	Solvent regeneration waste	Oil removal from water with low oil and grease content (<1000 mg/L) or removal of trace quantities of oil and grease prior to membrane processing. Oil reservoirs and thermogenic natural gas reservoirs usually contain trace amounts of liquid hydrocarbons.
Ozone	Strong oxidizers oxidize soluble contaminant and easy operation, efficient for primary treatment of soluble constituents remove them as the precipitate	Easy operation, efficient for primary treatment of soluble constituents	On-site supply of oxidizer, separation of the precipitate, byproduct CO2.	Solids precipitated in slurry form	
Adsorption	Porous media adsorbs contaminants from the influent stream	Compact packed bed modules, cheaper, efficient	High retention time, less efficient at a higher feed concentration	Used adsorbent media, regeneration waste	These technologies typically require less power and less pretreatment than membrane technologies. Suitable produced waters will have TDS values between 10,000 and 1000 mg/L. Some of the treatments remove oil and grease contaminants and some of them require oil and grease contaminants to be treated before these operations.
Lime softening	Addition of lime to remove carbonate, bicarbonate, etc. hardness	Cheaper, accessible, can be modified	Chemical addition, post-treatment necessary	Used chemical and precipitated waste	
Ion-exchange	Dissolved salts or minerals are ionized and removed by exchanging ions with ion-exchangers	Low energy required, possible continuous regeneration of resin, efficient, mobile treatment possible	Pre- and post-treatment require for high efficiency, produce effluent concentrate	Regeneration chemicals	
Rapid spray evaporation	Injecting water at high velocity in heated air evaporates the water which can be condensed to obtained treated water	High quality treated water, the higher conversion efficiency	The high energy required for heating air, required handling of solids	Waste in sludge form at the end of evaporation	
Freeze–thaw evaporation	Utilize natural temperature cycles to freeze water into crystals from contaminated water and thaw crystals to produce pure water	No energy required, natural process, cheaper	Lower conversion efficiency, long operation cycle	–	
Microfiltration	Membrane removes micro-particles from the water under the applied pressure	Higher recovery of freshwater, compact modules	High energy required, less efficiency for divalent, monovalent salts, viruses, etc.	Concentrated waste from membrane backwash during membrane cleaning, concentrate stream from the filtration operation	Removal of trace oil and grease, microbial, soluble organics, divalent salts, acids, and trace solids. Contaminants can be targeted by the selection of the membrane.
Ultrafiltration	Membrane removes ultra-particles from the water under the applied pressure	Higher recovery of freshwater, compact modules, viruses and organics, etc. removal	High energy, membrane fouling, low MW organics, salts, etc.		
Reverse osmosis	Pure water is squeezed from contaminated water under a pressure differential	Removes monovalent salts, dissolved contaminants, etc., compact modules	High-pressure requirements, even trace amounts of oil and grease can cause membrane fouling		Removal of sodium chloride, other monovalent salts, and other organics. Some organic species may require pretreatment. While energy costs increase with higher TDS, RO is able to efficiently remove salts in excess of 10,000 mg/L.
Activated sludge	Using oil-degrading microorganisms to degrade contaminants present in water	Cheaper, simple and clean technology	Oxygen requirement, large dimensions of the filter	Sludge waste at the end of the treatment	Removal of suspended and trace solids, ammonia, boron, metals, etc. Post-treatment is normally required to separate biomass, precipitated solids, dissolved gases
Constructed wetland treatment	Natural oxidation and decomposition of contaminants by flora and fauna	Cheaper, efficient removal of dissolved and suspended contaminants	Retention time requirement, maintenance, temperature and pH effects		

2.7 Oil Removal Using Nanoparticles

Recently, the use of magnetic nanoparticles (MNPs) in the treatment of produced water has generated great interest due to their large surface area per unit mass, surface properties, and potential recyclability (Ko et al., 2017; Lu et al., 2017, and Villa et al., 2016). Chemical demulsifiers (emulsion breakers) such as amines polyols and polyurethanes are commonly used in the oil field to destabilize oil-water emulsions and extract residual oil from produced water. Nevertheless, the use of these breakers still has some environmental and economic constraints. Furthermore, optimizing the dosage requirements of the chemical demulsifiers is very challenging. The use of low demulsifier concentration may not be effective in destabilizing produced water. On the other hand, high concentrations are not favorable because the excessive addition of demulsifiers may increase emulsion stability. In addition, chemical demulsifiers can be used only once; hence, recovering and recycling impose another restriction on their application in the oilfield. To overcome the recycling challenges and material waste, a new treatment technique has been developed (Ko et al., 2017) using inorganic nanoparticles coated with organic demulsifiers.

Recent studies (Liang et al., 2015; Ko et al., 2017) have shown encouraging results using coated superparamagnetic magnetite (Fe_3O_4) nanoparticles to separate oil from oil-in-water nano emulsions using a magnetic field. In addition to magnetite, other iron oxide nanoparticles such as maghemite (γ-Fe_2O_3) have also been used for removing oil layers when oil unintentionally contaminates a water source such as an oil spill (Chun et al., 2001). Maghemite and magnetite are both ferromagnetic materials, which have low toxicity and magnetic moments of 4.0 and 2.5 μB/f.u. (Bohr magnetons per formula unit), respectively (Villa et al., 2016; Gubin 2009). Among iron oxide nanoparticles, magnetite, maghemite, and hematite (α-Fe2O3) are the most widely used MNPs as adsorbents for heavy metal removal in produced water (Cao et al., 2016). Of the three common iron oxide nanoparticles, functionalized magnetite is the most considered for residual oil removal applications. Several experimental studies (Goh et al., 2019; Ko et al., 2017) have demonstrated the use of functionalized iron oxide nanoparticles for extracting residual oil from produced water at low concentrations. Comparatively, magnetite exhibits the highest saturation magnetization (Villa et al., 2016; Gubin 2009). Previous studies (Goh et al., 2019; Ko et al., 2017) have focused mainly on the magnetite nanoparticles for three major reasons including high saturation magnetization, ability to graft demulsifiers on the surface, and recyclability. Recycling of the MNPS is a relevant factor that makes the economic feasibility of this technology possible, in **Fig 2.3** can be observed the results (removal efficiency vs number of cycles) obtained from recycling experiments with coated magnetite in previous studies. Also, magnetite nanoparticles are biocompatible and are currently used in medical applications such as drug delivery. They provide a simple, efficient, and safe method for removing residual oil from produced water. The superparamagnetism and surface charge displayed by the nanoparticles allow fast and simple oil removal.



Magnetite MNPs coated with oleic acid

(Wang et al, 2018)

Magnetite MNPs coated with 5010 demulsifier

(Liang et al, 2015)

Magnetite MNPs coated with amine

(Li et al, 2014)

Figure 2.3. Magnetite recycling experiments results in different studies.

Chapter 3. Experimental Studies

In this chapter, all experimental procedures completed during the development of this thesis will be explained in detail.

3.1 Synthesis of Maghemite

During the experimental stage, different types of maghemite nanoparticles were manufactured. Among different chemical methods, the co-precipitation technique was chosen to produce maghemite because of its advantages over the rest of the methods. The benefit of co-precipitation includes simplicity in terms of equipment and process, low cost, high yield, and short production time. In this study, three different co-precipitation methods were utilized for producing maghemite nanoparticles. Each of the resulting batches of nanoparticles from the experiments was characterized to ensure that their properties were suitable for oil removal application.

3.1.1 High Yielding Method

The maghemite synthesis method presented in a previous study (Nazari, et. al., 2014) is simple and high yielding. The reagents for this method are shown in **Table 3.1**. The experimental setup consists of a 1000 mL jacketed reactor (**Fig. 3.1**) with a speed-controlled agitator, pH, and temperature meters, scale, heating, and cooling system, vacuum chamber, pump, and a permanent Neodymium magnet.

Table 3.1 Reagents for high yielding method

Reagent	Chemical Nomenclature	CAS No.	Purity
Iron (III) Chloride hexahydrate	$FeCl_3.6H_2O$	10025-77-1	99+%
Iron (II) Chloride tetrahydrate	$FeCl_2\cdot 4H_2O$	13478-10-9	99+%
Ammonium hydroxide	NH_4OH	1336-21-6	28-30%

Figure 3.1 Reactor setup for MNPs synthesis

To manufacture the nanoparticles, a thermometer and pH meter were first installed on the reactor to keep track of the process parameters. Warm water (27 °C) was circulated through the reactor jacket. Then, 125 mL of deionized water was transferred to the reactor while mechanical stirring at 400 rpm. Once the desired temperature was reached, 33.7 g of ferric chloride hexahydrate and 49.8 g of ferrous chloride tetrahydrate were added to the reactor to prepare a precursor solution (**Fig. 3.2**). The amount of reagent used in this procedure ensured a 2:1 molar ratio needed for the synthesis of maghemite. When the precursor solution was homogenized, 125 mL of 28% ammonium hydroxide solution was poured into the reactor. The reactive mixture was mixed for 40 minutes and a brown precipitate was obtained. For the duration of the reaction, the pH level was continuously monitored, and the final pH was approximately 9.8. The resulting solution was transferred into a beaker (**Fig. 3.3**) where the maghemite nanoparticles were collected by applying a magnetic field. The synthesized maghemite nanoparticles were washed with deionized water (three times) and ethanol (3 times). The samples were dried in an oven for 6 hours at 70°C. After drying, they were ground by a lab grinder (mortar and pestle). By using this method, 24.74 g of maghemite nanoparticles were produced. The obtained product was labeled as B001 and stored in plastic containers.

