“TREATMENT OF PRODUCED WATER USING FERRATE (VI) AND DIRECTIONAL SOLVENT EXTRACTION.”

A Thesis

By

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ABSTRACT

“Treatment of Produced Water Using Ferrate and Directional Solvent Extraction.”

(May 2021)

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Oil field fracking operations creates by-product “produced water” that is highly variable in composition and difficult to treat. This study aims to examine two novel treatment processes together in improving the quality of a synthetic, hypersaline produced water, and examines if effluent would be suitable for reuse. Here, we examine the ability of ferrate (VI) to coagulate organic and inorganic compounds to reduce turbidity while the efficacy of diisopropylamine (DIPA) in water extraction from the subsequent hypersaline solutions was also assessed under a variety of temperature ranges. For the final product water that is separated and treated through both processes, various characteristics were examined. Of note, significant reductions in turbidity (95.07% - 97.66% removal) and salinity (94.2% - 99.13% rejection) were observed at a variety of hypersaline concentrations and temperature ranges. Results indicate that this treatment process may show a favorable per-unit treatment cost compared to conventional processes.

DEDICATION

To my parents, who have given me their endless love.

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While it may appear to be the work of a single individual, this thesis would never have been completed without the substantial help provided by others.

I would first like to gratefully acknowledge the mentorship, guidance, and encouragement that my advisor Dr. Walter Den has provided over my time in the program. His willingness to listen to my ideas, his support for me in my journey forward, and his help in allowing me to create my own unique experience have been nothing short of amazing. My journey to this point has been unconventional, but his advice has never been wrong for me. I hope to continue working with him in the future.

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CHAPTER I: INTRODUCTION

NATURE OF THE PROBLEM

Within any industry, waste production is a major concern from an operational perspective. It is well established within the literature that waste management and disposal (irrespective of industry) occupies a significant portion of capital and operational expenditures, and innovation in reducing those costs is becoming a promising sector to focus on for a variety of benefits (e.g.: Abdallah et al., 2021). For example, reductions to operational costs and environmental risks as well as increases in productivity have been documented (e.g.: Brunner & Rechberger, 2015) among other side-effects on optimizing waste management. A more prominent shift in how waste management is perceived could be a result of more conventional economic forces exert on an industry. Market forces such as consumer demand, speculation, and other externalities have forced industries into examining all areas for optimization given the possibility of further tangential benefit that could be derived from it while reducing overhead costs. The oil and gas (O/G) industry is an example of this. Novel ("unconventional") methods of production (such as through hydraulic fracturing) and examining the waste stream from exploration and production appears to be the best candidate for decreasing operational costs or increasing profitability for this industry given the wild shifts[1] in consumer and market demand.

Unconventional oil and gas (UOG) development and exploration within the United States over the last decade has allowed a previously unavailable source of fossil

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[1] As an example, Jan 6 2020 – Apr 20 2020, where the daily price for West Texas Intermediate crude oil pricing went from $63.27/ bbl to $-36.98/bbl (U.S. Energy Information Administration, n.d.)

fuels to be available for consumption. Here, UOG production is defined as being sourced from low-permeable shale, sandstone, and carbonate rock formations (US EPA, 2013) through stimulation via processes such as hydraulic fracturing (HF). Estimates from U.S. Energy Information Administration (EIA) indicate that production methods such as HF for UOG accounted for roughly 65% of domestic crude oil and natural gas production in 2019, compared to 2% from 2000. UOG does possess notable disadvantages; the U.S. Environmental Protection Agency (EPA) identified several concerns with respect to UOG production: air pollution and contamination of groundwater and surface waters from production and disposal of wastewaters, the unresolved impact of discharge of waste into underground wells for disposal, and the full extent of the stress on water supplies needed for exploration and production (US EPA, 2013). Complicating these concerns is the myriad of regulations (and subsequent exemptions) that exist at a variety of levels of legislation governing oil and gas exploration and the nature of public perception and the resulting intractable relationship regarding energy generation.

PROBLEM SCOPING

Produced Water - Definition

Produced water is a by-product of the oil and gas exploration process. There is not a totally agreed upon definition of it (Clark & Veil, 2009 versus Orem et al., 2014, as an example)[2], but for this proposal I follow the definition[3] provided by Walsh (2019): "…any water stream that flows from an oil or gas producing reservoir…[including]:

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[2] Synonyms include: brine, saltwater, formation water, flowback water, formation brine, co-produced water

[3] Provided explicitly to prevent any misunderstanding or alternative interpretation.

formation (reservoir) water from primary production…interstitial water…condensed water…water from water flood, chemical enhanced oil recovery, steam flood, etc.” This is an admittedly wide-ranging definition, although some differentiation can be made based on the lifespan of the well as the overall composition of the water removed will change over time. Initially, water may be used as a carrying fluid for cutting through rock and returned to the surface. This “flowback water” is widely considered to be the hardest to treat (Blewett et al., 2017; Walsh, 2019) due to additives incorporated into the carrying fluid for performance gain and constituents introduced from the surrounding rock. Orem et al. (2014) considers flowback water to fall within the produced water “schema”, while Walsh classifies it as a separate waste stream due to its inherent purpose; the flowback water is not “created”[4] as a function of the drilling of the well. After drilling is completed, further stimulation of the well may occur, where water may be returned to the surface from a variety of processes (both natural and anthropogenic). This water, regardless of its origination or purpose, will vary in composition due to the geology of the area, additives to increase performance of the fracturing operation, or the nature of the hydrocarbon being reached.

Importance of Treatment

Disclosure of composition of produced water

A lack of comprehensive legislation at a federal level and a disparate implementation of state-level regulation has created an unclear understanding of the composition of HF fluid. The on-going development of the FracFocus database aims to

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[4] Thus the definition of “produced” from water already present within the reservoir.

reduce this information gap while being accessible to wider public in the interest in disclosure. The FracFocus database allows an individual to search for a well using a variety of parameters including by date of operation, operator, geographical location, and ingredients through CAS number. According to this database, several states have some level of reporting for its composition, but the database remains incomplete. It should be noted that some operators and companies voluntarily disclose the compositions of HF fluids where able, but proprietary formulations remain elusive.

Produced water volumes

By volume, produced water is the largest source of waste from hydraulic fracturing and remains a difficult by-product to address. Volumes of water and hydrocarbons being produced are (unsurprisingly) inconsistent even from the same well. Averages at the initial production stage can be as low as 3 barrels for every barrel of hydrocarbon recovered, and as high as 8-10 barrels at the end of a well’s lifetime (Clark & Veil, 2009). Various estimates of total domestic, onshore produced water have been suggested to be as high as 14-21 billion barrels per year (Clark & Veil, 2009). With such a large volume of waste being produced, there has been a rising interest in determining the relationship between water usage for UOG development, the amount of energy being produced, and the amount of waste being co-produced. Work such as Kondash & Vengosh (2015) and Scanlon et al. (2014, 2017, 2020) have highlighted this relationship and the shift in perception in how water usage is viewed. Compared to more conventional O/G development, these authors suggest that UOG is more likely to be constrained by waste disposal operations than the more conventional perception of being limited by available water supply. These authors do not discount the considerable amounts of water needed for UOG exploration and development, nor do they ignore the effects of permanently removing water from the larger hydrological cycle through deep injection wells. Rather, they seek to emphasize the unique nature of this waste stream.

Breakdown of composition of produced water

Secondary to the considerable volumes that are produced with UOG is the composition of the produced water. Due to the underlying nature of the geologies that the hydrocarbons cohabitate, large quantities of salts are typically present within solution. The estimated TDS (total dissolved solids) of the waters can range from above seawater[5] to values exceeding seven times that of seawater (FracFocus Chemical Disclosure Registry, n.d.). Under the EPA's National Pollutant Discharge Elimination System (NPDES), these waste streams would need significant treatment to be able to be discharged to surface waters, while outright bans exist for some reuse[6] opportunities. Jiménez et al. (2018) identified several parameters that would need to be met based on current regulations on surface discharge and for potential reuse.

In lieu of complete disclosure by operators and companies, a considerable amount of effort from other interested parties has gone into determining what the exact nature of the composition of produced water and its effects across a multitude of species. Work such as by Danforth et al. (2020) has tried to illustrate the lack of prioritization of treating for these unknown compounds, with an estimated 24% being

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[5] Conventionally viewed as 35,000 mg/L TDS, with water containing 3,000-10,000 mg/L TDS considered as brackish, in excess of 10,000 mg/L TDS as saline, and in excess of 35,000 mg/L as brine. (Godsey, n.d.). Fresh water is defined as under 1,000 mg/L TDS by WHO, and under 500 mg/L TDS by US EPA (US EPA, 2018; World Health Organization, 1984).

[6] Here defined as being treated for out-of-industry usage, while define recycling to mean end-usage within the industry, such as further operations.

able to be readily identified, and 56% having no data available from a variety of databases on potential toxicological effects. Radionuclides (termed in the literatures and industry as Naturally Occurring Radioactive Materials, rather than the diagnostic-purpose tracers used in mapping) and heavy metal contamination are also of concern for both operators and communities (Vengosh et al., 2014). More conventional solids such as sands or silicas see usage for breaking or keeping fissures within the rock open during stimulation, with clays and other viscosity-increasing additives used for sealing and thickening purposes (Clark & Veil, 2009). Finally, a variety of agents for corrosion resistance, biocide control, and pH control is often added. This complicated formulation presents a considerable barrier to conventional treatment; where one process may seem viable, another constituent usually prevents full efficacy from being realized (Chang et al., 2019).

Texas water scarcity and relationship to oil and gas exploration

Within the state of Texas, water resources availability is complicated by the nature of ownership compared to other states. Surface waters are owned by the state with access controlled by a system of permitting for withdrawals based on age of the permit, with permits transferable to other entities (Griffin & Characklis, 2002). Conversely, ground water is largely controlled through the ‘rule-of-capture’, where property owners are able to withdraw and use as much as they please, even to the detriment of their neighbors. Groundwater withdrawal can be mediated by larger agencies (“groundwater conservation districts”) tasked with managing over-exploitation, protection, and movement of water within each district (Cook & Webber, 2016).

Cook & Webber (2016) and Scanlon et al. (2020) also summarized the nature of water use needed for HF. Under current projections aligned with state's Water Plan, 25-31% of groundwater supplies[7] would be used by HF alone. Movement of water to support this industry can be limited by conservation districts (through permitting or outright banning), or through appropriating groundwaters for other use. Cook & Webber (2016) also noted that due to the nature of the product being produced, water costs were adsorbed into the larger operational/ capital expenditures (e.g.: drilling) and were thus insensitive to the larger regional water supply issues than other industries (e.g.: agriculture) were not able to avoid. New water acquisitions with the O/G industry continues to be largely dictated by consumer demand for hydrocarbon products.

Legal issues involving produced water

Another consideration, but not fully discussed here are the legal issues surrounding produced water. As an example, recent work by Waggoner (2020) has outlined the difficulties involved with the nature of the ownership of produced water under Texas law (*Robinson v. Robbins Petroleum Corp., Inc.*, (1973) compared to Tex. Water Code Ann. § 35.002(5); Tex. Admin. Code § 297.1(21)). More research is needed to assess the legal nature of this waste stream to better determine where it exists within the waste management strategy. Action at a state level, such as in New Mexico ("New Mexico Land Boss Ends Fresh Water Sales for Oil and Gas," 2020), suggests that the

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[7] Permian and Eagle Ford tight oil plays. Scanlon et al. (2020) noted that for the Eagle Ford play, HF in conjunction with other industries over the 50-year period is projected to use up to 250% of groundwater supplies in that area.

usage of water within the mining industry is being placed under greater scrutiny given the increasing stress on water supplies available for use.

Economic cost consideration

Work by Collins (2018, 2019a, 2019b) has offered preliminary research into the economic value in treating produced water. When properly optimized, the tantalizing possibility of a multibillion-dollar market from disposal of produced water, treatment for reuse, and sourcing water for operations in the various oil plays can be visualized. As discussed in the previous section, water usage is largely dictated by consumer demand given the relatively low influence water costs impose on the greater expenditures needed for exploration. Conversely, waste disposal exercises significant influence on costs, so operators choose the most cost effective option that regulatory policy and weighing of (potential future) liability allows (Puder & Veil, 2006). As water resources become constrained, alternatives to conventional management of produced water (e.g.: injection for disposal) should become more attractive.

Global water supplies and water scarcity

As previously discussed, the water used for O/G exploration and development is considerable, with withdrawals estimated at 248 billion gallons, most of which is returned as produced water (Kondash & Vengosh, 2015). This amount is difficult to visualize, especially compared to global water supplies. The current amount of fresh water available for use is estimated to be at 0.3% of global water, with 0.014% to be both easily accessible and suitable for human consumption (Eakins & Sharman, 2010). Of that, 19% of the fresh water available to humanity is used for industrial usage, 11% is diverted for municipal purposes, and approximately 70% is used for agricultural purposes (Food and Agriculture Organization, n.d.; Hanasaki et al., 2013). The large, remaining portion of global water is seawater or inaccessible due to being locked up as ice. Kondash and Vengosh (2015) therefore suggest that while the water used for O/G exploration is a relatively small fraction of the water available for (global) human use, the increasing waste volume that is difficult to treat and the removal of water is the real issue. Indeed, many of the areas that feature heavy O/G development are also some of the most water scarce areas and complete with other industries for available water resources (Scanlon et al., 2020).

Water scarcity, as defined by Grey and Sadoff (2007), is the “availability of an acceptable quantity and quality of water for health, livelihoods, ecosystems and production, coupled with an acceptable level of water-related risks to people, environments and economies.” The statistics are sobering: 71% (4.3 billion) of the current global population by some estimates experiences “moderate-to-severe water scarcity ,” 66% (4.0 billion) will experience “severe water scarcity ” at-least one month of the year, up to 2.9 billion for “4-6 months”, and 0.5 billion “persistently year round” (Mekonnen & Hoekstra, 2016). This roughly equates to roughly 35% of the population having less than 1000 m^3 / capita / year for usage (Kummu et al., 2010). Notably, the terms “water scarcity”, “water crisis”, and “water shortages” are often used interchangeably within many fields, with no clear distinction as to what constitutes a more severe event over another. In response to the growing need for clear communication, some institutions – such as the World Economic Forum (WEF) – have changed how they are perceived from a problem-solving approach (see Global Risk

Impact reports 2009-2019), redefining what was “water shortages” as “water crises” indicating some progression of severity.