Figure 3.2 Chemical co-precipitation method schematic

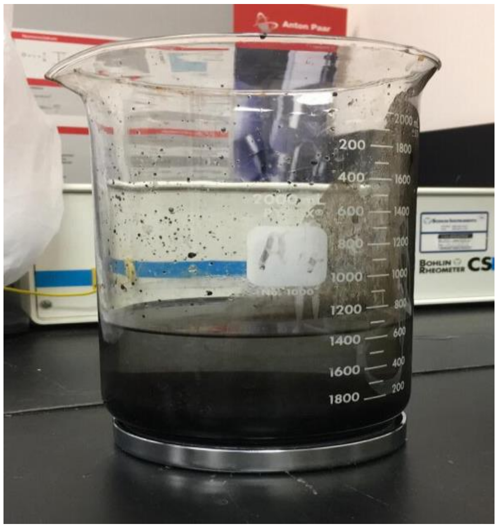


Figure 3.3 Produced maghemite nanoparticles in brine after synthesis

3.1.2 Low Yielding Method

In the method, the procedure presented by Wu and Gao (2012) was followed. The reagents utilized in this method are presented in **Table 3.2**. The equipment used in this method included: a 1000 mL jacketed reactor with a speed-controlled agitator, pH and temperature meters, scale, heating, and cooling system, vacuum chamber, metering pump, and a magnet.

Table 3.2. Reagents used in the low yielding method

Reagent	Chemical Nomenclature	CAS No.	Purity
Iron (III) Chloride hexahydrate	FeCl3.6H2O	10025-77-1	99+%
Iron (II) Chloride tetrahydrate	FeCl2·4H2O	13478-10-9	99+%
Ammonium hydroxide	NH4OH	1336-21-6	28-30%
Urea	CH4N2O	57-13-6	99%

The nano synthesis was carried out by dissolving 21.67 g of $FeCl_3 \cdot 6H_2O$, 7.95 g of $FeCl_2 \cdot 4H_2O$ (with a molar ratio of $FeCl_3 \cdot 6H_2O$ to $FeCl_2 \cdot 4H_2O$ to be 1:2), and 6.0 g of urea were completely dissolved in 400 mL of deionized (DI) water in a reactor which is open to the atmosphere. The reactor was placed in a water bath to control the temperature. It is equipped with a pH meter and temperature sensor. After this step, the solution was stirred and gently heated to the desired temperature (80°C) for one hour under reflux condition to decompose the urea. Then, 320 mL of 28% ammonium hydroxide solution was injected using a metering pump while mixing the solution. Brown precipitate appeared in the reactor once the ammonium hydroxide injection was started. The injection was continued until complete precipitation of maghemite, which was indicated by the solution pH reaching 10.02. The reaction was allowed to continue for additional 30 minutes. Then, the reactor was cooled down using a cooling water bath (27°C) and the brown solution was collected in a beaker for further separation and washing. MNPs were separated by using a magnet. The beaker was placed on top of the magnet to collect the MNPs and decant the floating liquid.

The precipitate was washed five times with DI water to make sure all the reaction residues were removed. Subsequently, these MNPs were put in a vacuum chamber for about an hour to evaporate part of the remaining water. Finally, MNPs were heated in an oven at 70°C for about six hours. The dry product was ground using a simple mortar until reduced to powder and labeled as B002. The amount of product obtained by using this method was 7.75 g of maghemite nanoparticles.

3.1.3 Medium Yielding Method

This method was implemented following the procedure presented by Nurdin et al. (2014). The reagents utilized in this method are presented in **Table 3.3**. The equipment used in this method included: a 1000 mL jacketed reactor with a speed-controlled agitator, pH meter and temperature sensor, scale, heating and cooling system, vacuum chamber, metering pump, and a magnet.

Table 3.3 Reagents used in the medium yielding method

Reagent	Chemical Nomenclature	CAS No.	Purity
Iron (III) Chloride hexahydrate	FeCl3.6H2O	10025-77-1	99+%
Iron (II) Chloride tetrahydrate	FeCl2·4H2O	13478-10-9	99+%
Ammonium hydroxide	NH4OH	1336-21-6	28-30%
Nitric Acid	CH4N2O	57-13-6	99%

Synthesize the nanoparticles, 67.5 g of $FeCl_3 \cdot 6H_2O$ and 24.85 g of $FeCl_2 \cdot 4H_2O$ (with molar ratio 2:1) were mixed with 125 mL of DI water in a reactor placed in a water bath maintained at 27°C. After this solution was well mixed using a mechanical stirrer, 125 mL of 28% NH_4OH solution was added to the reactor rapidly under vigorous stirring. This process was held for 20 minutes. The brown precipitate was formed after 20 minutes and the suspension was placed in a beaker to separate the MNPs from the remaining liquid. To recover the nanoparticles, MNPs were collected at the bottom of the beaker by placing the beaker on top of a magnet and the liquid was decanted. The MNPs were washed thoroughly 4 times with DI water.

Recovered nanoparticles were put in 20 ml of 2M nitric acid solution while stirring. The solution was stirred for 10 minutes, then the MNPs were collected and washed with DI water four times. To ensure complete oxidation, MNPs were mixed with a 0.25M ferric nitrate solution for 30 minutes. Finally, these MNPs were placed in a vacuum chamber for about an hour to evaporate part of the remaining water. Finally, the MNPs were dried by placing them in an oven at 70°C for about 6 hours. The dried MNPs were ground using a simple mortar until reduced to powder and labeled as B003. The total amount of maghemite nanoparticles powder produced with this method was 12.48 g.

3.2 Characterization of Nanoparticles

Characterization of nanoparticles was performed by applying different methods. Particle size, FTIR mineralogy, surface charge, and saturation magnetization were measured to have a better understanding of the behavior of the synthesized maghemite nanoparticles.

3.2.1 Dynamic Light Scattering

Dynamic light scattering (DLS) is often performed to measure the hydrodynamic size of the particles, this is one of the most popular techniques because it allows particle determination down to 1 nm. A laser beam illuminates (**Fig. 3.4)** a solution that contains macromolecules and the changes of the scattered light are detected at a known angle by a photon detector. This technique measures mainly the Brownian motion of macromolecules in the solution sample, as a result, the diffusion coefficient that is related to the hydrodynamic size can be obtained. If this technique uses simple DLS instruments that are measured at a fixed angle, particle size can be determined; however, if it is used with a multi-angle device, it can determine a complete size distribution (Stetefeld. et al., 2016).

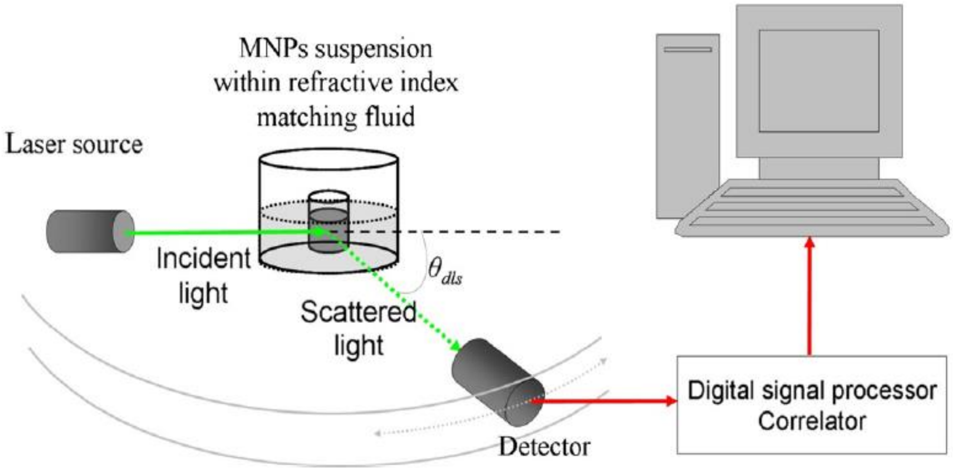


Figure 3.4 Typical experimental setup for DLS measurement (Lim et al., 2013)

In this study, a DLS particle sizer with an auto-titrator (Brookhaven NanoBrook Omni 90Plus Zeta Potential Analyzer) that uses phase analysis light scattering (PALS) was utilized to measure the hydrodynamic size of the MNPs obtained after co-precipitation. During the measurement, each sample of nanoparticles was dispersed in Millipore water and was sonicated for 15 minutes or until the sample reached dispersion with no visible particle settling. The measurements were repeated five times (Theurer et al., 2020).

3.2.2 FTIR Analysis – Fourier Transform Infrared

FTRI is the most common method of infrared spectroscopy. Analysis of infrared spectra can show the type of molecular bonds present in a sample and subsequently, the concentration of the compounds associated with the detected bonds. In FTIR analysis, infrared light is applied through a sample; part of this energy is absorbed by the sample, the rest of the radiation continues to pass through. The molecular absorption and transmission of the IR energy will be displayed on the obtained spectra, an infrared spectrum is created by different molecules that do not produce the same IR pattern (Faix, 1992). FTIR is performed using a spectrometer in which the sample is placed, and the spectra are recorded. FTIR was used to characterize the composition of the synthesized maghemite nanoparticles (Smith, 2011). This technique was performed using a NICOLET 6700 FTIR instrument.

3.2.3 Saturation Magnetization

Defined as the maximum of the magnetization value achieved in a sufficiently large magnetic field, Saturation Magnetization is one of the most significant properties of magnetic nanoparticles. This property is a function of temperature. The values of magnetization in nanoparticles are usually lower than the ones measured in bulk material at a determined temperature. (Lu et al., 2007). The property of the MNPs is directly related to their characteristics when a magnetic field is applied to recover them after being dispersed. The higher the value of saturation magnetization the easier to recover the MNPs when a magnetic field is applied. To measure saturation magnetization the MNPs were sent to a commercial laboratory where a KOERZIMAT MS instrument was used. In addition to saturation magnetization, the magnetic characteristics of the nanoparticles were directly measured with a force gauge. This was performed to develop a relationship between saturation magnetization and direct force measurement in the laboratory for a quick magnetization assessment after synthesizing MNPs.

3.3 Oil Removal Experiments

To calculate oil removal efficiencies and find ways to recycle maghemite nanoparticles, laboratory demulsification experiments were performed. For each test, a given set of materials, test parameters, and techniques were utilized to ensure repeatability of the experiments and determine the effect of different parameters on the removal efficiency. The focus is to optimize reagents and the conditions required for synthesizing maghemite nanoparticles to maximize oil removal efficiencies and maintain the characteristics of MNPs after several cycles of use. At the same time, this study is aimed at ensuring other critical factors such as economic feasibility and short separation times. In this section, materials, equipment, procedures, and data collection techniques used during the investigation are described in detail.

3.3.1 Materials

The materials used to fulfill the purpose of this study are listed below.

- In-house produced maghemite nanoparticles. Three different types of maghemite nanoparticles were synthesized via chemical co-precipitation.
- Commercial maghemite nanoparticles (Iron III oxide nanopowder, < 50 nm particle size) were purchased from Sigma-Aldrich.

- Deionized (DI) water with 0.23 MΩ resistivity was obtained from LabChem.
- Sodium chloride (NaCl, ≥ 99.0 %) was purchased from Fisher Bioreagents
- Produced water was collected from a well in Oklahoma (PW-OK) with residual oil of 80-95 ppm (measured in the lab). This water was orange in color and contained visible solids suspended.
- Produced water was collected from a well in Argentina (PW-ARG). Oil concentration between 20-40 ppm was measured from this sample. Unlike the other samples, this one presented a transparent color (it was assumed that this sample was pretreated before it was sent).
- Produced water was obtained from a well located in Macalester Oklahoma (PW-OKF), with a measured residual oil content of 70-85 ppm. This sample was clear gray and contained visible suspended solids.
- Ethanol (Histoprep, 100% alcohol) was used for solvent washing.

3.3.2 Equipment

Oil Content Analyzer

The oil concentration of produced water before and after treatment is the most relevant variable to evaluate the removal efficiency of MNPs. The instrument (**Fig. 3.5**) used for measuring the oil concentration was an oil content analyzer (Horiba OCMA-550). This instrument uses a solvent extraction technique with non-dispersive infrared absorption analysis. The measurements were made by injecting the extracted water sample into the attached cell and placing it on the equipment. This instrument was selected due to its simplicity to obtain the necessary measurements without additional testing. Non-dispersive infrared absorption analysis is frequently used to measure a single component of a sample. The detector cell is equipped with the required analytic. Infrared radiation passes through the cell to determine the fraction of incident radiation that is absorbed at a given energy level or wavelength (Stuart, 2004).

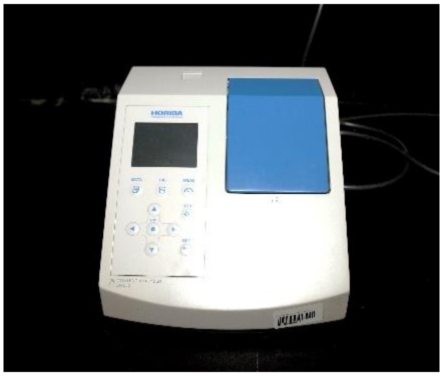


Figure 3.5 Oil content analyzer Horiba OCMA 550

Hydrocarbons have an absorption band in the vicinity of wavelengths 3.4 to 3.5 mm (2941 cm^{-1} to 2857 cm^{-1}) based on the activity of organic chemical groups such as methylene ($-CH_2$) and methyl ($-CH_3$) that are particular to hydrocarbons. This is how the oil content analyzer achieves accurate results when measuring oil concentration in produced water samples. In addition to the accuracy, this instrument complies with the ASTM D7066-04 standard method which covers the determination of oil, grease, and nonpolar material in the water, also uses as a reference the wavelength corresponding to the CH_2 stretch vibration frequency, about 2930 cm^{-1} (Yang 2011). The solvent used in the oil content analyzer is called S-316. The compounds present in the solvent S-316 are polychlorotrifluoroethylene (65-75%) and chlorotrifluoroethylene (25-35%). This solvent presents optimal characteristics for oil removal applications such as:

- Applicability for measuring a wide range of temperature due to the boiling point of 134°C and the melting point of -143°C.
- Chemical stability in acid, alkali, oil, and water
- Low volatility, low vapor pressure.

- Non-flammable and low toxicity for the human body

Properties of S-316 are presented in **Table 3.4**. Separation of oil dispersed in produced water is achieved by creating a water-solvent solution in a 1:1 ratio, this mixture was agitated for at least 30 seconds. The success of the measurement will be determined by the layer separation after this step. 6.5 ml of the solvent layer should be removed with a syringe and poured into the measurement cell.

Table 3.4 Properties of solvent Horiba S-316

Properties of S-316	
Chemical Formula	$Cl(CF_2\text{-}CFCl)_2Cl$
Molecular weight	304
Boiling point	134 °C
Melting point	-143 °C
Density	1.75 g/mL (25°C)
Vapor pressure	0.0015 MPa (25°C)
Saturated solubility in water	0.0048 g/100 g (25°C)
Acute oral toxicity (LD50)	52.5 g/kg

Zero and span calibration must be performed daily when using the oil content analyzer because as the surrounding environmental conditions change, the results can be affected. For zero calibration, 6.5 mL of clean S-316 solvent is required. For span calibration, a solution of solvent with known B-heavy oil (**Fig. 3.6**) concentration must be used. This oil comes with the instrument. Accurate measurements are achieved in less than 3 minutes.

Recycling of solvent S-316 is possible if solvent reclaimer is used. The reclaimer uses a 2-layer column of activated carbon and aluminum. It minimizes costs and facilitates residual oil handling of the entire procedure.

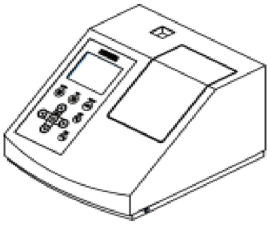
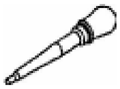
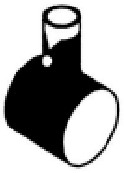
Main Unit OCMA 550	Dropper	B-heavy oil	Measurement Cell	Cell cap
				

Figure 3.6 Oil content analyzer Horiba OCMA 550 with its accessories

Sonifier

The sonifier used during the experimental stage was Branson SFX550 (**Fig. 3.7**). This device was utilized to disperse uniformly maghemite nanoparticles in sodium chloride brine. The sonifier produces a sonic wave at 20 kHz or 40 kHz. The wave creates an intense agitation in the working sample. The wave is transmitted through a disrupting horn that is attached to the instrument. The sonifier can be set up to provide energy in continuous mode or as pulses. It is also possible to control time, temperature, the mixing energy, and process samples from 0.2 to 1000 mL.

Figure 3.7 Sonifier Branson SFX550

During the experiment, different maghemite samples were sonicated to create nanosuspensions. The nanosuspensions were mixed for 3 minutes using the continuous mode and a preset amplitude of 20%. Homogeneous dispersions of maghemite nanoparticles in brine were prepared using the parameters mentioned previously.

Vortex Shaker

A Benchmark Scientific BV1000 vortex mixer (**Fig. 3.8**) was utilized to homogenize samples during the demulsification of produced water by nanosuspension. Also, it was used to mix produced water with a solvent when performing measurements with the oil content analyzer. In each one of these procedures, 10 mL glass vials with lid were used, 30 seconds was the optimal mixing time for the samples. The instrument can be operated by touch or in continuous mode varying the speed from 200 to 3,200 rpm for a tube with volume up to 50 mL. The instrument provided strong agitation and reduced mixing time of the samples.

Figure 3.8 Vortex Mixer Benchmark Scientific BV1000

3.3.3 Oil Removal Procedure

Produced water samples (**Fig. 3.9**) with different oil concentrations (0-90 ppm) were used in this study. At the start, the oil contents of the produced water samples were measured. The concentrations were measured following these steps:

Step 1: 10 mL of produced water and 10 mL of S-316 solvent were transferred with a syringe to a glass vial with a lid.

Step 2: The vial was placed on the vortex mixer for 30 seconds.

Step 3: The vial was put on a flat surface until the separation of the phases.

Step 4: When the separation was completed, 6.5 mL of heavy phase (solvent) was taken from the vial to the measuring cell.

Step 5: The measurement cell was set in the oil content analyzer.

Step 6: Concentration was read.

Residual oil concentrations were taken as initial concentration and recorded for future calculations.

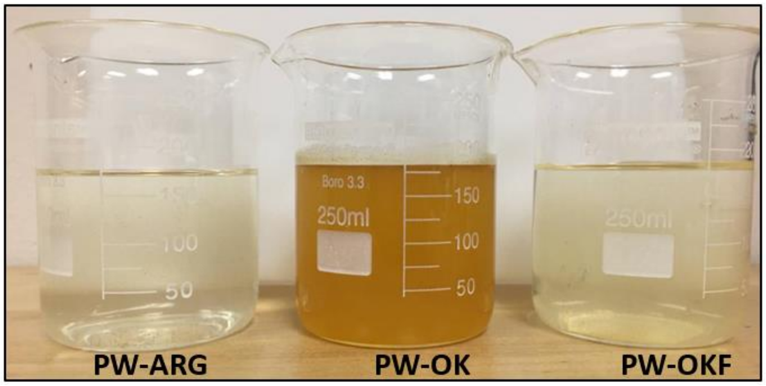


Figure 3.9 Produced water samples

Brine solution was made by mixing DI water and analytical grade sodium chloride purchased from Sigma Aldrich. The purpose of the brine was to disperse maghemite nanoparticles and form nanosuspension (**Fig. 3.10**). The chosen brine concentration was 3%. This concentration has been found (Wang et al., 2018; Theurer et al., 2020) to be favorable for the demulsification of produced water. To prepare nanosuspension, brine and maghemite nanoparticle powder were mixed and sonicated in a beaker at 20% amplitude for 2 minutes, 5 mg/mL was the chosen concentration for the nanosuspension. Multiple tests were conducted varying the concentration of nanoparticles. To establish the minimum required MNP concentration for water treatment, concentrations as low as 2.5 mg/mL were used. However, the reduction in concentration increased the time necessary to achieve the desired efficiency. Once the components were homogenized, the nanosuspension (10 mL) was mixed with produced water (10 mL) in a 1 to 1 ratio. A vertex mixer was used to mix the nanosuspension with produced water and achieve quick demulsification.