According to the WEF, water crises and water shortages have dominated the top five most impactful issues to affect the global population since 2011 (World Economic Forum, 2019). In spite of this, the same report continues to recognize the likelihood of such an event to be slightly more likely than the “failure of a regional or global governance,” “inter-state conflict,” or “large scale involuntary migration”, as the WEF now views water scarcity to be a social issue. What many agree on, is that water management and water usage is fast becoming a priority. While there is enough fresh water for the entire current global population (presuming a highly theoretical, evenly balanced distribution), there exists inequality at all levels due to factors ranging from the socio-political and economic to temporal and simple physical variations (Van der Bruggen et al., 2010). Complicating current supply demands, the global population is currently expected to grow to 9 billion by 2045 (Department of Economic and Social Affairs, United Nations, 2016). With such a milestone in mind, and pronounced existing demand upon the natural resources available, a projected reduction in global availability of 30% of fresh water by 2025 suggests higher rates of water scarcity to be a fast-approaching reality (Richard, 2015), irrespective of relative usage amounts.

Current Technologies

The growing shift from conventional oil and gas (COG) to unconventional oil and gas (UOG) development has forced the industry to evaluate how this produced water can be repurposed, especially given the growing constraints of available fresh water supplies and how public perception of how that water should be used. Surveys of the field have documented the increasing incorporation of conventional and unconventional treatment pathways into industry in an effort to minimize the fresh and brackish water withdrawals that UOG demands, while also examining the effluent qualities for reuse (Al-Ghouti et al., 2019; Fakhru'l-Razi et al., 2009; Jiménez et al., 2018). Literature, such as Walsh (2019), have echoed this shift as the adoption from desalination and municipal processes rises due to the well-established nature of these sectors and cost of operations.

Produced water management

Previous strategies of managing produced water as documented by Arthur et al. (2011) and Clark & Veil (2009) are useful as a historical reference to the various management schemes that are still in use. While the overall percentages cited within such literature have changed, they are still useful to emphasize from where the industry and need for treatment came. At the time of their publication, they described a variety of treatment pathways (from domestic production, excluding off-shore), summarized here: underground injection, reinjection for enhanced recovery, evaporation, offsite commercial disposal, and beneficial reuse. Of the total volume handled, less than 2% was estimated to be repurposed for beneficial reuse with over 90% being disposed of through underground injection (American Petroleum Institute, 2000). The remaining percentages were used for enhanced recovery or surface discharge after treatment.

Additional produced water treatment

More recently, the shift from managing the waste stream to treating to alternative usage has become more attractive due growing concerns regarding underground disposal injection and induced seismicity (Keranen & Weingarten, 2018; Ries et al., 2018), as well as constricting water resources. Briefly discussed here, treatment of produced water to create an effluent suitable for either recycling or reuse.

Recycling of produced water is focused on removal of hydrocarbons and solids from solutions so that the waste stream can be reinjected for further recovery. This is largely accomplished through physical and limited chemical means, such as the employment of cyclones and coagulants (Fakhru'l-Razi et al., 2009), while ignoring salinity due to the shift in salt-tolerant formulations for fracking (Halliburton, 2013).

Treatment for reuse opportunities can necessitate considerable cost and investment, mostly pertaining to relevant regulatory requirements. While all states adhere to the minimum that federal legislation requires, some states have higher requirements for reuse, usually revolving around characteristics such as salinity/ sodicity, pH, organic loading, and toxicity of compounds (Puder & Veil, 2006). As discussed in previous sections, parallel to the development of new treatment options is the assessment of constituents effects to organisms (Danforth et al., 2020). Work in this area is critical to assessing if a technology or management scheme is viable in the long-term. Many options that operate past physical treatment processes (e.g.: chemical/secondary, tertiary treatments) are focused on reducing these constituents.

PURPOSE OF THE STUDY

Research Question

The purpose of this study looks to examine several facets of treating produced water to an acceptable standard for either recycling or reuse opportunities. We seek to examine several gaps in the usage of these treatments, primarily revolving around the conditions produced water provides.

Currently, there is little work on using use ferrate (VI) as an effective pretreatment of incoming waste streams under saline or brine conditions. Correspondingly, while there is research on using ferrate (VI) as an advanced oxidative treatment in more conventional waste streams, there are few reasonable examples to illustrate the similar potential for its treatment of produced water, especially under the prominent saline conditions. Despite that, many currently used methods of treating produced water for reduction in turbidity and organic loading of water suffer from a variety of operational constraints. Therefore, an investigation into if ferrate (VI) can be used for reducing turbidity and the organic loading of the water while evaluating its potential cost performance against other treatments is needed.

Directional solvent extraction (DSE) occupies a similar role to ferrate (VI) compared to its conventional treatment alternatives. Currently, it remains an experimental treatment method, and few have examined it under more challenging operating conditions. DSE has primarily been examined for traditional desalination efforts, but few examples show the potential to reject turbidity and dissolved constituents while simultaneously operating under hypersaline environments under the solvent treatment pathway proposed.

What is critical the development of any treatment process, including that of produced water, is the economic cost and ultimately the viability of treatments across a multitude of conditions. Being able to satisfy both is arguably the biggest barrier to adoption within the field. The growing demand for water coupled with the changes in legislation regarding disposal suggest a prominent opportunity for novel recovery technologies. Given the wide range of constituents that can be observed in produced water (Al-Ghouti et al., 2019; Camarillo et al., 2016; Maguire-Boyle & Barron, 2014), continued need for reinjection, disposal, or reuse from operators, and current progress in treating this water, this combined ferrate-directional solvent extraction process has promising relevance in large-scale application in hydraulic fracturing wastewater treatment area.

Goals and Objectives

By examining these objectives, we can demonstrate a treatment process that has to potential to fill several voids in the understanding of different fields of water treatment. First, we investigate if ferrate (VI) is an effective method of pretreatment for reduction of turbidity of the produced water under hypersaline conditions. We also examine the efficacy of ferrate (VI) in breaking stable suspensions that are common with produced water. Next, we investigate if a directional solvent extraction (Boo et al., 2019; Choi et al., 2021) can be performed on the ferrate (VI) - pretreated produced water, and if experimental results correspond with prior experiments under hypersaline solutions for producing a product effluent with a lower TDS. Finally, the study looks to establish economic calculations in determining the role of this novel treatment process in the industry by looking at a per-unit treatment cost compared to other currently used processes.

CHAPTER II: REVIEW OF THE LITERATURE

STATUS OF CURRENT RESEARCH

Conventional and Unconventional Treatment of Produced Water

Current treatment of produced water can be categorized in a number of ways. Aside from waste management schemes where the goal is primarily safe and long-term disposal, blending of waste streams and adjustment of (initial) fracking fluids are also ways that have been documented to reduce overall volumes of produced water, usually with little-to-no reduction in efficacy (Arthur et al., 2011; Halliburton, 2013).

Further treatment of the produced water for recycling and reuse (termed “polishing” by Jiménez et al.) has been well-documented by Fakhru’l-Razi et al. (2009) and Jiménez et al. (2018). These authors have extensively described the various ways produced water is current managed along with proposed treatment standards and reuse opportunities through additional treatment. Both have identified that treatment is dictated by a variety of factors including the volumetric flow of the waste, characteristics of the waste, and prospective end-use. Summarized in **Table 1**, this summary includes a proposed use or targeted pollutant, considerations regarding said process, an efficiency for removal, and prospective cost ranges (where available, preferably within industry). Given that this an aggregation of several sources, this represents a non-exhaustive list of treatments or possible end-results and attempts to demonstrate the variety of options available. A lack of cost for treatment either indicates technologies that are not mature enough to see wide-spread implementation (e.g.: experimental, bench, or pilot-scale) or a lack of response from operators. Puder & Veil (2006) noted that some disposal and treatment facilities declined to offer specific costs (offering ranges) or processes to protect competitiveness.

***Table 1**: Conventional and unconventional treatment technologies of produced water*

Technology	Treatment Process	Targeted pollutant/ use	Considerations	Efficiency	Cost ($/bbl)
Reuse or recycle					
	Re-injection for enhanced recovery	Steam flood for oil sands	Need to ensure chemical compatibility with receiving formation.		0.05–1.25
	Injection for future water use	Aquifer storage and recovery	Need to ensure that water meets water standards, public opposition		0.10–1.33
	Injection for hydrological purposes	Subsidence control	Need to ensure chemical compatibility with receiving formation.		
	Agricultural use	Irrigation	Need to ensure that water meets water standards, public opposition, may not be permitted through local law		5.18-26.25
		Livestock and wildlife watering	Need to ensure that water meets water standards, public opposition, may not be permitted through local law		5.18-26.25
	Industrial use	Oil and gas industry application	May need treatment in order to meet operational specifications.		

Technology	Treatment Process	Targeted pollutant/ use	Considerations	Efficiency	Cost ($/bbl)
		Power plants	May need treatment in order to meet operational specifications, significant volumes needed.		
		Other (vehicle wash, firefighting, dust control on gravel road)	Will need storage facilities and possibly treatment to meet local standards.		
	Treat to drinking water quality	Use for drinking water.	Cost to treat may be high. Need good quality control. May encounter public opposition.		
Disposal					
	Injections	Disposal	Disposal into EPA regulated wells. Requires adherence to SWDA.		0.30–10.00
	Discharge	Disposal	May need treatment in order to meet local permitting (where available) for surface discharge.		2.25-3.50
	Evaporation	Disposal	Salt and sludge production and disposal volumes		0.40-3.95

Technology	Treatment Process	Targeted pollutant/ use	Considerations	Efficiency	Cost ($/bbl)
	Offsite commercial disposal	Disposal	Cost to treat may be high with large volumes and distances to treatment area.		0.30- 22.00
	Burial	Disposal	Not available in areas with high seasonal water tables, marshy environments, or tundra. May be limited to solid or semisolid, low-salt, low-hydrocarbon content inert materials. Requires dewatering.		3.00-22.00
	Discharge to municipal treatment plants	Disposal	Cost to treat may be high with large volumes, distances to treatment area, and to municipal influent standards.		0.75-3.50

Technology	Treatment Process	Targeted pollutant/ use	Considerations	Efficiency	Cost ($/bbl)
Physical treatment					
	Adsorption	Organic, inorganic compounds, BTEX, oil, heavy metals	Suspended particles can clog substrate, CAPEX/OPEX	100% recovery water, 80 - 85% heavy metal adsorption	
	Cyclones	Disruption of dispersed/dissolved oil phase	low removal efficiency, no removal of dissolved hazardous components		
	Enhanced flotation	Disruption of dispersed/dissolved oil phase	May require pretreatment prior, salinity dependent, sludge removal costs	< 93% removal of oils	0.05 [A]
	Filtration (coarse)	Removal of fine solids	Initial pH, oxygen adjustment. High retention time. Periodic sludge removal. Low throughput. Used as part of other treatments	95.8% removal of oil and grease (as part of ozone treatment)	
Biological treatment					
	Microbial biodegradation	suspended oil, dissolved organics, ammonia	No reduction in TDS, other recalcitrant components may not be degraded, possibly affected by TDS and organic loading of feed water, high sludge volumes produced, high operation time	99% removal of TPH, 30-50% removal of COD	
	Wetland construction	suspended oil, dissolved organics, ammonia	Need to ensure that effluent meets water standards, large space requirements, extensive oversight/ management. May encounter public opposition.	~98% removal of TPH, 40-78% removal of heavy metals	0.01-2.00 [B]

Technology	Treatment Process	Targeted pollutant/ use	Considerations	Efficiency	Cost ($/bbl)
Membrane treatment					
	Ceramic Microfiltration (MF)/ Ultrafiltration (UF) membrane	removal of oils, salts, suspended solids	Limited to low TDS feed waters; fouling, higher energy requirements as TDS/TSS increases, may require pretreatment, periodic cleaning of membrane, disposal of membrane backwash stream	95-97% removal of oils, 100% removal of TSS, 90%-100% recovery of product water	
	Polymeric MF/UF membrane	removal of oils, salts, suspended solids	fouling, higher energy requirements as TDS/TSS increases, may require pretreatment; periodic cleaning of membrane, disposal of membrane backwash stream	100% removal of TSS, 85%-100% recovery of product water	
	Nanofiltration (NF)	removal of oils, salts, suspended solids	Not a standalone solution; limited TDS operating range, fouling, higher energy requirements as TDS/TSS increases, may require pre-treatment; sensitive to organic/inorganics in feed. Feed limited to 45C, periodic cleaning of membrane, disposal of membrane backwash stream	90-99.9% removal of TSS, 75%-90% recovery of product water	
	Reverse Osmosis (RO)	removal of oils, salts, suspended solids	fouling, higher energy requirements as TDS/TSS increases, requires extensive pretreatment; sensitive to organic/inorganics in feed. Feed limited to 45C, periodic cleaning of membrane, disposal of membrane backwash stream	90-99.9% removal of TSS, 75%-90% recovery of product water	2.50-3.50

Technology	Treatment Process	Targeted pollutant/ use	Considerations	Efficiency	Cost ($/bbl)
Thermal treatment					
	Thermal incineration/ desorption	Destruction of organics, intermediate treatment	High temperatures needed, preferential to high hydrocarbon concentration feeds.		10.50-105
	Multi-stage flash	Recovery of water	pH adjustment to prevent scale formation, large footprint required, post-treatment needed	21 - 25 Wh/l	0.30-0.36 [C]
	Multi-effect distillation	Recovery of water	pH adjustment to prevent scale formation, large footprint required	8 - 12 Wh/l	0.10-0.17 [C]
	Freeze-thaw/evaporation	Recovery of water	requires sub-zero ambient temperatures and large footprint	removal of 90% of TPH, TSS, TDS, volatile organic compounds, semi-volatile organic compounds, heavy metals	2.65–5.00
Chemical treatment					
	Chemical precipitation	suspended and colloidal particles	Cannot remove dissolved components, sludge formation volumes	97% removal	2.20-2.30 [D]
	Electrodialysis	Removal of salts	limited ability to remove non-ionic constituents		0.02–0.64
	Photo-electrocatalysis	Dispersed and dissolved hydrocarbons	Limited to experimental-phase implementation	reduction of 90% of COD and BOD, reduction of muta-genicity	

Technology	Treatment Process	Targeted pollutant/ use	Considerations	Efficiency	Cost ($/bbl)
	Ion exchange	Heavy metal removal	High OPEX costs, other supplies for regeneration of resins, requires pretreatment for removal of solids. May be used with other processes. Ineffective at higher salinities	90-95% removal	
	Macro-porous polymer extraction technology	Dispersed and dissolved hydrocarbons	Requires pretreatment, high CAPEX/OPEX, high cost per treatment	99% removal of BTEX, 95-99% for aliphatic compounds below C20, and total aliphatic removal efficiency of 91-95%	
Advanced Oxidation processes					
	H_2O_2 and H_2O_2/UV	Removal of organic compounds	Requires pretreatment, requires optimization of reagent and reaction time, H_2O_2 production/delivery to site	69% removal of TPH (after 8 days)	
	Fenton and Photo-Fenton processes	Removal of organic compounds	Low pH requirement, sludge removal required after process, dissolved constituents can cause complexing/scavenging	75% TPH, 99% TOC removal, BTEX to n.d.l.	

Technology	Treatment Process	Targeted pollutant/ use	Considerations	Efficiency	Cost ($/bbl)
	Ozone (O_3)	Removal of organic compounds	High production costs, needs to be produced on site, low efficiency with higher TDS	"markedly reduced O/G content," met current discharge requirements for total O/G content	
	Heterogeneous photocatalysis	Removal of organic compounds	Limited to experimental-phase implementation	90% removal after 4 hrs (TiO2/UV)	
	Electrochemical oxidation	Removal of organic compounds	Cl2, H2 side-formation	40-70% removal of COD	
	Wet air oxidation and supercritical water oxidation	Removal of organic compounds	Used as an intermediate treatment, needs high temperature/pressure	90% of COD removal within 30 mins	

[A]: Cost does not reflect further disposal that is required.

[B] Remediation over 20+ years, unknown if this includes land purchase and upper volumes able to be treated.

[C] Evaluated at $0.09 per kWh

[D] Cost does not reflect additional treatment and further disposal.

Sources: Al-Ghouti et al. (2019); Arthur et al. (2011); Earthworks (2008); Fakhru’l-Razi et al. (2009); Jiménez et al. (2018); Puder & Veil (2006)

***Table 2**: Summary of reported costs for treatment options*

Management option	Minimum Cost ($/bbl)	Maximum Cost ($/bbl)
Disposal	0.30	22.00
Reuse or recycle	0.05	26.25
Chemical treatment	0.02	2.30
Membrane treatment	2.50	3.50
Thermal treatment	0.10	105.00
Biological treatment	0.01	2.00

Usage of Ferrate for Treatment of Wastewater

Currently, usage of ferrate occupies three distinct niches within wastewater treatment. Much work has been performed to examine ferrate's viability as additive for coagulation and flocculation to reduce turbidity (not a complete list, but see: de Luca et al., 1992; Graham et al., 2010; Jiang & Lloyd, 2002; Lv et al., 2018; Zheng & Deng, 2016), with varying results. This is currently theorized by Lv et al. to be the result of three main factors: laboratory-scale implementation, implementation of a buffer solution to mediate the pH of the reaction, and the inability to separate ferrate's dual effects of oxidation and coagulation (Lv et al., 2018). Widespread variation in dosage (Cui et al., 2018; Mendonça et al., 2017), target contaminant (Jiang et al., 2018), and operational application (Goodwill et al., 2016) appear to have profound affects for ferrate's efficacy for pretreatment.

Ferrate's second and third application can be observed at both ends of a wastewater treatment process when used as an oxidizer to reduce downstream turbidity for filtration (Goodwill et al., 2016), for targeting recalcitrant compounds (Sharma, 2010, 2011, 2013), and for disinfection. Destruction of recalcitrant compounds may be substances that are not susceptible to traditional processes within municipal wastewater streams (e.g.: pharmaceuticals), or where conventional treatments (e.g.: ozone, peroxide) have unwanted down-stream (e.g.: trihalomethane) or side-product formation. Jiang et al. (2014)[8] also demonstrated ferrate's ability at low doses (1.5 mg/L) for

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[8] Jiang et al. also demonstrated in the same paper ferrate's ability to remove a variety of endocrine disruptors, personal care products, and heavy metals from solution, the last of which is of more concern for this study as a direction for future work.

disinfection of a variety of microorganisms. Ferrate's biggest advantage over more conventional treatments is the variety of roles it may be applied to, with the final end-product being a stable ferric ion that precipitates readily out of solution (Han et al., 2019; Lv et al., 2018), and is easily dealt with through conventional settling and clarification operations while not being considered a toxic by-product.

To date, there is relatively little work with usage of ferrate in treating produced water from hydraulic fracturing operations, although some exists. Wang et al. (2016) looked at the usage of ferrate an advanced oxidation treatment to target polyaromatics, one ring aromatics, and naphthenic acids from the production of oil sands wastewater. Compared to other studies using ferrate for municipal waste streams, Wang et al. (2016) reported effective dosages requiring between 1 – 400 mg/L as Fe, with a moderate of oxidation occurring for high carbon-count compounds, suggesting that oxidation rather coagulation is the main removal mechanism (Wang et al., 2016). Mendonça et al. (2017) examined a highly concentrated sodium ferrate (VI) application in under acidic conditions to treat produced water from oil-field operations in Brazil. At a pH level of 3 and using a 2000 mg/L dosage of ferrate (VI), the final oil and grease content of the water was able to be reduced by 94% to 4.7 mg/L after 24 hours. Alternatively, Han et al. (2019) looked at using ferrate for demulsifying the stable oil-water emulsions that are formed in produced water by targeting the thickeners that increase the viscosity and chemical oxygen demand (COD) of the water. At a much lower dose (5 mg/L) and at 45 C, ferrate was able to substantially reduce the COD loading of the wastewater (~74% reduction) while reducing the suspended solids (~70% reduction) and viscosity (removal efficiency of 91.8%). These three studies, along with the prior work in using ferrate (VI) as an unconventional waste stream treatment, provides excellent justification in its usage for treating produced water from hydraulic fracturing operations.

Direction Solvent Extraction for Desalination

Directional solvent extraction[9] (DSE) utilizes a low-grade heat, membrane-free process that has promising results in disrupting the sea water desalination treatment field. First identified by Davidson et al. (1960) and Hood & Davison (1960), a variety of alcohol and amine solvents show selective solubility to water (rather than salts) that could operate at lower operating temperatures than other convention desalination treatment. More recently, the work in DSE has been focused on optimization of solvent choice (Choi et al., 2019, 2021; Garciadiego et al., 2020), process design (Alotaibi et al., 2017, 2019; Bajpayee, 2012), and the possible explanations behind the molecular movement between solvent and water (Luo et al., 2011). Most of the prior work has looked at sea water and brackish water for candidates for desalination, although (Bajpayee, 2012; Boo et al., 2019, 2020) looked at the possibility of “hypersaline” brines for further extraction of water and for zero-liquid discharge processes.

DSE can be compared to two predominate[10], but different methods of desalination currently used. Reverse osmosis (RO) utilizes a semi-permeable membrane that selectively allows for rejection of feed water constituents. However,

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[9] Other names for the process include “temperature swing solvent extraction” and “ionic liquid extraction” with the latter focused on a select solute extraction rather than water.

[10] We acknowledge the presence of other technologies, but these two represent the mature majority of the current methods of desalination. Other technologies are perceived to be unviable due to energy requirements or operating parameters of brine concentration but show promising applications for hybridization with existing technologies.

significant mechanical force to overcome osmotic pressure across the membrane is required, resulting in a limited range of concentrations of brines that can be treated. Membrane fouling and replacement as well as pretreatment of feed water are also operational concerns that need to be considered when using RO. Conversely, thermal-based processes, such as Multi-Stage Flash (MSF) or Multi-Effect Distillation (MED) require large physical footprints, high energy input, and high thermal output to condense evaporated water from saline solutions, with a disproportionate thermal energy usage required for viability. Final disposal of brine reject (or “raffinate”) for both thermal- and RO-based operations is also of concern, as discharge of concentrated brine has adverse ecological impacts on the environment (Bazargan, 2018; Bleninger et al., 2010). DSE’s advantages over conventional treatments are thought to include no fouling potential, lower energy usage/operating parameters, and wider tolerance to brine concentrations and incoming feed water (Bajpayee, 2012; Garciadiego et al., 2020), suggesting it is well suited as a candidate for hydraulic fracturing wastewater treatment.

CHAPTER III: MATERIALS AND METHODS

FLOWCHART OF PROPOSED TERATMENT PATHWAY

We propose the following as a possible treatment pathway for an initial proof-of-concept operation. We separate this treatment pathway into two distinct processes: ferrate (VI) oxidation/ coagulation and directional solvent extraction. First, we presume that the raw wastewater has been pretreated to remove the “free” oil content, leaving suspended oil and particles, which is common for current treatment schemes.

Raw wastewater is then subjected to rapid mixing (600 RPM), where ferrate (VI) is introduced after being rehydrated. After pretreatment with ferrate (VI), wastewater is allowed to settle. Treated wastewater should then be quenched (such as through sodium thiosulfate addition) to remove residual ferrate (VI) before introduction into the directional solvent extraction process if needed. With no pH control and no buffer solution used, ferrate (VI) should rapidly decompose to non-reactive species. Suspended oils should now be a distinct layer and able to be removed with skimming, while settled solids removed through coarse filtration or clarification.

For directional solvent extraction, treated wastewater (now nominally a brine solution) would be introduced into the solvent into a sealed container (termed “cold” treatment). Container would be vigorously agitated to promote water uptake. After an appropriate measure of time, a change in the respective volumes of solvent and brine will occur, with the brine appearing to reduce in volume while the solvent increases. This would indicate that solvent hydration had occurred. Rich solvent mixture is then removed from brine through pipetting. Brine not fully adsorbed into solvent (“raffinate”) could be either retained for further solvent extraction until excess salt precipitated (under a zero-liquid discharge scheme proposed by Boo et al., 2020) or reintroduced into the treatment stream. The rich solvent is then placed into a hot bath under sealed conditions with adequate headspace for an appropriate amount of time. After heat treatment, separation of solvent and water should be observed, with the solvent being the top layer and water the bottom layer. Now a solution that exhibits a defined bi-layer, mixture is separated through gravitational separation, with solvent being able to be reused for repeated extraction once cooled.

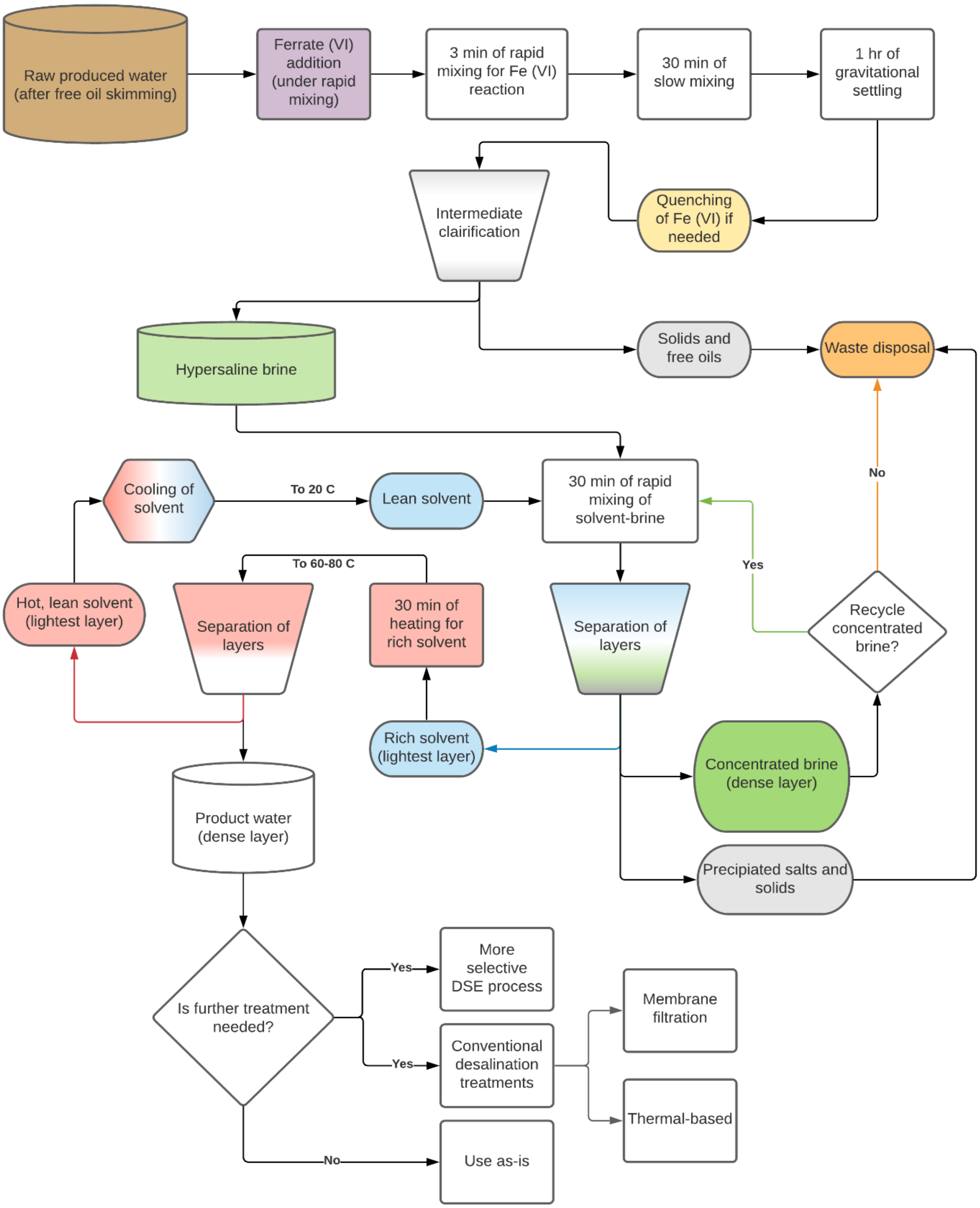

Figure 1: Proposed treatment pathway

Adapted from Boo et al. 2019 and Choi et al. (2021)

MATERIALS

Chemicals

Diisopropylamine ("solvent", CAS#: 108-18-9, BeanTown Chemical) was used as received. 4 M saline brines were prepared by dissolving table salt ("Quality Salt" HEB) or sodium chloride (CAS# 7647-14-5,VWR Life Sciences) in deionized water ("DI", 18.2 μΩ) obtained from a Milli-Q ultrapure water purification system. Potassium ferrate was prepared by Dr. Virender Sharma's laboratory at Texas A&M University (College Station) by the method of Thompson et al. (1951), and kept in sealed bottles under desiccant until use. Oil Red O (CAS#: 1320-06-5, BeanTown Chemical) was dissolved in DIPA to yield 0.12 w/w% solutions, and a few drops were added to the solvent for visual distinction from the brine solution. Sodium thiosulfate pentahydrate (CAS#: 335-95-5, Strem Chemicals) was dissolved into DI water to create a 100 mM solution and maintained under refrigeration until use. Sodium bentonite clay ("Aquagel Gold Seal Viscosifer", Baroid) was used as received. NaOH (CAS#: 1310-73-2, VWR BDH Chemicals) and H_2SO_4 (CAS#: 7664-93-9, JT Baker) were used to create 100 mM solutions using DI water. Hexadecane (CAS#: 0000544-76-3, Acros Organics) was used as received.