Figure 3.10 Maghemite nanosuspension

After demulsification, the sample was subjected to an external magnetic field by placing the sample on a small magnet. The goal of this step is to collect the nanoparticles covered with oil by taking advantage of their superparamagnetic properties. The water treatment with nanoparticles was collected and its residual oil content was measured following the steps described previously. The nanoparticles saturated with oil were recovered and collected in a different beaker to be washed with ethanol and reused in different cycles. The oil removal efficiency ($\eta_{removal}$) is calculated from the initial (C_i) and treated C_{pw}) produced water residual oil concentrations as:

$$\eta_{removal} = \frac{C_i - C_{pw}}{C_i} \, x \, 100 \qquad (3.1)$$

3.3.4 Validation

To validate the results of the present study, it was necessary to ensure the repeatability and accuracy of the experiments performed in the laboratory. To this end, the oil removal experiments were repeated in approximately 6 months in which enough information was collected to obtain the fundamental statistical parameters. Two different types of maghemite nanoparticles were used in 3 different types of produced water. In **Table 3.5**, the removal efficiencies of different produced water samples obtained from repeated experiments are presented. To compare the performance of the iron oxide nanoparticles synthesized in the laboratory and those of commercial maghemite, basic statistical parameters (mean, standard deviation) were calculated for the removal efficiency (**Table 3.6**).

Table 3.5 Removal efficiencies in different samples using maghemite

	In-house maghemite			Commercial Maghemite		
	C_i [mg/mL]	**C_f [mg/mL]**	**$\eta_{removal}$ [%]**	**C_i [mg/mL]**	**C_f [mg/mL]**	**$\eta_{removal}$ [%]**
PW-OKF	70.3	2.8	96.02	70.3	1.1	98.44
	70.3	1.5	97.87	70.3	0.9	98.72
	70.3	1.4	98.01	70.3	0.7	99.00
	70.3	2.1	97.01	70.3	1.5	97.87
	70.3	0.6	99.15	70.3	0	99.99
	70.3	0.8	98.86	70.3	0.6	99.15
PW-ARG	45.5	1.2	97.36	45.5	0.4	99.12
	45.5	0.5	98.90	45.5	0	99.99
	45.5	0	100.00	45.5	0.6	98.68
	45.5	0	100.00	45.5	0.7	98.46
	45.5	0	100.00	45.5	0.6	98.68
	45.5	0.7	98.46	45.5	0	99.99
PW-OK	82	0.2	99.76	82	1.2	98.54
	82	0	100.00	82	0.9	98.90
	82	0	100.00	82	1.1	98.66
	82	0.8	99.02	82	0.9	98.90
	82	2.2	97.32	82	0.6	99.27
	82	1.8	97.80	82	1	98.78

Table 3.6 Basic statistic parameter for oil removal efficiency

	Synthesized maghemite		Commercial maghemite	
	Mean Removal Efficiency	**Standard Deviation**	**Mean Removal Efficiency**	**Standard Deviation**
PW-OKF	97.81	1.16	98.86	0.72
PW-ARG	99.12	1.09	99.16	0.69
PW-OK	98.98	1.17	98.84	0.25

3.4 Nanoparticle Recycling Test

The recyclability of the nanoparticles was one of the most relevant factors during the development of this study due to the need to optimize the process in economic terms. As it is shown in this study, there are different ways to reduce the amount of emulsified oil in the produced water, but most of them are expensive or use materials or equipment that can only serve their purpose once. It is where the reuse of iron oxide nanoparticles becomes relevant, firstly because it maximizes economic profitability and secondly because it reduces the number of by-products or residues that can cause damage to the environment. The materials used in repeated treatment experiments include maghemite nanoparticles recovered from previous treatment, DI water, and analytical grade ethanol. The equipment needed for the recycling includes a vortex mixer, sonicator, magnet, and oil content analyzer.

3.4.1 MNP Recycling Procedure

The maghemite nanoparticles recycling process (**Fig. 3.11**) is described as follows:

i. After separating the nanoparticles by collecting them at the bottom of the vial using a magnet, the treated water was decanted from the vial.
ii. The remaining nanoparticles that are covered with oil were washed with ethanol three times (the content of the vial was set in the vortex mixer for 30 seconds) and the MNPs were

collected with the magnet every washing step. This step was performed to ensure the complete removal of the residual oil from the nanoparticles.

iii. Then, MNPs were washed three more times using brine (1180 ppm NaCl) to remove ethanol from their surface.

iv. 10 ml of 1180 ppm NaCl brine was poured into the vial and sonicated for 2 minutes at 20% amplitude to prepare nanosuspension needed to restart the next treatment cycle.

Following this procedure, nanoparticles were recycled up to 12 times without losing their effectiveness in demulsifying water samples.

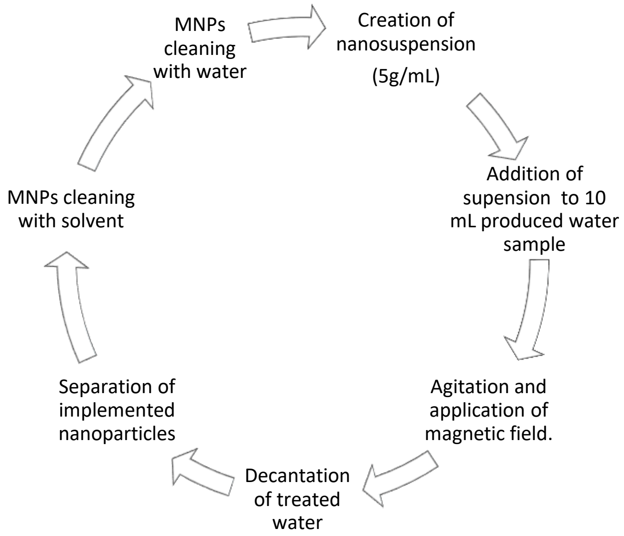


Figure 3.11 Nanoparticle Recovery procedure

Chapter 4. Results and Discussion

The main intent of this study is to find an optimal method for synthesis on MNPs and analyze the performance of maghemite nanoparticles to remove the hydrocarbons present in produced water. For this purpose, the oil concentration of treated water must comply with the discharge limits (maximum 42 ppm daily and 29 ppm monthly average) established for disposal. The use of maghemite nanoparticles as a new water treatment method is beneficial when compared with the methods (membranes filtration, gas flotation, use of emulsifiers, and others) currently utilized involve either high cost, long retention time, and product that can be harmful to the environment. On the other hand, maghemite NPs can achieve oil removal efficiencies higher than 98%, offering at the same time an alternative mitigation method for the issues mentioned previously.

4.1 Nanoparticle Synthesis

The synthesis of MNPs is one of the major challenges for the implementation of the technology presented in this study because the characteristics of MNPs that are critical for their performance depend on the manufacturing method. Within all existing synthesis techniques, different parameters need to be adjusted to synthesize MNPs with suitable characteristics such as particle size, and surface and magnetic properties. The chemical co-precipitation methods explained in Chapter 3 used iron chloride hydrates as main precursors, which have been widely studied for the synthesis of iron oxide nanoparticles. The dissolution of the different iron salts, in the presence of oxygen (to ensure the production of maghemite), resulted in a brownish precipitate (**Fig. 4.1**).

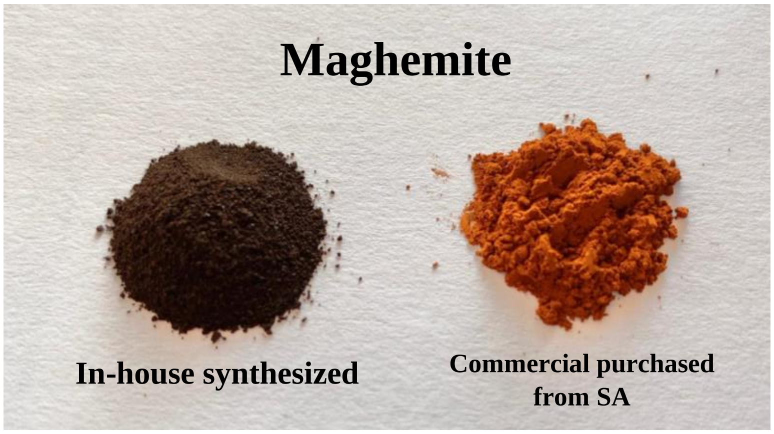


Figure 4.1 Maghemite nanoparticles used for produced water treatment

After synthesis, each nanoparticle manufacturing method is evaluated based on their ease of production, characteristics, and ability to remove oil from produced water. The batch labeled as B001 was chosen for its oil removal efficiency as shown in the study conducted by Theurer et al. (2020) and for the simplicity of its synthesis as compared to the other methods as described in Chapter 3. The high-yielding synthesis method is simple and allows good control of process parameters. When this synthesis method was used, the final pH obtained was 9.8; therefore, no additional reagent was needed to adjust it. Maghemite production is favored when the pH shows a value between 9 and 11. Also, this method requires the least amount of manufacturing time and produces the largest amount of magnetic nanoparticles per reactor volume (**Table 4.1**).

Table 4.1 Synthesis methods of maghemite nanoparticles (Theurer et al., 2020)

Co-precipitation Method	Batch No.	Production Time (min)	Yield per reactor volume (g/L)
Nazari et al. 2014	B001	40	82.4
Wu and Gao 2012	B002	150	10.76
Nurdin et al.2014	B003	65	41.6

4.2 Nanoparticle Characteristics

In addition to higher removal efficiencies shown by B001, characterization was performed to assess its properties and have a better understanding of the mechanism of oil removal. After the synthesis of nanoparticles, various characterization techniques were applied to determine relevant properties such as particle size, mineralogy, magnetic saturation, and surface charge of the particles.

4.2.1 Particle Size Measurement

Dynamics Light Scattering (DLS) technique was implemented to measure the hydrodynamic size of the maghemite nanoparticles. The instrument used for these measurements was the Brookhaven NanoBrook Omni 90Plus Zeta Potential Analyzer shown in **Figure 4.2**.