Instruments

A Thermo Scientific Orion Star A329 multimeter was used in conjunction with Orion DuraProbe 4-Electrode Conductivity Cell probe and Orion ROSS Ultra Low Maintenance pH/ATC Triode for salinity and pH/temperature measurements. Vernier LabQuest 2 with ORP sensor was used for measuring ORP of samples. Hach's DR1900 Portable Spectrophotometer was used to determine ferrate (VI) concentration through optical absorbance. An Ohaus precision balance (PX163) was used for all dry measurements. VWR's Signature Ergonomic High Performance Single-Channel Variable Volume Pipettors were used for additions and removals of various liquids. Oakton T100 turbidity meter was used for measuring turbidities and a Hamilton Beach Commercial blender (soil attachment) was used for making emulsions.

METHODS

Preparation of synthetic produced water

Initial formulation (formula #1) of synthetic produced water (SPW) was prepared by emulsifying 60 mg calcium bentonite clay into appropriately diluted 4 M NaCl stock solutions to create 300 mL 1 M, 2 M, and 4 M brines. 35 µL of TruSyn 200i was added after clay addition and continued to be emulsified using the Hamilton Beach blender to ensure full incorporation.

For formula #2, sodium bentonite clay and hexadecane were added to 1 M, 2 M, and 4 M brine solutions[11] to create mixtures that would possess an initial turbidity of approximately 50 NTU and an organic content equivalent to 100 mg/L. SPW was mixed using the Hamilton Beach blender to create a stable suspension. Formula #3 followed formula #2 but increased initial turbidity to approximately 100 NTU.

Ferrate stock solution was prepared by dissolving dry, premade potassium ferrate into DI water or a buffer solution. Ferrate concentration was determined through optical spectrometry at 510 nm after filtering through a 0.45 µm filter following the Lee et al. (2004) methodology and used immediately afterwards.

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[11] Brine stock solution was created using table salt rather than the reagent grade salt in formula #1

Pretreatment of synthetic produced water

Five sets of trials were performed to develop the proposed treatment process. Trial 1 was used to determine the adequate ferrate (VI) dosage under conditions that had dissolved solids and oils, but no salt. This was necessary given the wide range of opinions within the literature on appropriate ferrate (VI) dosage for inducing simultaneous oxidation and flocculation. Trial 2 was a variation of trial 1 where a dosage amount was hypothesized to be appropriate given varying levels of salt content. There were some indications within the literature that suggested that dosage levels may be affected by the dissolved ions present within brine solutions. Trial 3 was used to determine the role of pH control with respect to ferrate (VI) under hypersaline conditions after observations from trial 1 and 2. Larger volumes were used in trial 3, but still followed the ratio of constituents observed in trials 1 and 2. Trial 4 re-assessed the ferrate (VI) dosage using a different formulation for SPW and under modified operating conditions following. Trial 5 capitalized on the findings from trial 4 for ferrate (VI) dosage and pH control. For trials 4 and 5, a control was included to observe if suspensions were maintained throughout mixing and settling periods. Negligible loss of turbidity was observed in either trial, confirming that suspension of hydrocarbon and dust was stable.

Initial tests to determine appropriate ferrate dosage was performed under triplicate replication, starting with a 0 M salt solution. 100 µM, 50 µM, and 25 µM (equating to an approximate 12, 6, and 3 mg/L as Fe dosage, respectively) were selected as candidates based on prior usage in the literature (Talaiekhozani et al., 2017) and feasibility of preparation. Ferrate (VI) concentration was estimated at a 10 mg/L as Fe for Trial 2, and 12 mg/L as Fe for Trial 3.

For trials 1 and 2, SPW solutions were placed onto a programable paddle stirrer (Phipps and Bird, model 7790-400) and set to 200 RPM for rapid mixing for 60 seconds prior to addition of ferrate solution, then continued to mix for another 60 seconds; pH was monitored and allowed to rise. After rapid mixing, the paddle stirrer was set to 50 RPM for 45 minutes for slow mixing to enhance floc formation. SPW was quenched with $Na_2S_2O_3$ (100 mM) to halt ferrate (VI) residual reactions and allowed to continue mixing for 30 minutes. Paddle blades were removed, and gravitational settling was allowed to occur for 45 minutes, with sampling for turbidity taken as before at the conclusion of the trial.

For trial 3, the setup of tests followed trial 2 arrangement, but pH was controlled during ferrate (VI) incorporation through NaOH and H_2SO_4 addition to maintain 7.0 pH. Samples of each treatment level were collected before and after introduction of ferrate for assessing turbidity and salinity. Turbidity was assessed using a turbidity meter while salinity was determined through measuring the conductivity of the water.

Trial 4 was conducted using formula #2 following further research and insight provided by the previous trials. Notable deviations from previous trials included not using a buffer solution and not employing any pH control. Prior research by Lv et al. (2018) documented earlier research using ferrate (VI), noting that many used buffer solutions and pH control to eliminate iron hydroxide formation, as the primary interest was using ferrate (VI) as an oxidizer rather than a coagulation. Here, the interest was to examine ferrate (VI)'s performance as a coagulation, so the change in pH was allowed to occur unhindered. Ferrate (VI) doses were added under rapid mixing conditions (600 RPM) and allowed to continue for 180 seconds (Figure 2). Doses ranged from 1.0 to

15.0 mg/L as Fe. SPW were transferred to the programmable paddle stirrer and set to 30 RPM for 30 minutes to allow for floc formation. After the slow mixing, samples were allowed to gravity settle for one hour, after which samples were collected for turbidity. Samples were collected by pipetting 3 cm under the waterline.

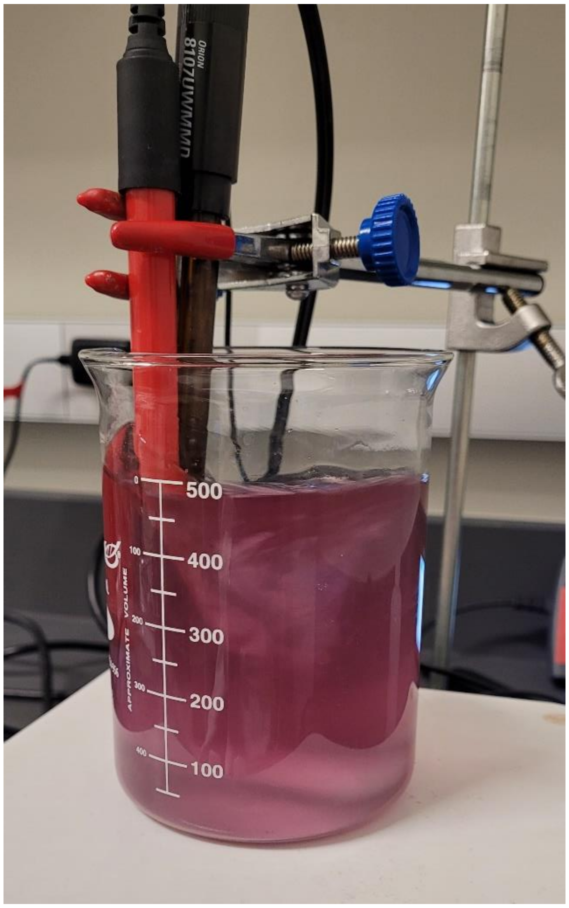

Figure 2: Rapid mixing of SPW

Trial 5 was conducted with formula #3. A 5 mg/L as Fe dosage was selected due to the research done by Han et al. (2019). Ferrate doses were added under 600 RPM mixing for three minutes, then transferred over to the paddle stirrer for 30 minutes (Figure 3). Samples were allowed to gravity settle for one hour, after which turbidity was recorded (Figure 4). Samples were collected by pipetting 3 cm under the waterline.

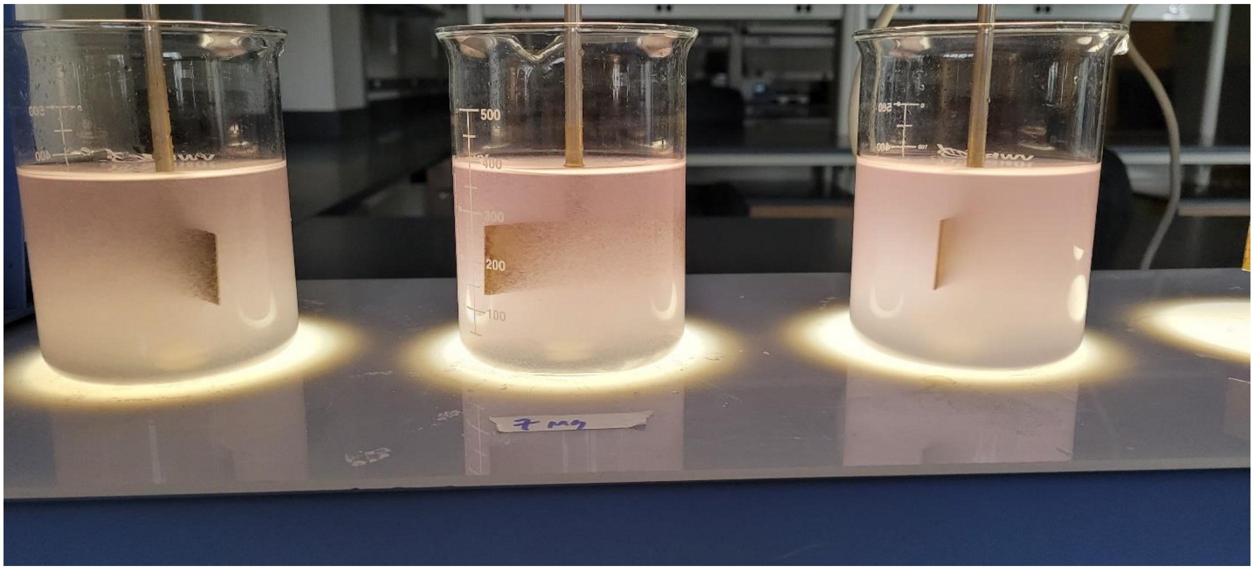

Figure 3: Slow mixing of SPW to encourage flocculation.

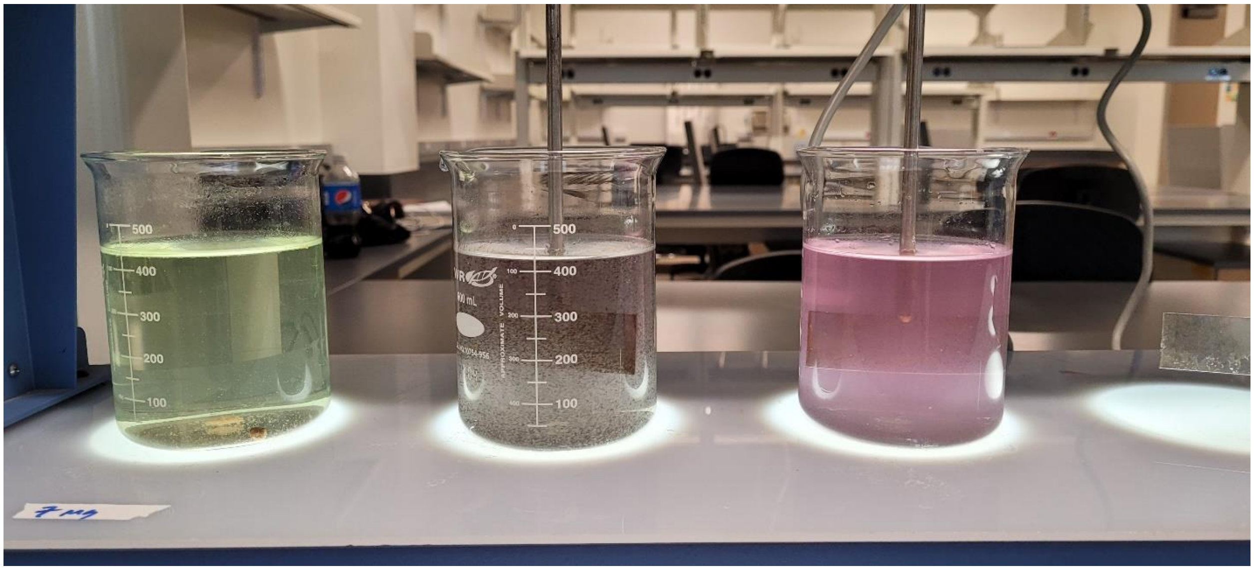

Figure 4: Samples undergoing gravitational settling and continued stirring. From left to right, an approximate 10 min difference between samples.

Directional solvent extraction of product water

For initial testing of solvent extraction (trials 1-3), sealed containers of solvent were placed into a refrigerator and allowed to cool up to one hour before use. Solvent was doped with an Oil Red O dye to further differentiate solvent from SPW. Supernatant from ferrate treated-SPW was collected through pipetting off liquid, filtering to remove large solids, added to prechilled solvent, and agitated for 60 seconds. Containers were placed back into refrigerator to cool for one hour, with re-agitation every 15 minutes. After one hour, rich solvent mixture[12] was decanted from raffinate by pipetting and separatory funnel. Rich solvent was bottled, placed into water bath to heat for 1 hour at 70 C, and agitated every 15 minutes for 60 seconds. After heating cycle, water and lean solvent layer separation was observed, with layers being removed through the usage of separatory funnel decanting. Volumes of solvent and product water recovered were measured, and aliquots for turbidity, and salinity of the product water were collected. Samples were diluted to create a greater volume where needed and then back-transformed.

Adjustments to extraction of product water through solvent extraction were also made. Following new research in the field by Choi et al. (2021), the need for the prolonged “cold” extraction period was reevaluated. While Boo et al. (2019) used a one hour period that did not employ any agitation (therefore allowing adsorption through a diffusion-like process), Choi et al. (2021) used a vigorous (i.e: via handshaking) mixing for one minute at 25 C. A median option between the two was devised for trial 5; rapid mixing by orbital shaker at 140 RPM for thirty minutes at room temperature (Figure 5). This would differentiate from Boo et al. (2019) by being shorter in time, higher in initial

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[12] While not explicitly declared in works such as Boo et al. (2019) and Choi et al. (2021), full uptake of a solute into a solvent can be described as being “rich”, while solute-poor solvents as “lean” following a similar terminology for amine gas treatment or gas sweetening.

temperature (20 vs 15 C), and including a physical motion, while being more quantifiable than Choi et al. (2021).

Figure 5: Modified orbital shaker

Similar to trial 4, after bilayer clearly formed a portion of the rich solvent layer was removed through pipetting and placed into a sealed container (Figure 6). Different from previously trials, pipetting allowed only a portion of the solvent to be removed while preventing any inadvertent mixing of layers or cross-contamination that separatory flasks would include at the lower temperature for previous trials. The rich solvent was then placed into a hot bath for thirty minutes. Similar to Choi et al. (2021), the hot bath was set to a variety of temperatures to assess the solvent’s performance at each salt concentration level. Temperatures of 60, 70, and 80 C were selected due to the boiling point of the solvent used, and to compare against previous literature who only employed one “high” temperature (Boo et al., 2019). After the heating phase, product water was removed through a separation flask, measured for volume, and evaluated for salinity (Figure 7). Removal through a separation flask was appropriate here as the solvent would be less soluble in the product water at the higher temperatures

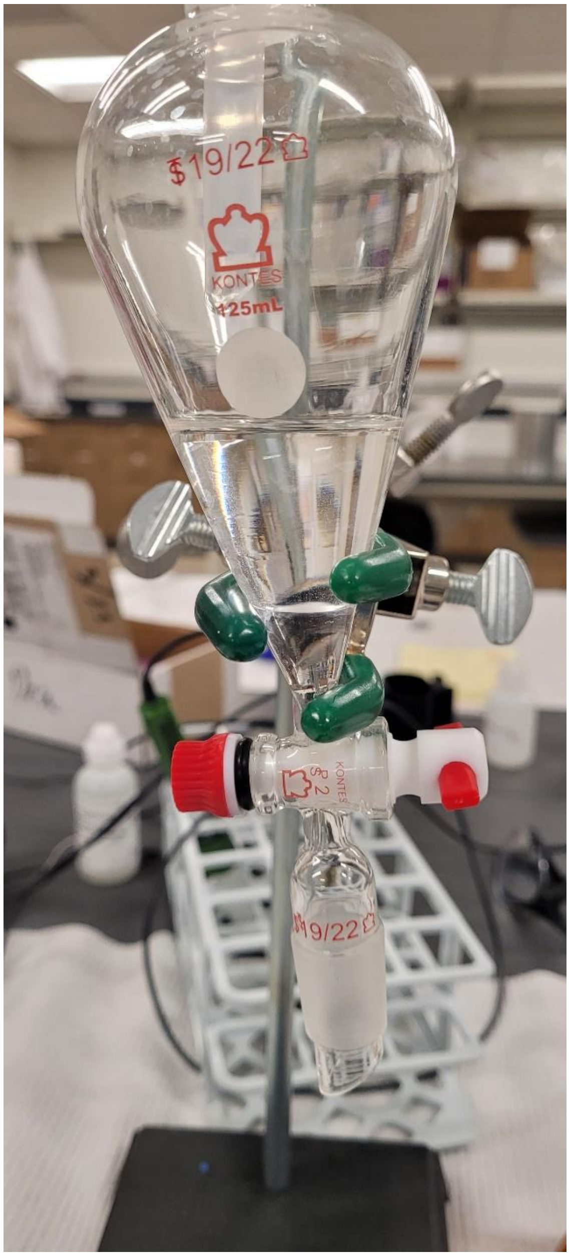

Figure 7: Separation of lean solvent and product water. Bottom layer is water, top layer is solvent.

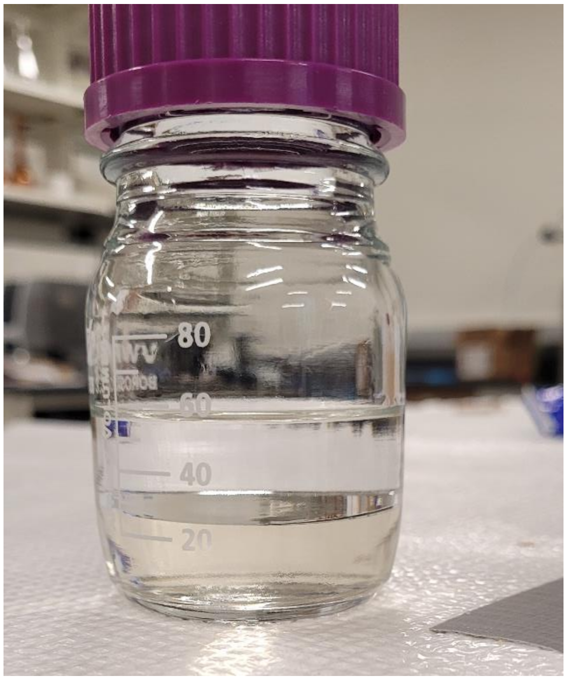

Figure 6: SPW with DIPA. Bottom layer is SPW, with top layer as DIPA.

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CHAPTER IV: RESULTS

PRETREATMENT OF SYNTHETIC PRODUCED WATER

Trials 1 through 3

Usage of ferrate (VI) to pretreat SPW through oxidation of organic compounds and subsequently inducing coagulation and flocculation produced mixed results at a variety of treatment levels. For initial dosage determination of ferrate (trial 1), 100 µM resulted in an average 60% reduction in turbidity for supernatant collected, while the 50 µM and 25 µM treatment levels yielded an average increase of 90% and 53% in turbidity. Under trial 2 where salt was present (83 µM ferrate dosage at all levels), turbidity measurements post-ferrate treatment increased by an average of 83% for brine treatment levels, while trial 3 (100 µM ferrate at all levels, pH controlled) turbidity was reduced by 87% post-ferrate treatment (**Table 4**).

Trial 4

Utilizing no pH control and formula #2, ferrate (VI) doses had a wide range of effects at the various salt concentration levels. For 1 M brines, a 1.5 mg/L as Fe dose removed 93.0% of turbidity after treatment and settling. For 2 M brines, a dosage of 1 to 7 mg/L as Fe presented a removal ranging from 99.6 to 95.7% turbidity removal, with 10 mg/L as Fe removing 84.6% and 15 mg/L as Fe removing 93.2%. 4 M brines presented a diminishing removal as doses increased, with 1 mg/L as Fe removing 96.0% of turbidity, and 15 mg/L as Fe only removing 39.9% of turbidity (**Table 5**).

Trial 5

Utilizing no pH control and formula #3, the 5 mg/L as Fe dose was able to remove an average of 96.52% of turbidity across all three salt concentrations, for an average turbidity of 3.27 NTU. For 1 M brines, an average final turbidity was 2.99 NTU, equating to a removal efficiency of 96.83%. For 2 M brines, the average final turbidity was 2.23 NTU, equating to 97.66% efficiency for removal. Finally, for 4 M brines, the final turbidity was 4.60 NTU corresponding to a 95.07% removal efficiency (**Table 6**).

DIRECTIONAL SOLVENT EXTRACTION OF PRODUCED WATER

For trials 2 and 3, supernatant was collection for addition into solvent treatment. For Trial 2, raffinate, and final product water volumes were recorded. 1 M solutions recovered 55% of feed water (rejected 38%) by volume, 2 M recovered 23% (rejected 53%), and 4 M recovered 5% (rejected 73%). For Trial 3, salinity was compared against initial conditions. 1 M solutions reduced salinity by 37%, 2 M reduced salinity by 65%, and 4 M reduced salinity by 84% (**Table 4**). Solvent treatment reduced on average turbidity by 87% for Trial 2 and 84% for trial 3 when compared to supernatant turbidity.

For trial 5, treated SPW supernatant was collected similar to trials 2 and 3. After solvent extraction, product water was examined for volumes and salinity. For 1 M brines, an average water extraction efficiency was calculated at 25.15%. For 2 M and 4M brines, average water extraction efficiency was 13.07% and 2.93%, respectively. These efficiencies represent the average across the three ΔT that were examined, with more granular breakdown provided in **Table 7**. Salt rejection was calculated similar to turbidity, with the results aggregated in **Table 8**. Of note, average feed concentration was observed to be reduced by 94.73% for 1 M brines, 97.40% for 2 M, and 98.94% for 4 M brines, equating to product waters that yielded averages of 3078 ppm, 3039 ppm, and 2473 ppm, respective to brine concentrations (**Table 8**). .

***Table 3**: Initial and final conditions of SPW for turbidity*

Trial, Test	Average of Initial Turbidity (NTU)	Average of Turbidity after Fe(VI) treatment (NTU)	TRE - Fe (VI)	Average of Turbidity after Fe(VI) and solvent treatment (NTU)	Total TRE
1, No Salt					
3 mg/ L Fe (VI) *(n=3)*	48	73.6	(-53%)	--	--
6 mg/ L Fe (VI) *(n=3)*	48.2	91.7	(-90%)	--	--
12 mg/ L Fe (VI) *(n=3)*	46.2	18.34	60%	--	--
2, Salt					
1 M, 10 mg/ L Fe (VI) *(n=3)*	60.7	95	(-57%)	10	84%
2 M, 10 mg/ L Fe (VI) *(n=3)*	56.3	118.6	(-111%)	13	77%
4 M, 10 mg/ L Fe (VI) *(n=3)*	58.4	106.8	(-83%)	18	69%
3, Salt - pH controlled					
1 M, 12 mg/ L Fe (VI) *(n=3)*	81.7	7.9	90%	2.12	97%
2 M, 12 mg/ L Fe (VI) *(n=3)*	126	14.9	88%	1.44	99%
4 M, 12 mg/ L Fe (VI) *(n=3)*	146	24.5	83%	3.08	98%

***Table 4**: Initial and final conditions for SPW for salinity, Trial 3 only*

Trial, Test	Average of Initial Salinity (mS/cm)	Average of Salinity after Fe(VI) and solvent treatment (mS/cm)	SRE
3, Salt - pH controlled			
1 M, 12 mg/ L Fe (VI) *(n=3)*	81.37	50.95	37%
2 M, 12 mg/ L Fe (VI) *(n=3)*	129.6	45.22	65%
4 M, 12 mg/ L Fe (VI) *(n=3)*	221.6	34.8	84%

***Table 5**: Trial 4 results, turbidity removal with varying ferrate (VI) doses and no pH control*

Salt concentration	Dosage (mg/L as Fe)	Initial Turbidity (NTU)	Final Turbidity (NTU)	TRE
1 M	1.5	21.6	1.51	93.0%
1 M	3.5	27	13.49	50.0%
1 M	7	27.6	22.4	18.8%
1 M	10	43.4	13.11	69.8%
1 M	14	31.9	23.1	27.6%
2 M	1	43.2	0.16	99.6%
2 M	2.5	46.5	0.84	98.2%
2 M	5	48.7	1.43	97.1%
2 M	7	51.5	2.23	95.7%
2 M	10	42.4	6.55	84.6%
2 M	15	50.7	3.44	93.2%
4 M	1	48.8	1.95	96.0%
4 M	2.5	51.9	6.06	88.3%
4 M	5	48.3	7.95	83.5%
4 M	7	49.3	11.11	77.5%
4 M	10	55.7	14.4	74.1%
4 M	15	49.6	29.8	39.9%

***Table 6**: Trial 5, Aggregated results for removal of turbidity by 5 mg/L ferrate (VI) dose.*

Salt concentration	Average of Initial Turbidity (NTU)	Average of Final Turbidity (NTU)	Average of TRE
1 M *(n=6)*	94.32	2.99	96.83%
2 M *(n=6)*	94.75	2.23	97.66%
4 M (*n*=6)	93.73	4.60	95.07%
Average	94.27	3.27	96.52%

***Table 7**: Trial 5, Average of water extraction efficiencies at various ΔT from 20 C*

	ΔT from 20 C			Average of water extractions V_{water} / $M_{solvent}$ (mL/g)
Salt Concentrations	40 C	50 C	60 C	
1 M *(n=6)*	21.83%	25.23%	28.35%	25.14%
2 M *(n=6)*	10.80%	14.24%	14.16%	13.07%
4 M *(n=6)*	1.56%	2.95%	4.28%	2.93%

***Table 8:** Trial 5, Salt rejection and product water and feed concentrations*

Salt Concentrations, ΔT from 20 C	Average of initial Salinity (mS/cm)	Average of final Salinity (mS/cm)	Average of product concentration (ppm)	Average of SRE
1 M (~58,440 ppm)	92.46	4.81	3078	94.73%
40 C	92.18	5.29	3388	94.20%
50 C	91.89	4.59	2938	94.97%
60 C	93.31	4.54	2908	95.02%
2 M (~116,880 ppm)	181.71	4.75	3039	97.40%
40 C	182.03	5.40	3453	97.05%
50 C	182.18	4.12	2637	97.74%
60 C	180.93	4.73	3028	97.41%
4 M (~233,760 ppm)	365.48	3.86	2473	98.94%
40 C	365.20	4.92	3147	98.65%
50 C	365.56	3.49	2232	99.05%
60 C	365.69	3.19	2040	99.13%

CHAPTER V: DISCUSSION

PRETREATMENT OF SYNTHETIC PRODUCED WATER

Preliminary examinations of ferrate (VI)

The aim of trial 1 was to determine the appropriate dosage of ferrate at a controlled, initial turbidity. The 12 mg/L dosage was the only treatment level that resulted in a lower turbidity, while the other dosage amount of 6 mg/L and 3 mg/L increased overall turbidity at the conclusion of the trial. Determination of an appropriate ferrate dosage appeared to conflict with the prior research across both treatment levels. At one end of the spectrum, doses of up to 2000 mg/L[13] have been reported in the literature (de Luca et al., 1992; Mendonça et al., 2017; Wang et al., 2016), while others have indicated a much more approachable dosages of ≤10 mg/L (Jiang & Lloyd, 2002). This variability in dosage and efficacy for oxidation, coagulation, and flocculation is theorized to be a function of initial turbidity, the dissolved ion concentration of the water, pH control, and the organic loading of the incoming wastewater. In this study, the incoming turbidity and dissolved ion concentration is considerably higher than most municipal waste streams. The high dissolved ion concentration that is inherent to the nature of this study is thought to rapidly accelerate the self-conversion of Fe (VI) to colloidal iron oxide particles that do not participate in charge neutralization for coagulation to occur (Jiang & Lloyd, 2002; Sharma et al., 2001). While some iron floc has been observed in other studies (Goodwill et al., 2016), it appears that nanoscale flocculation is occurring, but not true large-scale sweep flocculation that would result in

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[13] Albeit for oxidation and removal of oils and greases, rather than removal of non-hydrocarbon solids

a decrease in turbidity. The variability experienced in these initial trials as wells as other studies can be traced back to incoming characteristics of the water, but also retention times for settling to occur. In trials 1 and 2, ferrate was quenched rather than allowing for a natural degradation to occur while also having a shorter gravity-induced settling period than other trials had used. The degree at which rapid and slow mixing is performed to induce the initial oxidation of organic materials and to allow for floc formation to occur is equally variable.