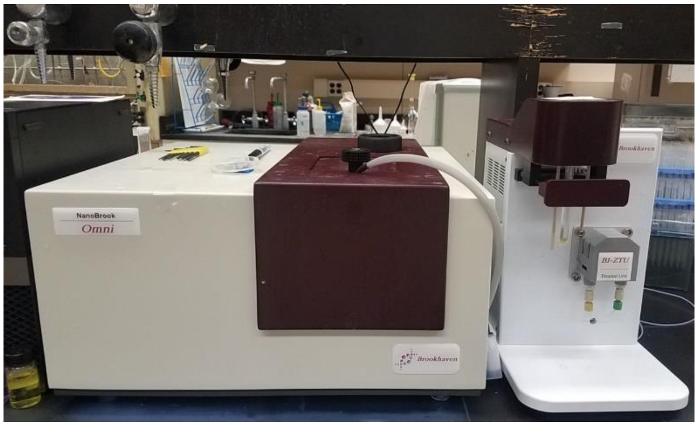


Figure 4.2 Nanobrook DLS Equipment

Each measurement was repeated 5 times to ensure the accuracy of the data. The average of the measurements was taken as the main hydrodynamic diameter of nanoparticles. The hydrodynamic diameters reported in **Table 4.2** were found to be close to the diameters reported in previous studies (Nurdin et al., 2014; Wang et al., 2018; Li et al., 2014; Ko et al., 2017) that used the same synthesis method of maghemite. The batch of nanoparticles chosen for this study is B001.

Hence, all experiments were performed with nanoparticles having a hydrodynamic diameter of 112.10 nm.

Table 4.2 Hydrodynamic diameter of maghemite NP samples

Nanoparticle type	Batch No.	Hydrodynamic diameter (nm)	Standard deviation	Standard Error
Commercial γ-Fe_2O_3	B000	241.89	57.31	25.63
Synthesized γ-Fe2O3	B001	112.10	41.01	112.1
	B002	221.00	26.1	26.10
	B003	33.22	24.31	7.69

4.2.2 FTIR Analysis

To assess the mineralogical composition of maghemite nanoparticles, a Fourier transform infrared spectroscopy (FTIR) analysis was performed. The instrument used for this purpose was NICOLET 6700 FTIR. The FTIR spectra obtained after the characterization of maghemite samples (B001, B002, B003) shown in **Fig. 4.3**. The absorption bands observed around 3340, 1604, 1388, and 588 cm^{-1} are consistent with the spectra presented in a previous study (Wu and Gao 2012). The observed bands can be attributed to O-H bond stretching at 3340 cm^{-1} and the most characteristic interaction, Fe-O bond at 588 cm^{-1} (Mishra et al., 2013; Sohrabijam et al., 2015).

The results of FTIR analysis for the low wavenumber range (200 to 800 cm^{-1}) are presented in **Fig. 4.4** to analyze the characteristic peaks that could not be seen in the FTIR spectra presented for the wide wavenumber range. In Fig. 4.4, several peaks (444, 588, 640, and 692 cm^{-1}) can be observed between 400 to 692 cm^{-1}. The spectrum for both samples (B000 and B001) show similar characteristic peaks of lattice absorption bands at the same wavenumber. These peaks are typical for iron oxide crystal structures (Tartaj et al., 2003). γ-Fe_2O_3 form of iron oxide presents a crystalline structure confirms that the powder synthesized in the laboratory was maghemite with an acceptable level of purity. According to the results of the FTIR analysis, it can be inferred that the procedure chosen for the synthesis is a suitable technique for producing technical grade maghemite.

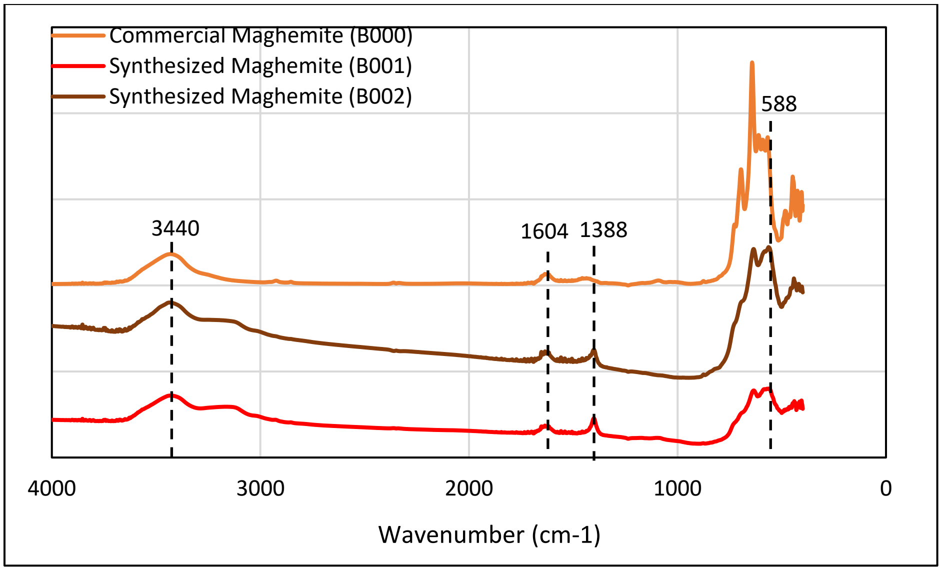


Figure 4.3 FTIR spectra for maghemite nanoparticles samples (Theurer et al., 2020)

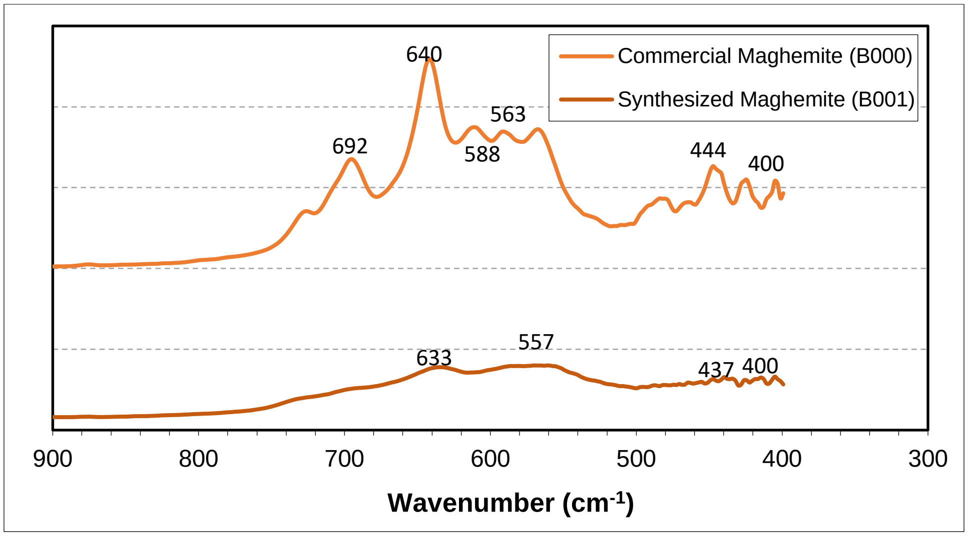


Figure 4.4 FTIR spectra for different maghemite nanoparticles at low wavenumber (Theurer et al., 2020)

4.2.3 Magnetic Force

Saturation magnetization is an indicator of the recycling capability of the MNPs when there is a magnetic field to collect the particles. For removing the oil and the recovery of nanoparticles, magnetization is a very important characteristic. The higher the saturation magnetization of nanoparticles, the easier to collect them from treated water. After confirming the production of maghemite with the selected method, it was imperative to test their magnetic properties. The magnetic force applied to the nanoparticles was measured using a digital force gauge (**Fig. 4.5**). To achieve this, a specific amount of maghemite powder was placed on the force gauge and a magnet was placed under a sample holder. The distance between the magnet to sample and the holder was 6.4 mm.

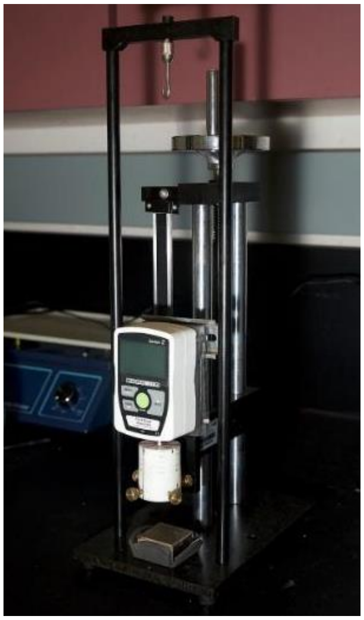


Figure 4.5 Digital force gauge

Samples of the three batches of synthesized nanoparticles as well as the commercial one were sent to a commercial laboratory where saturation magnetization was measured using a KOERZIMAT MS instrument. The measurements of magnetic force and saturation magnetization for the samples are presented in **Table 4.3**.

Table 4.3 Magnetic properties for magnetite and maghemite nanoparticles

Iron oxide MNPs	Batch No.	Magnetic Portion (%)	Measured SM (Gauss*cm^3/g)	Magnetic Force (N/g)	Predicted SM (Gauss*cm^3/g)
Maghemite (γ-Fe_2O_3)	B001	26.90%	43.03	0.59	45.66
	B002	36.63%	58.59	0.80	61.68
	B003	24.97%	39.95	0.54	41.65
	Commercial NPs	-	-	0.63	48.06

The magnetic force measurements obtained in the lab were correlated to the data provided by the commercial laboratory **(Fig. 4.6)**, showing a correlation coefficient of 0.9. The goal was to develop a simple and quick method that allows us to get saturation magnetization of produced maghemite in future experiments. Data collected throughout this research for saturation magnetization was consistent with the results reported by Kucheryavy et al. (2013).