For trial 3, pH control was examined due to the sharp spike in pH after ferrate (VI) was added into solution during trials 1 and 2. With acid addition, color of the solution changed from characteristic purple of iron (VI) to the yellow-brown color of iron (II /III), with floc formation occurring immediately. pH control through acid addition seems to present appreciable results, with an obvious change in turbidity reduction efficiency compared to the previous trials (**Table 3**). Further work needs to be performed to determine if oxidation is truly occurring with the organic components of the SPW at all dosage levels used within this study. Analysis at this current stage was not able to be performed due to the initial high salinities and low organic loading that prevented accurate COD or TOC (total organic carbon) results.

Further refinement of treatment pathway

Following the results and feedback received on trials 1-3 for experimental setup, trial 4 was used to examine the removal efficiency of ferrate (VI) without buffer or pH control. While some gains in TRE could be had with pH control, maintaining the pH at an appropriate level proved difficult using acid addition. Examination of the Pourbaix diagram of iron suggested an explanation of observed phenomena for earlier trials

(Figure 8). When adding the acid or maintain the pH through a buffer, the ferrate (VI) was shifted to aqueous $Fe^{2+ / 3+}$ or complexed (with the buffer) rather than the desired iron hydroxide species precipitating out. Turbidity would then increase as colloidal iron particles formed into solution, preventing coagulation from occurring. As noted by Lv et al. (2018) and Zheng & Deng (2016), this would explain the earlier increases in turbidity as buffers and pH control was employed. Trial 4 tested a higher turbidity SPW under no pH control following a refinement for dosage mixing time and for floc formation. Ferrate (VI) was allowed to readily decompose to lower valency species and then to ferric hydroxide, while pH was monitored but not adjusted. After settling, every trial and salt concentration level had profound reductions in turbidity compared to previous trials (**Table 5**). The gradual decrease in efficacy in trial 4 for the 4 M concentrations can be attributed by the interactions by the dissolved ions, similar to what other studies have documented (Sharma et al., 2001; Talaiekhozani et al., 2017).

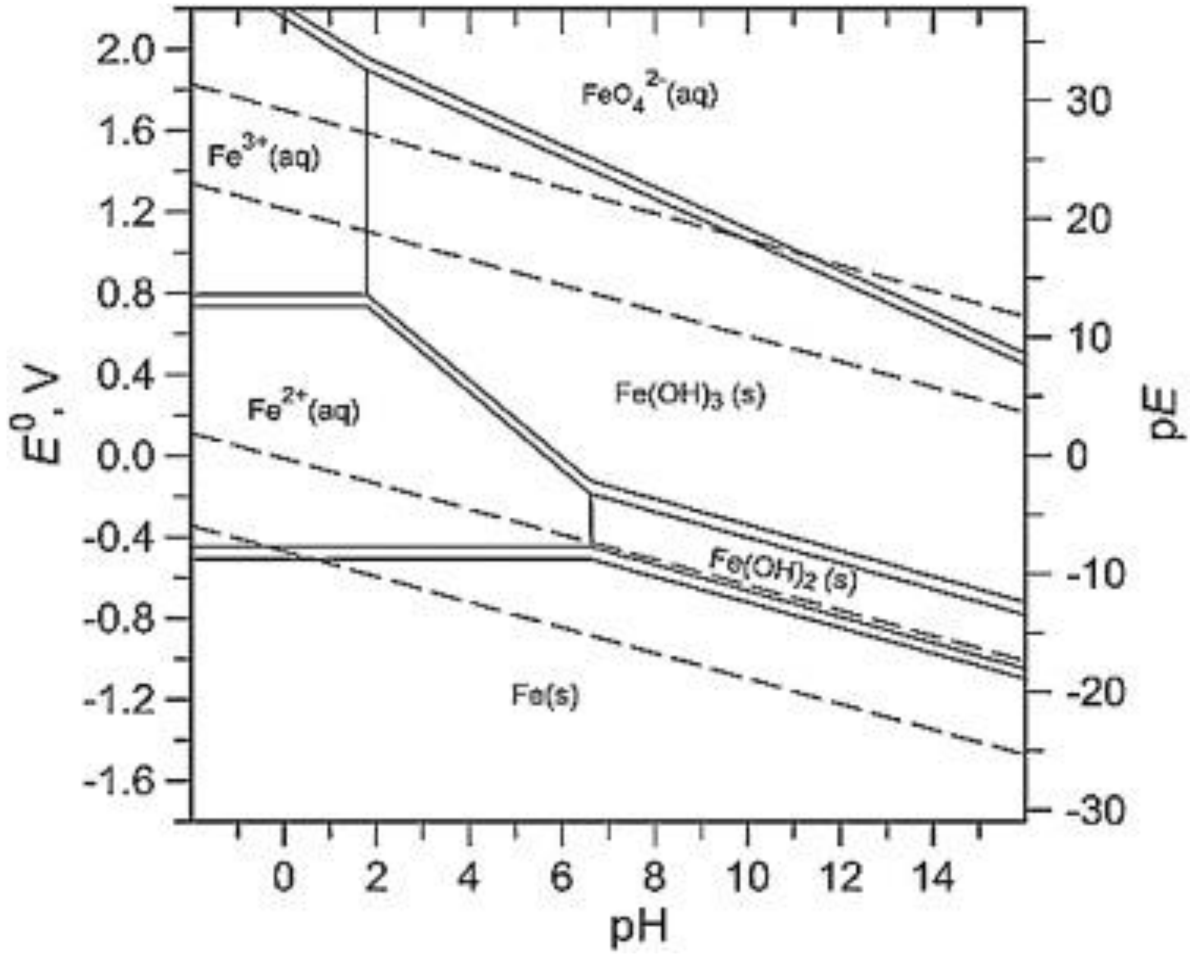

Figure 8: Pourbaix diagram of 1 M solution of Fe, (reprinted from Graham et al. (2004) with permission from Elsevier).

Trial 5 represented the culmination in refining the treatment procedure. Dosage was selected based on studies from Han et al. (2019) and Zheng & Deng (2016) who both used a 5 mg/L as Fe for treatment. While initial turbidities were increased compared to trial 4, the effectiveness for turbidity removal was not diminished (**Table 6**). Removal of turbidity to an average of 3.27 NTU presents an excellent opportunity for this treated water to be used for other purposes, although further work needs to be performed in examining the minimum dosage and reactant pathway needed for oxidation for more recalcitrant compounds present within produced water.

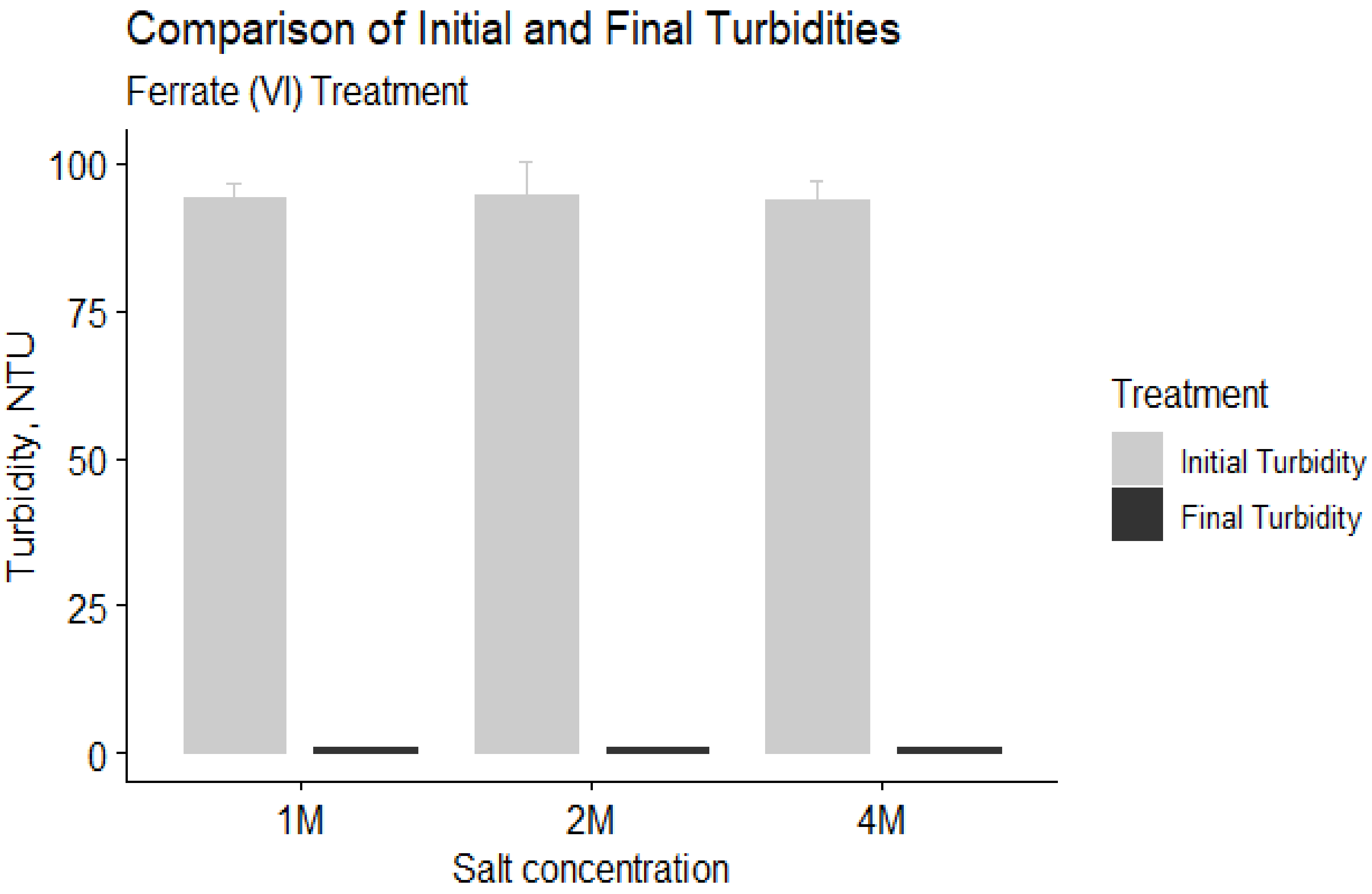

Figure 9: Comparison of turbidities with ferrate (VI) treatment

Statistical analysis of results for ferrate (VI) treatment

In order to determine if the initial salinity had an effect on the removal efficacy of the ferrate (VI), nonparametric analysis was used to analyze the final turbidities between each salt concentration level. An initial testing of assumptions from Levene's test for equality of variances indicated that the assumption of homogeneity of variance was violated (F = 11.289, p = 8.726 e-05), so nonparametric analysis was used.

Kruskal-Wallis rank sum test was used to determine if there were significant differences in final turbidities between salt concentration levels. Final turbidity was statistically affected by initial salt concentrations, H (2), p (1.283e-09) (Figure 10). Pairwise comparisons using Wilcoxon rank sum test (Holm correction) for post-hoc testing further indicated that all three salt concentrations were distinct from each other (**Table 9**).

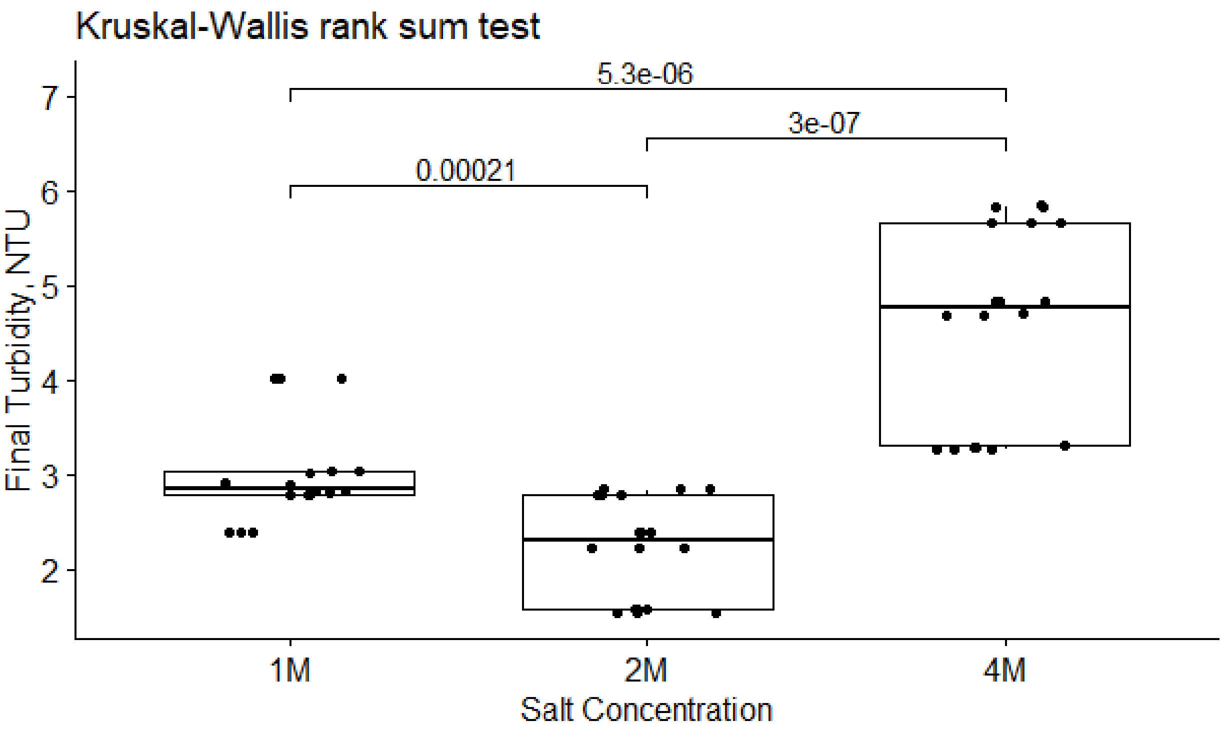

Figure 10: Kruskal- Wallis rank sum test for final turbidities

Table 9: *Pairwise comparison Wilcoxon rank sum test*

Pairwise comparisons using Wilcoxon rank sum test, Holm correction

	1M	2M
2M	1.967e-05	NA
4M	1.051e-05	8.902e-07

SOLVENT EXTRACTION OF PRODUCED WATER

Preliminary solvent extraction of treated produced water

For trial 2, despite an increase in turbidity after ferrate treatment, solvent extraction was able to reduce turbidity by 77% when compared to initial turbidity. As noted before, if the comparison was made to the supernatant collected, solvent extraction would show a reduction efficiency of 87%. Trial 3 show an average reduction of 95% of turbidity following solvent extraction when compared to initial turbidity, and reduced salinity by an average of 62% percent, although a wide variation in reduction rates was observed. Turbidity and Salinity reduction was evaluated as an efficiency formula where C_f is the reading after treatment, and C_i is the initial reading before treatment:

$$\text{Turbitidy/Salinity Reduction, TRE/SRE} = 1 - \left({}^{C_f}\!/_{C_i} \right)$$

Solvent extraction for salinity reduction appears to be in agreement with published literature, although further work needs to be performed in examining if residual solvent present in solution would increase the apparent salinity. Turbidity reduction efficiency of the solvent is unsurprising given the solvent’s preference for water; residual iron hydroxide, and colloidal clay particles were concentrated into the raffinate. Similar to the salinity, residual solvent may be to blame for what turbidity was reported but given that values were under 4 NTU with minimum values under 1.5 NTU, we feel that solvent extraction may present a potentially novel method of treating highly turbid waters.

The efficiency of the solvent to final water produced (at each treatment level) was expressed as a ratio of water volume (milliliters) to solvent mass (grams):

$$Solvent\ Efficiency, SE = {}^{V_{water}}\!/_{M_{solvent}}$$

Comparisons of raffinate volumes with final product waters indicates that a sizable portion of water remains in solution to solvent (at 1 M 8% unrecovered, ~24% for 2 M and 4 M), although this could be attributed to method of heating the solvent-water mixture. More elaborate setups such as using a simple distillation would eliminate this discrepancy but would increase treatment cost.

Further refinement of solvent process

As noted in the methodology section, progress in examining the molecular movement of solutes and salts (Choi et al., 2019, 2021) provided possible explanations to experimental results and improvements to future studies. Here, in the trial 5 a shorter hydration time between solvent and brine was employed while under mixing conditions following the insight provided by the continuous flow process employed by Choi et al. (2021). While this study did not employ a mixing condition to the degree that Choi et al. (2021) did (140 RPM orbital shaker vs 600/700/800 RPM impeller with unknown retention time to solvent-water extraction), the improvement in water recoveries from previous trials for both volume and final salinity cannot be understated. Rejections of 94.73% to 98.94% of feed salt concentrations within one hour at a temperature shift of 40 – 60 ºC highlights the ability for directional solvent extraction to produce near-consumable water (**Error! Reference source not found.**, Figure 12). While the results of this study do not entirely align with either Boo et al., (2019) or Choi et al. (2021) for recovery volumes or final salinities, it should be noted that at this current point further optimization of solvent hydration conditions and solvent choice seems to be the likeliest path forward for better results. A final product water of roughly 3000 ppm could be further extracted with a solvent exchange, passed through to more well-established desalination (such as reverse osmosis), or through consumer filtration systems.

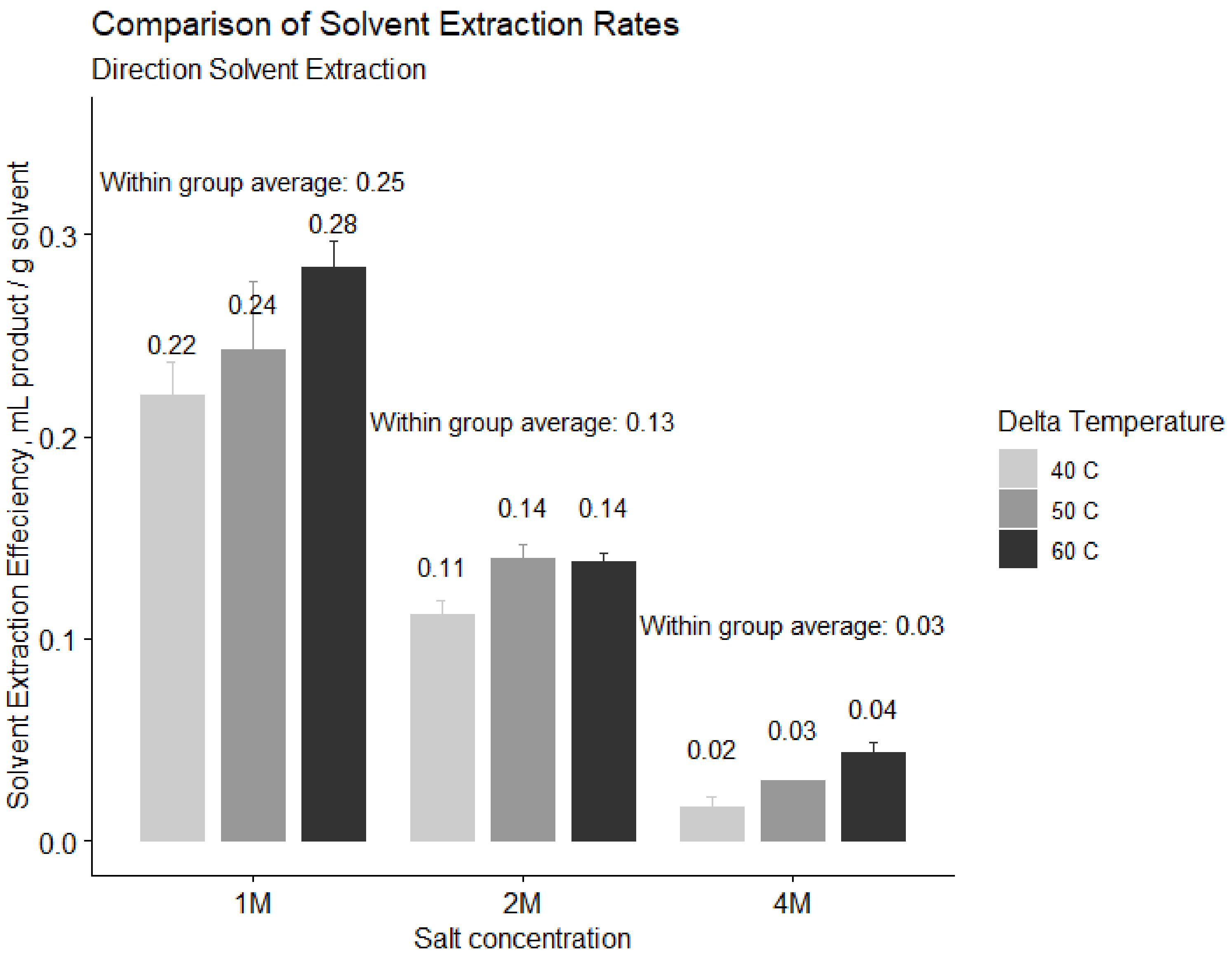

Figure 11: Comparison of solvent extraction efficiency rates, by salt and delta temperature. Labels indicate sub-group average, within group average.

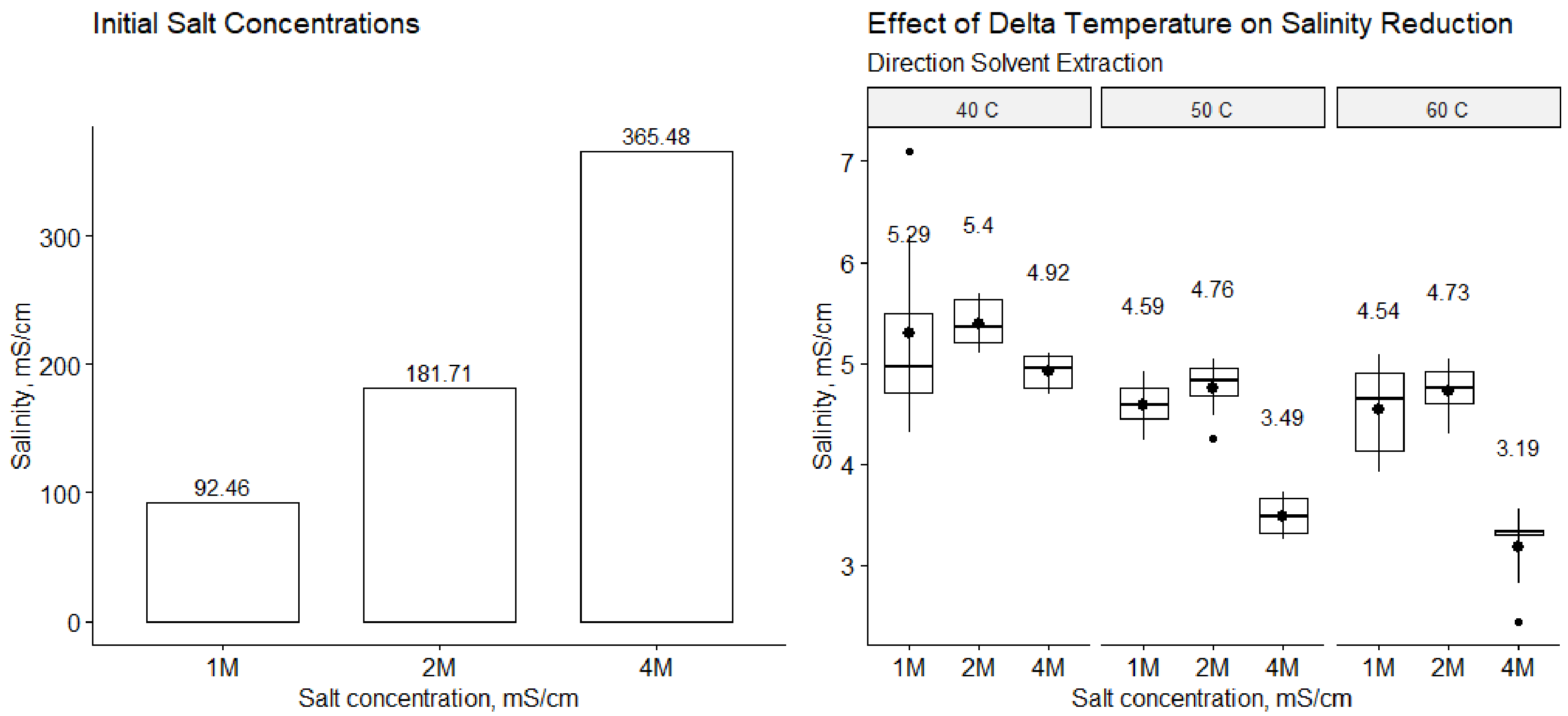

Figure 12: Effects of delta temperature on salinity reduction. Labels reflect average values for measurements.

Statistical analysis of results for DSE treatment

Analysis of the efficiency of the DSE treatment by salt concentration level and delta temperature (the difference from the low to high temperatures used) was performed through linear regression. An initial test for homogeneity of variance using Levene’s test with an interaction of salt concentration and delta temperature showed that all levels of salt concentration were homogenous for variance: F (1.9941), p (0.06904). Normality was assessed using Shapiro-Wilk’s normality test: W (0.84417), p (5.481e-06). Two-way ANOVA was carried out on the recovery rates by salt concentration and delta temperature. There was a statistically significant interaction between the effects of salt concentration and delta temperature on recovery rates: F (8,45) = 563.91, p (< 2.2e-16) (**Error! Reference source not found.**). Within group ANOVA comparison is indicated on Figure 12, with significance levels noted as well. Post-hoc testing using Tukey multiple pairwise-comparisons indicated that all three salt concentration levels were distinct from each other ($p < 0.05$), but there was some within-group interaction for the delta temperature for recovery rates.

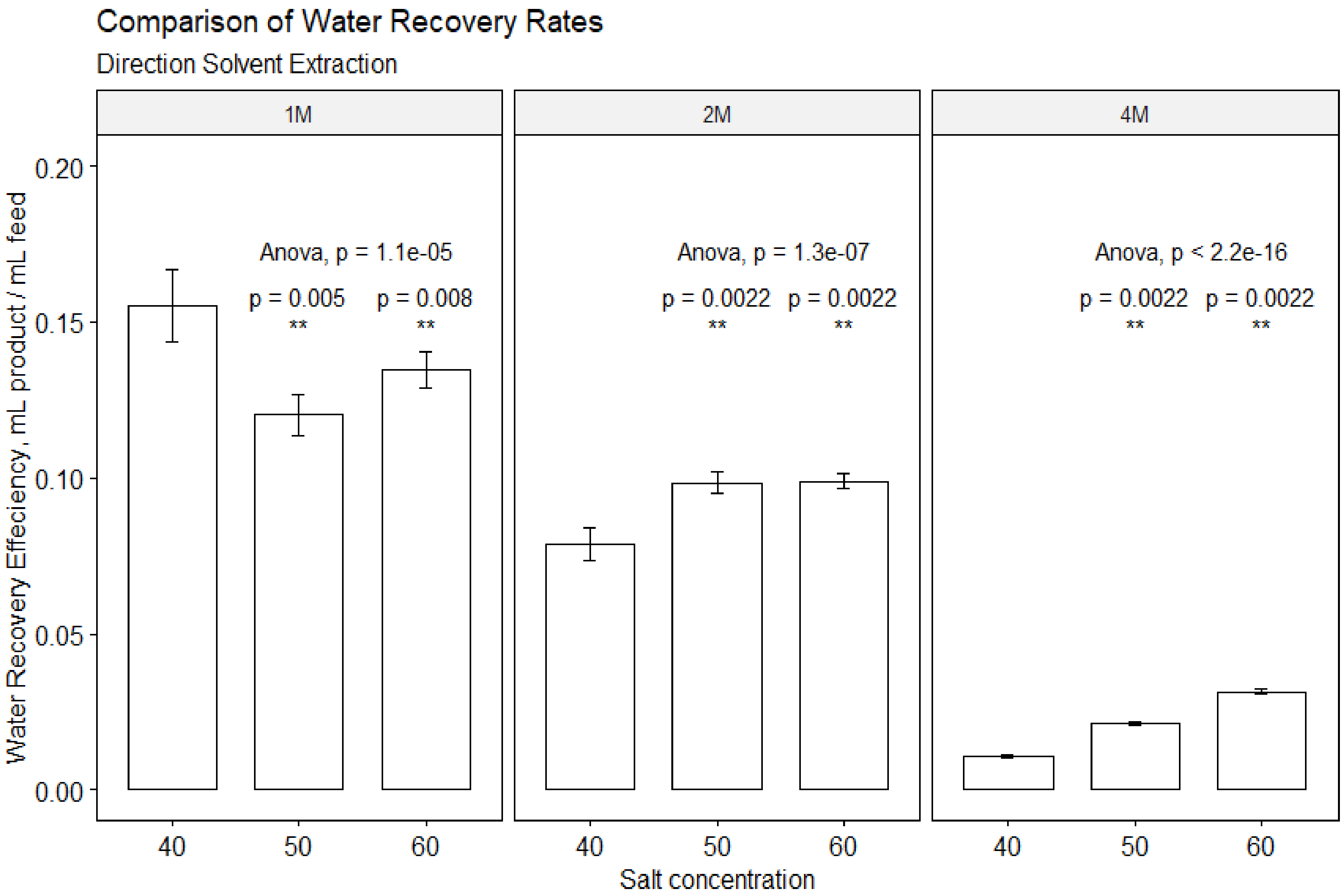

Figure 13: Comparison of water recovery rates by salinity and delta temperature. Significant differences between results are indicated with symbology and p-values.