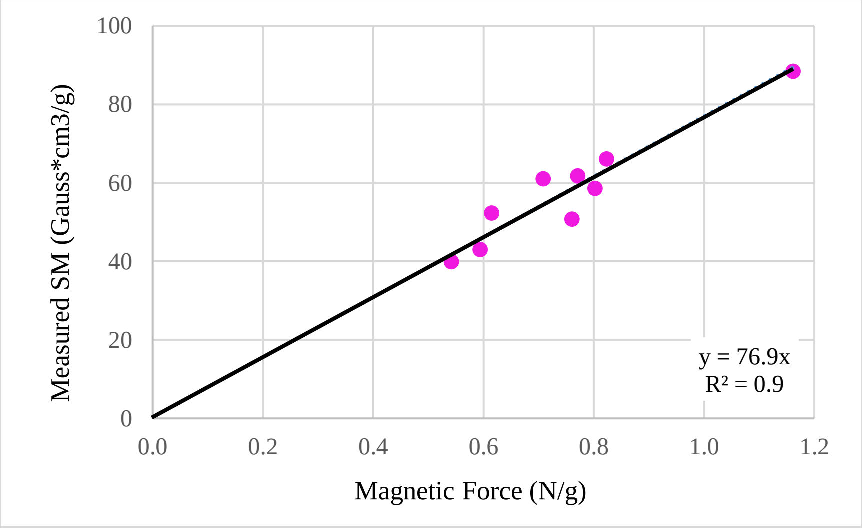


Figure 4.6 Measured magnetic force versus measured saturation magnetization

4.2.4 Zeta Potential

Dynamic light scattering was used to measure the zeta potential of the maghemite samples maintaining a solution pH of 5 during the measurements (Table 4.4). The measurements agree with those reported by other studies (Nurdin et al., 2012; 2014; Nurdin and Satriananda, 2016).

This feature ensures the attachment of the residual oil to the surface of nanoparticles. It indicates the oil removal efficiency of nanoparticles (Table 4.4).

Table 4.4 Zeta potential measurement of maghemite samples

Nanoparticle type	Batch No.	Zeta potential (mV)	Standard deviation (mV)
Commercial γ-F_2O_3	B000	-21.50	0.79
Synthesized γ-F_2O_3	B001	22.10	0.52
	B002	-3.87	0.62
	B003	30.91	0.22

4.3 Oil Removal Efficiency

The oil removal efficiency is the most important parameter measured in this research. The results obtained show that the use of maghemite nanoparticles has a great potential to be used in the treatment of produced water, with an efficiency of more than 97%. The technique presented in this thesis shows the ability of maghemite nanoparticles to reduce the content of emulsified and dissolved oil in produced water below the established standards for disposal. To ensure the correct functionality of this procedure, different factors were analyzed, including the characteristics of the synthesized nanoparticles, the nanoparticles-residual oil attraction mechanism, and the magnetic properties that allow their separation and reuse. Some of the advantages of using nanoparticles include the short retention time necessary for cleaning the water and the reduction in the production of secondary waste that pollutes the environment.

To analyze the functionality of maghemite nanoparticles, it is necessary to start with the characterization of the produced water samples used in this study. The three water samples obtained from various oilfields have different appearance and color (**Fig. 4.7**). These samples are identified as PW-OK, PW-ARG, and PW-OKF. The oil contents of the samples were measured using an oil content analyzer, which was previously subjected to a zero and span calibration to ensure the accuracy of the measurements.

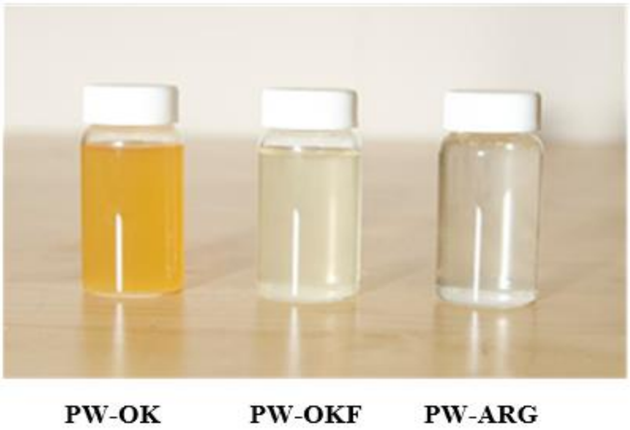


Figure 4.7 Produced water samples used in the investigation

The properties of the samples (**Table 4.5**) such as conductivity, total dissolved solids, salinity, and resistivity were measured with a handheld conductivity, resistivity, TDS, and salinity meter (Apera Instrument EC400S). The PW-OK and PW-ARG master data were taken from the study conducted by Theurer, 2019. The oil content of each sample is also included, and it is used in the calculation of oil removal efficiency.

Table 4.5 Properties of produced water samples

Water sample	Oil Concentration [mg/L]	Conductivity [mS/cm]	TDS [mg/L]	Salinity [ppm]	Resistivity [Ohm]
PW-OKF	70.3	140.8	83,000	76,000	9.8
PW-ARG	45.5	55	39,000	27,500	18
PW-OK	82	179.7	100,000	89,800	5.6

Following previous studies, the concentration of chosen nanoparticles to carry out the experiments was 5 mg /mL. The nanoparticles were suspended in a sodium chloride brine with a concentration of 1180 ppm. This level of salinity is optimal (Theurer, 2019) for the dispersion and suspension of nanoparticles. An overview of the test procedure is shown in **Fig. 4.8**.

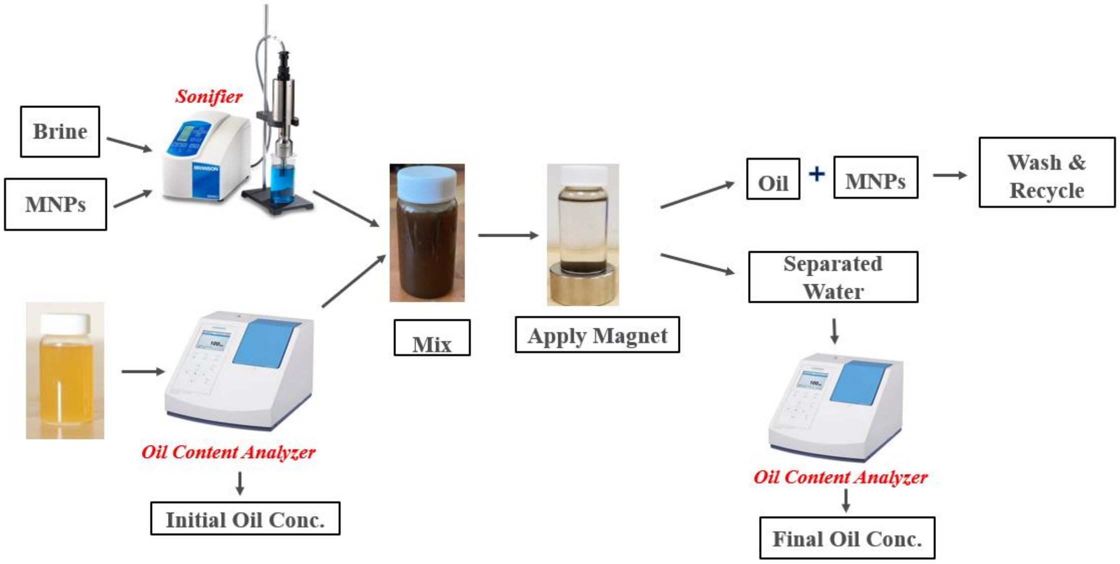


Figure 4.8 Water treatment procedure using maghemite nanoparticles

According to the data presented in Table 3.5, the maghemite nanoparticles show a great demulsifying capacity. The oil removal from the produced water samples shows the effectiveness of the oil attraction mechanism of the nanoparticles, as well as the successful recycling of maghemite using a permanent magnet, which facilitates the recovery and recycling of the nanoparticles. The results of the demulsification experiments were processed, the removal efficiencies of the synthesized and commercial maghemite were compared (**Fig. 4.9**). The nanoparticles showed uniform dispersion in the brine, this facilitated the attachment of the nanoparticles with oil droplets as well as the recovery.

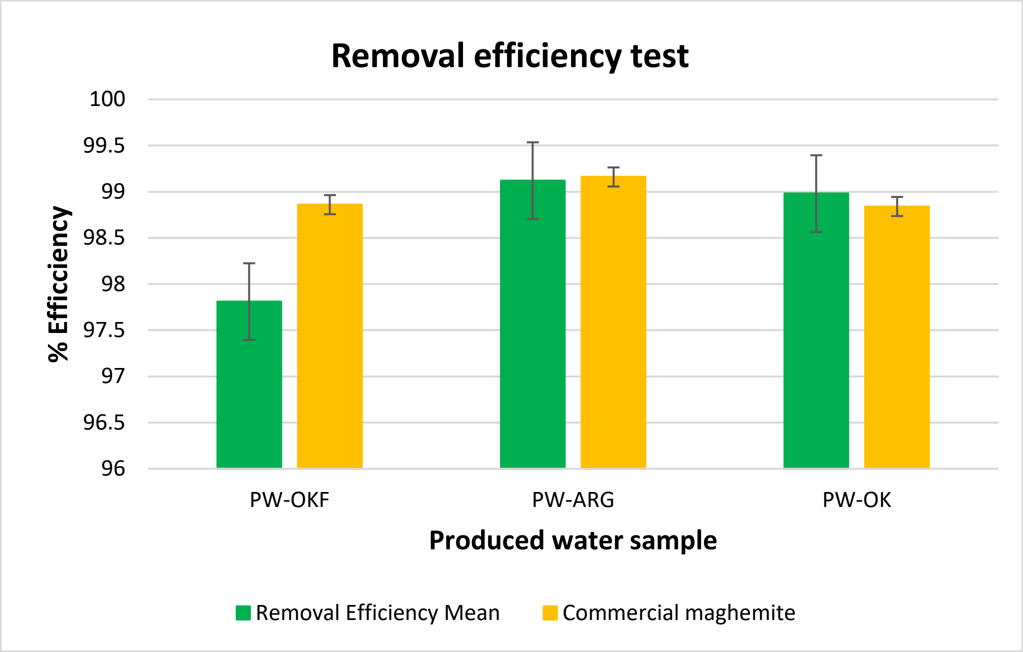


Figure 4.9 Removal efficiency test

4.3.1 Concentration of Nanosuspension

The separation of oil from the treated water was performed in approximately 20 seconds when a nanosuspension concentration of 5 mg/mL was used. However, this procedure must be optimized to maximize the technical and economic viability of the process. With this objective, nanosuspension concentrations of less than 5 mg/mL were used to treat produced water samples (**Fig. 4.10**). The sample chosen for this test was PW-OK because it was the one with the highest residual oil concentration. Concentrations from 1.5 to 7.5 mg/mL were considered. Tests were performed using synthesized and commercial nanoparticles.

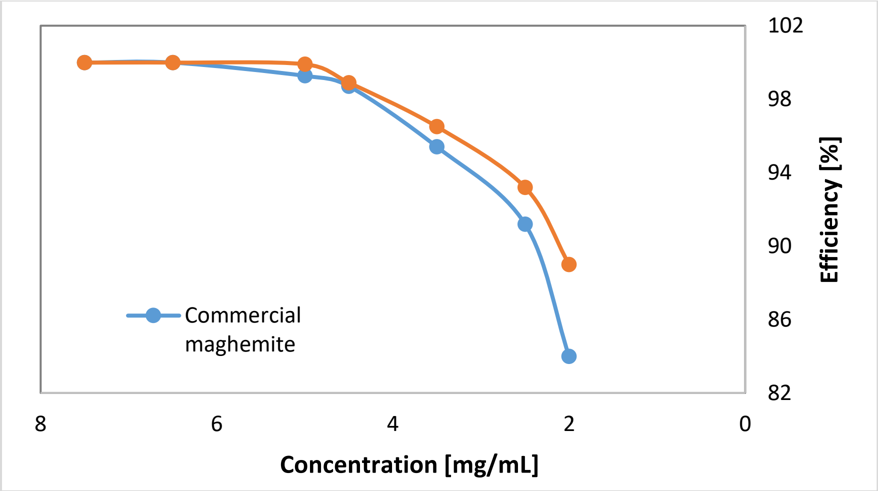


Figure 4.10 Oil removal efficiency of synthesized and commercial maghemite vs. concentration

As Fig. 4.10 indicates, concentrations as low as 2.5 mg/mL can be used to clean residual oil from produced water. When lower removal efficiency is acceptable, it might be feasible to use a nanoparticle concentration less than the one used in this study. However, the retention time needs to be increased to obtain the efficiencies presented in **Fig. 4.11**. The retention time increases when the concentration of maghemite in suspension decreases. As a result, 50 minutes of retention time was required when 2.5 mg/mL nanosuspension was used. Although the decrease in efficiency was observed, efficiencies greater than 90% are often sufficient to meet the required disposal limits for produced water.

Figure 4.11 a) Water treatment using 5mg/mL maghemite concentration, 30 seconds separation time. b) Water treatment using 2.5 mg/mL, 3 hours separation time

4.4 Gas Chromatography Analysis

Throughout the experimental work, the main method used to verify the effectiveness of the nanoparticles was an oil content analyzer, which uses the solvent extraction non-dispersive infrared absorption technique. To verify the oil removal, the sample with the highest oil content was subjected to gas chromatography (GC) analysis.

GC is one of the most common techniques used for the identification/quantification of many groups of non-polar and/or semi-polar compounds (Hasjslova and Cajka, 2007). This technique uses gas as the mobile phase and solid or liquid stationary phases. The limitations of this method to identify molecules arise because the compounds must have a boiling temperature of less than 350-400°C. In addition, the compounds must be easily evaporated without being decomposed or reacting with the other phases present in the material (Forgacs and Cserhati, 2003). The gas chromatograph unit (**Fig. 4.12**) used in this study was the Agilent 8860 GC system, which is equipped with a single quadrupole mass spectrometer that covers a wide range of routine GC application areas.

Figure 4.12 Agilent 8860 GC system

Initially, a PW-OK sample was run on the chromatograph to analyze the compounds present in the sample. **Figure 4.13** shows the characterization corresponding to the carbon chains C13, C14, C15, and C16. These were the compounds stored by default in the chromatograph, however, notable peaks can be observed around 2.8, 8.33, 7.342, and 7.404 minutes of retention time. It can be observed that the last two are the most intense. According to the literature, the peaks of greater intensity in the spectrum correspond to groups C21 and C23, this could be the result of taking a sample from a well that produces a moderately heavy oil.

Two samples were treated with maghemite nanoparticles and the treated water was again subjected to GC analysis. The results obtained are shown in **Fig. 4.14**, in which the samples are compared before and after the treatment, the proportional reduction in the intensity of the peaks indicated the removal of the hydrocarbons. The characteristic high-intensity peaks of C20+ hydrocarbon chains were disproportionately reduced. This could be an indicator of the presence of some resins and asphaltenes that are naturally present in crude oils and associated water.

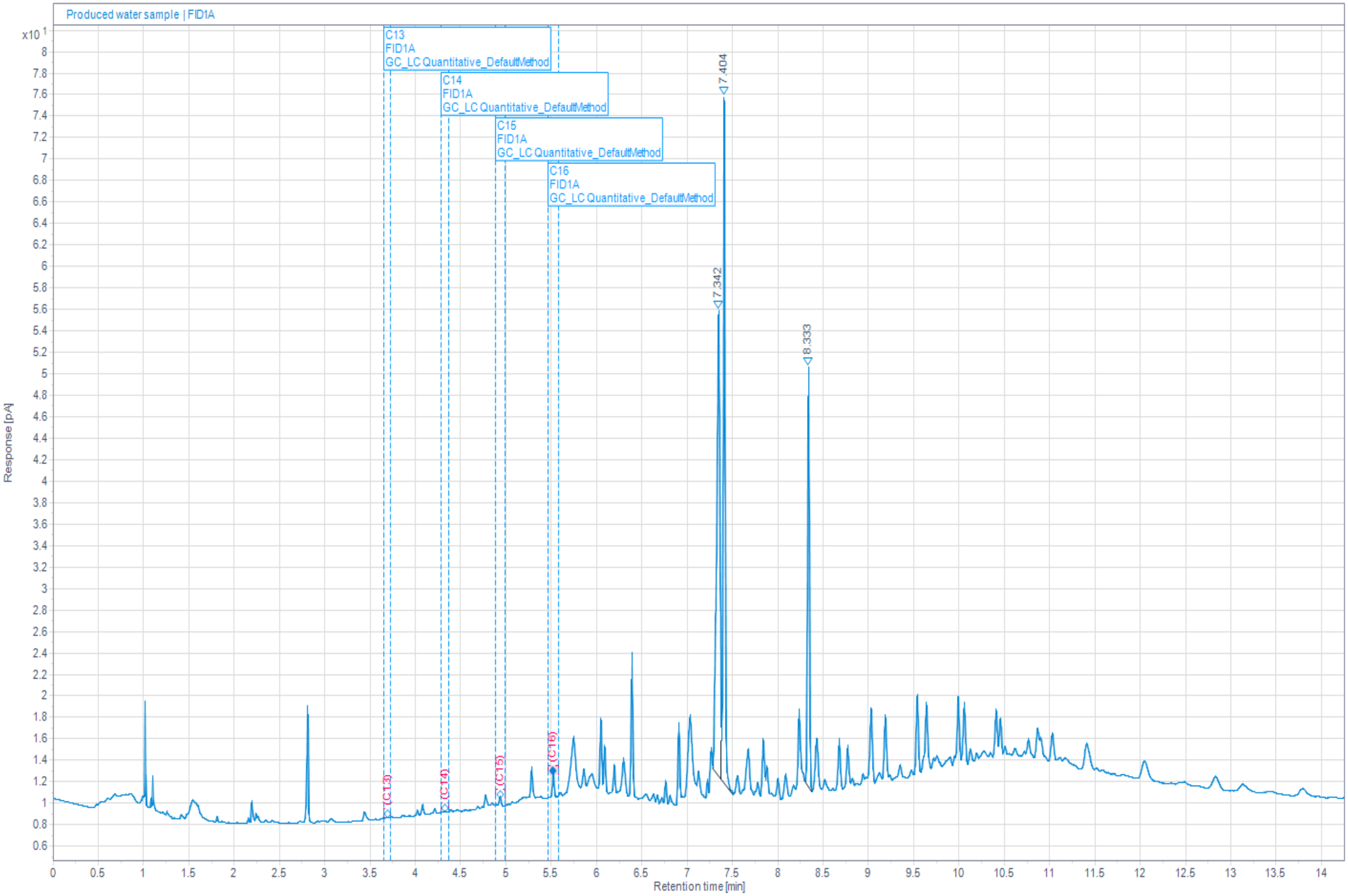


Figure 4.13 Chromatogram PW-OK sample

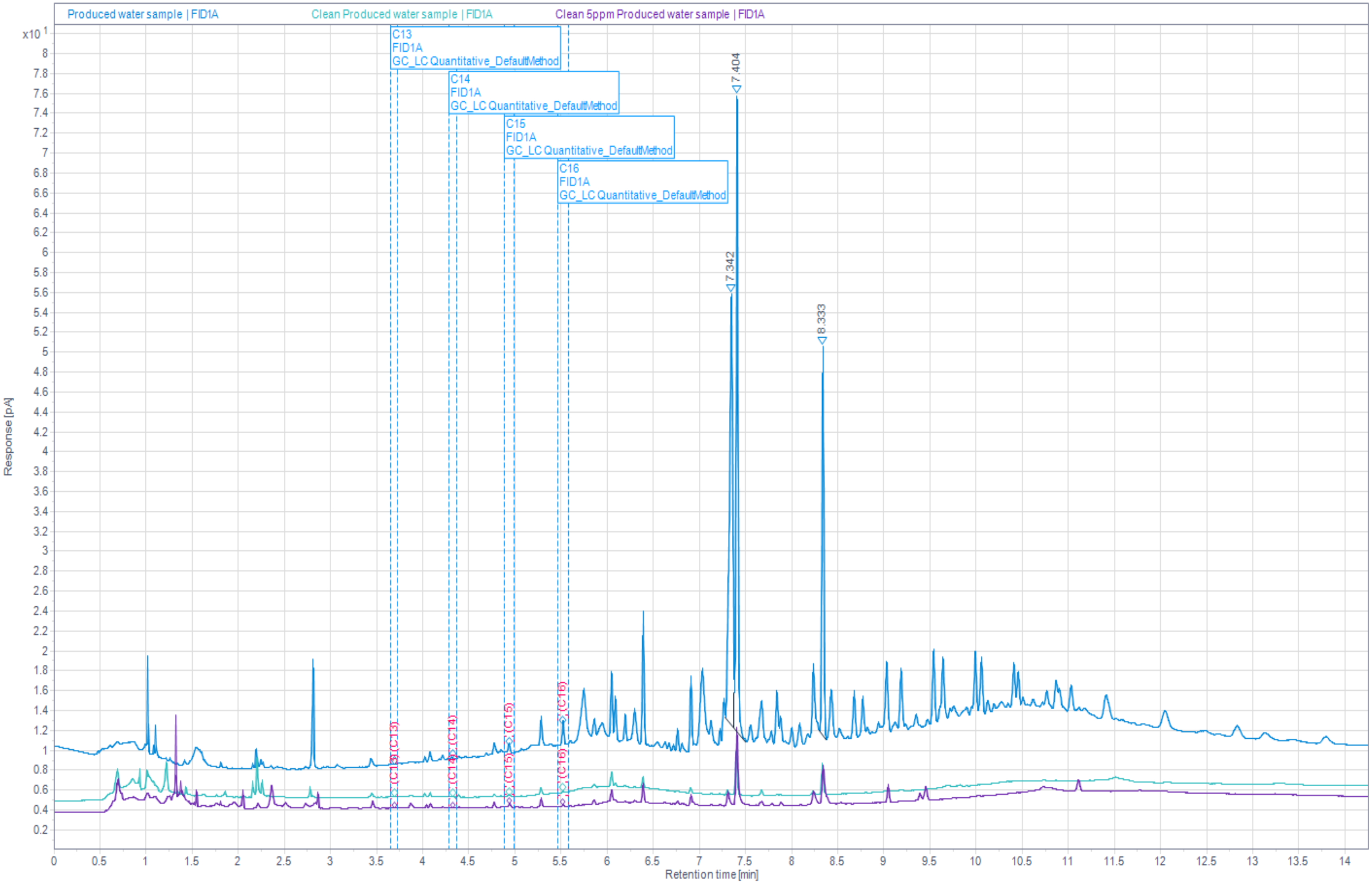


Figure 4.14 Chromatogram produced water sample and sample after cleaning with maghemite nanoparticles

4.5 Nanoparticle Recyclability

In the previous sections, the performance of maghemite particles is demonstrated. However, this method must be competitive in terms of economic feasibility. To achieve the required economic viability, it is necessary to recycle the expensive nanoparticles without losing their demulsifying properties. After applying the previously explained process, the nanoparticles were washed three times with ethanol and three times with brine to remove any remaining residue oil from the surface of the nanoparticles. Applying the established recycling technique, it was possible to repeat the treatment process up to 11 cycles before reducing the efficiency below 90% (**Figs. 4.15 to 4.17**).

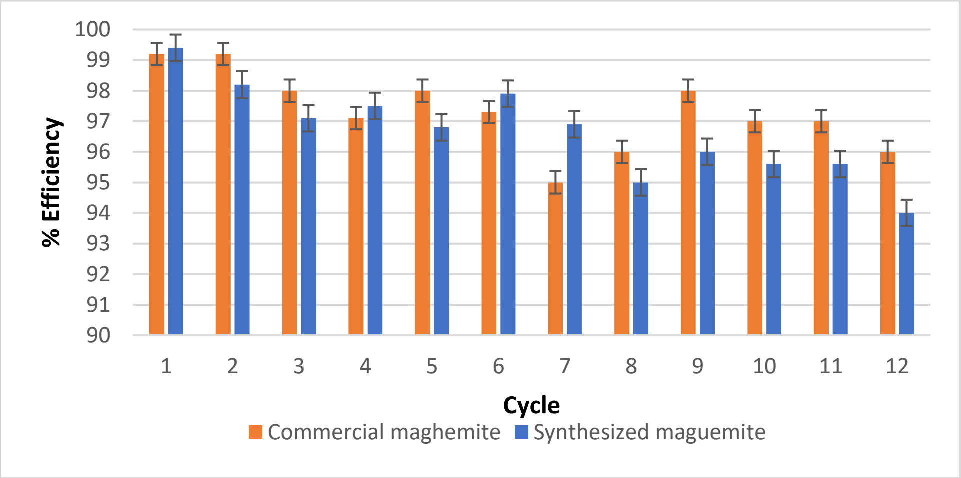


Figure 4.15 Recycling test PW-OK

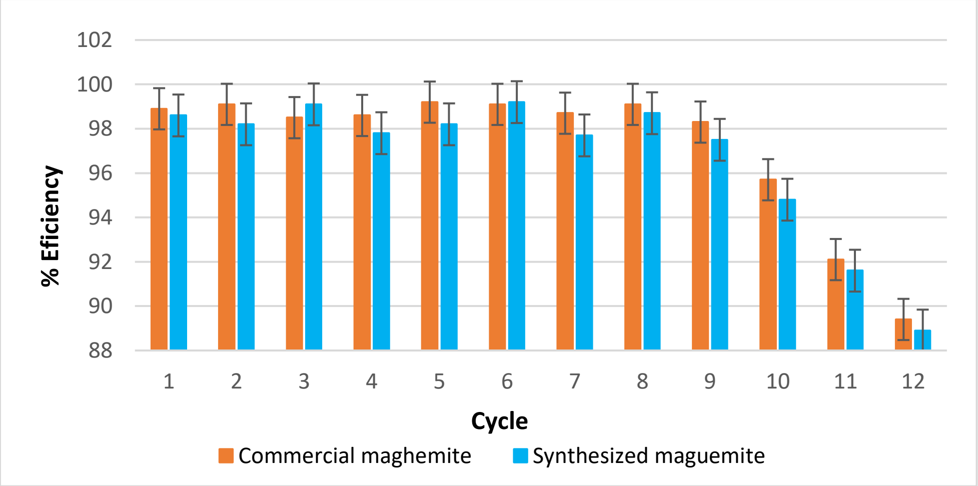


Figure 4.16 Recycling test PW-ARG

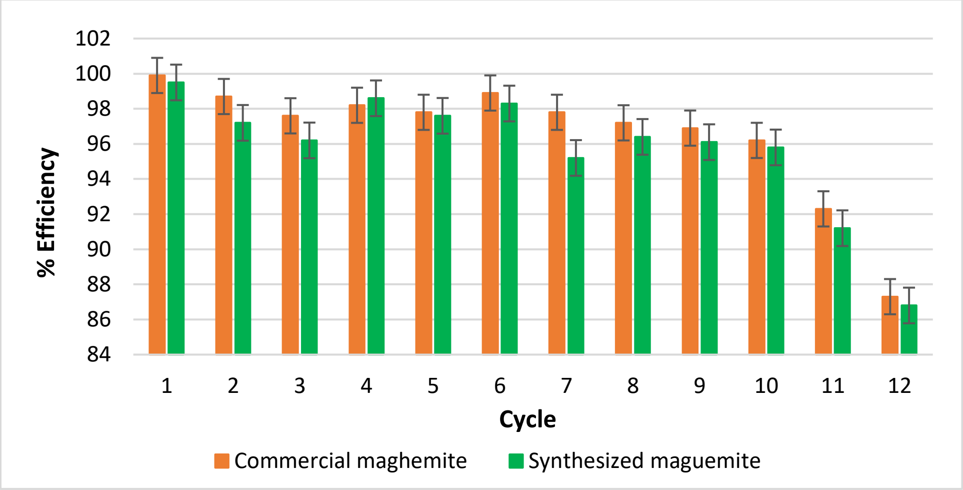


Figure 4.17 Recycling test with different samples of produced water

All the recycled MNPs were able to reduce oil concentrations below the established discharge limit. The removal efficiency obtained during the recovery of the nanoparticles was consistent throughout the eleven experiments. No coloration was observed in the brine or ethanol used for washing the nanoparticles, indicating the minimal dissolution of the nanoparticles.

After the treatment, water samples show noticeable color change. Some of the treated samples were slightly cloudy even though their oil content was minimal when tested with an oil content analyzer. Hence, there are other contaminants present in produced water that are not removed by the nanoparticles. The decrease in efficiency in the last four cycles may be due to the loss of mass during the washing and recovery. Consequently, the concentration of nanoparticles in suspension decreased causing a reduction in oil removal efficiency.

Chapter 5. Conclusion and Recommendations

5.1 Conclusions

The treatment of produced water using maghemite nanoparticles can be a novel and efficient alternative to existing residual oil removal methods. The advantages of this technique over the existing methods include a reduction in treatment cost and secondary waste, which requires further treatment or disposal efforts. After the extensive study of nanoparticles as a treatment method for produced water, it can be concluded that:

- Maghemite nanoparticles can remove emulsified residual oil in produced water with removal efficiency higher than 97%, meeting the required disposal concentration limits.
- The synthesis of nanoparticles using the chemical co-precipitation method resulted in maghemite nanoparticles with optimal properties for the demulsification process, including magnetic properties and surface charge.
- The concentration of nanoparticles in suspension to clean produced water affects the oil removal efficiency and required retention time. Thus, concentrations as low as 2.5 mg /mL can be used even if the retention time is increased considerably.
- One of the most relevant advantages of using maghemite nanoparticles is that after use they can be recovered, cleaned, and recycled. The cycles of use can be extended up to eleven times without showing a significant reduction in removal efficiency.
- Due to their low-cost, environmental compatibility, and repeated recyclability, maghemite nanoparticles offer a practical option for produced water treatment.

5.2 Recommendations

To continue with the development of this work and get closer to the application of the explained method, it is recommended to:

- Analyze the composition of the treated produced water to study how its components could inhibit or facilitates the action of maghemite nanoparticles.
- Scale-up the method for industrial application and develop a technique to perform the treatment in continuous mode.
- Investigate produced water with higher oil concentration to use this method in different applications such as oil spills.

Nomenclature

MNPs – Magnetic Nanoparticles

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

NORM – Naturally-occurring radioactive material

GC – Gas chromatography

PPM – Parts per million

MF – Microfiltration

NF – Nanofiltration

UF – Ultrafiltration

RO – Reverse osmosis

MSF – Multistage flash

VCD – Vapor compression distillation

MED – Multi-effect distillation

$\eta_{removal}$ – Oil removal efficiency

C_i – Initial oil concentration

C_{pw} – Produced water oil concentration

C_f –Final oil concentration

μ – Mean

σ – Standard deviation

FTIR – Fourier Transform Infrared

DLS – Dynamic Light Scattering

DI – Deionized

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