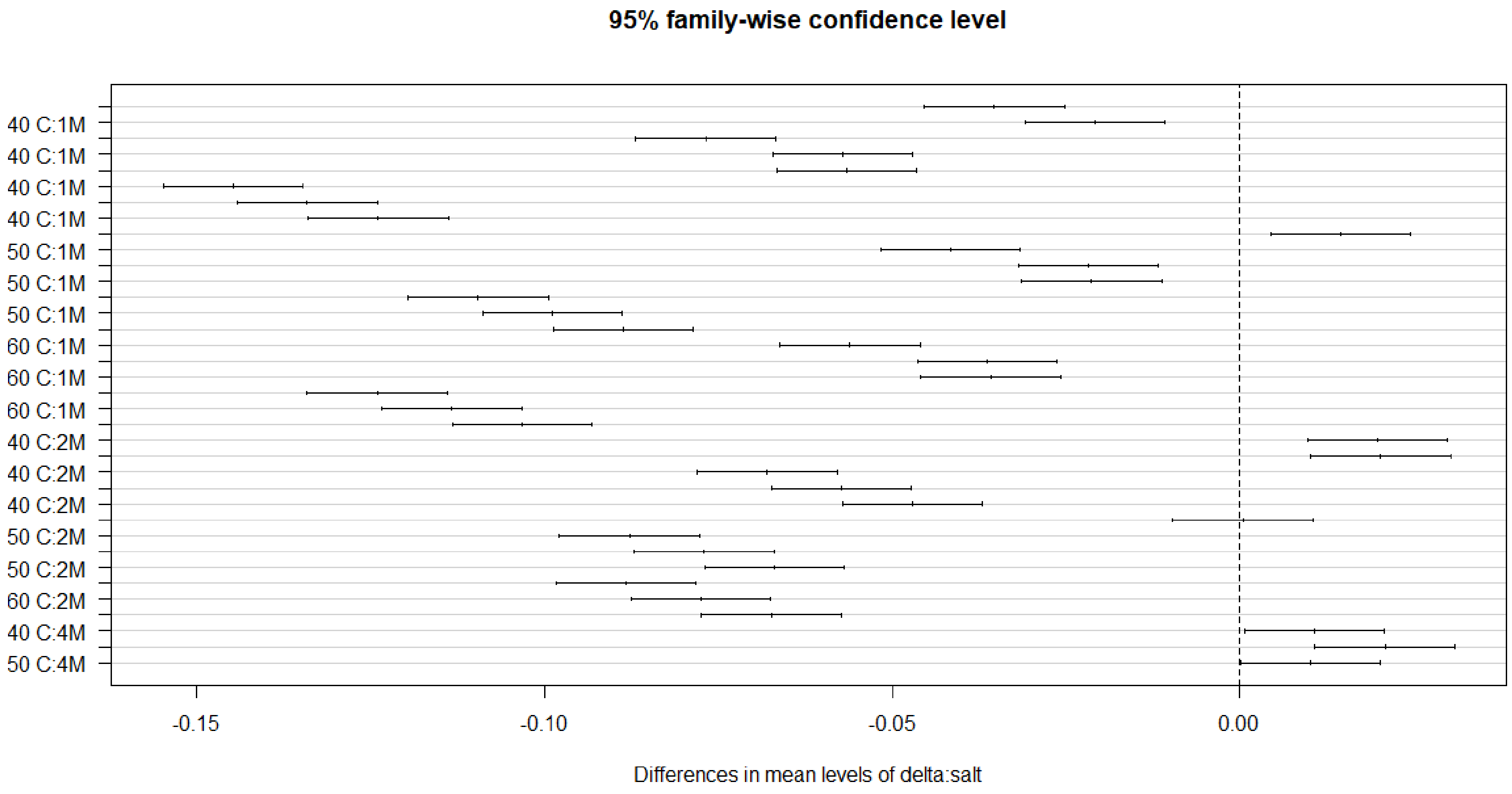

Figure 14:Results of Tukeys HSD post-hoc analysis.

Economic cost analysis

In order for this treatment regime to be considered beyond the experimental phase, a projected cost per treatment volume should be examined. As this treatment regime is functionally two distinct processes, a cost for pretreatment and then for solvent extract can be calculated using a variety of industry, commercial, and experimental values. Obviously, short of a pilot scale implementation, these costs merely provide a preliminary benchmark against the conventional technologies listed in **Table 1** and **Table 2**.

Ferrate (VI) proposed costs

Ferrate (VI) treatment cost can be distinguished by two main factors: synthesis and dosage. As noted by Talaiekhozani et al. (2017), production of a pure product is highly dependent on the reagents and synthesis pathway. The “wet oxidation” method produced relatively high purity (96%) at a low cost but is highly unstable and must be used immediately. Other electrochemical reactors have been considered, with low proposed costs ($0.02/g : Quino-Favero et al., 2018), although the scalability[14] of such efforts is unexamined. Currently, the best case for treatment cost comes from a presentation given by T.D Waite of Ferrate Solutions, Inc (Ferrate Solutions, 2021, and personal communications). He indicates that the proposed treatment cost is estimated at $0.07/ mg/L. We feel this is the best-case scenario for large-scale implementation of

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[14] While difficult to verify, there was a press release (2008) indicating that the synthesis company Battelle in conjunction with a start up was able to reduce the price down to $2.00 per gram (or $0.002 per mg) using a proprietary electrochemical reactor at high purity and volumes, but no further record of the product is able to be found for commercial implementation. Jiang et al. (2018) documents a pilot and full-scale implementation for a municipal wastewater treatment process, but no breakdown on cost is explicitly declared.

ferrate (VI) for immediate usage and use it as our cost for this treatment process. Should cheaper synthesis pathways become more available, this would drastically reduce the cost per treatment.

Directional solvent extraction costs

Directional solvent extraction's proposed costs are easier to project due to underlying operating conditions compared to ferrate (VI) dosage. DSE takes advantage of a low heat gradient and a solvent that has a temperature- dependent solubility. Cost per treatment is a calculation of the specific heat capacity of the solvent and the water. Boo et al. (2019) calculated the energy needed to create 1 m^3 from a 1.5 M brine[15] with a 50% recovery using DIPA (with heat recoveries of 80 and 90%) to be 77 - 39 kWh/ m^3 (respectively). Choi et al. (2021) using a similar solvent (DPA) was able to bring the cost to 5 – 6.9 kWh/ m^3 (95% heat recovery) for a saline solution through simulation.

If we use an additive specific heat capacity calculation for using DIPA to create 1 m^3 from the various salt concentrations, we can estimate the cost to range from 259.2 kWh/ m^3 – 3011.62 kWh/ m^3, with no heat recovery. With heat recoveries ranging 80 - 95%, the energy cost can be brought down to 15.77 – 602.32 kWh/ m^3. We attribute this range to two factors: the amount of solvent needed to extract an amount of water at a given salt concentration; as salinity increases, the amount of solvent needed[16] increase. Secondly, as salinity of the feed increases, DIPA seems to benefit from larger temperature swings. Despite that, even as efficiency may increase with the increase in

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[15] Repeated extraction on the 1.5 M brine until 50% recover of water was achieved.

[16] Not calculated here, but this calculation presumes a single work-cycle rather than reconcentrating the raffinate to further extract water out of it.

ΔT, the corresponding energy costs potentially outweigh the marginal volume produced. If DSE is to be viable, a solvent with a lower specific heat capacity must be used or significant heat recovery operations employed.

Total proposed treatment cost and comparison to other treatments

Using assumption laid out in the two previous sections, a total cost per treatment volume can be assessed. A dosage of 5 mg/L as Fe for ferrate (VI) at the Ferrate Solutions, Inc. synthesis cost was selected, and the cost for electricity for the directional solvent extraction was assessed at $0.09. The total cost with a variety of heat recoveries against the aggregation of other treatment technologies (from **Table 2**) are summarized in **Table 10**.

Costs are highly dependent on cost of ferrate (VI) synthesis, ferrate (VI) dosage, salt concentration of solution, employment of heat recovery processes, and at which ΔT C for DSE extraction occurs. 1 M brines follow seem to be less sensitive to increases in ΔT, while 2 M and 4 M brines benefit from increasing ΔT as salinity increases; lowest costs were achieved at ΔT of 50 and 60, respectively (**Error! Reference source not found.**). This is theorized to be a result of the propensity of the solvent to retain water even after a dehydration cycle. These values also align with calculations performed by Boo et al. (2019) when accounting for differences in water extraction efficiencies . **Error! Reference source not found.** and Figure 16 show the massive difference in energy to produce 1 m^3 of water, with the respective mass amounts of solvent needed, determined through interpolation for a single-pass operation. Beyond this initial scale, a continuous process could be used where the solvent is successfully regenerated (as proposed in Figure 1).

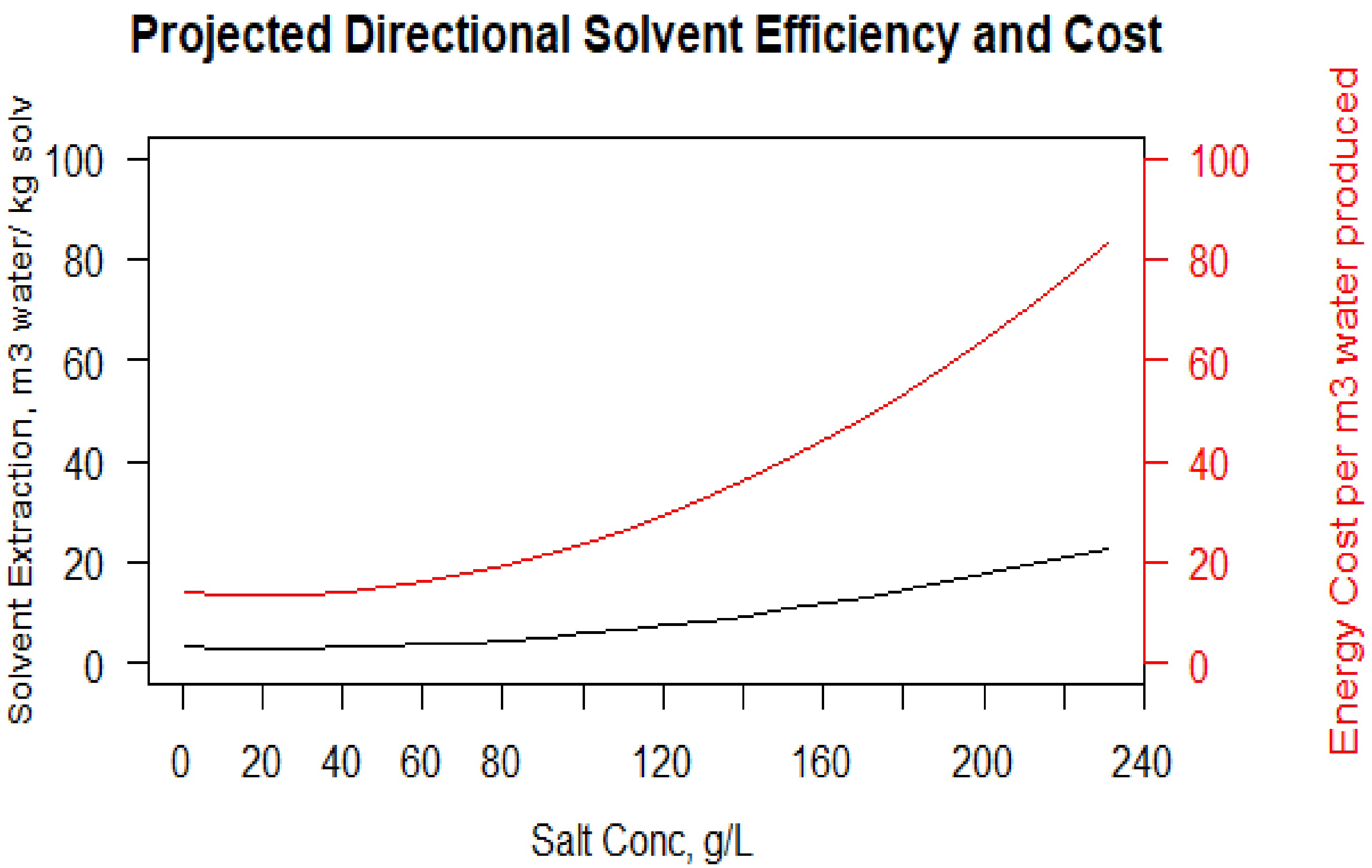

Figure 15: Projected DSE and energy cost (kWh) with 95% HR at 50C dT to create 1 m3 of water.

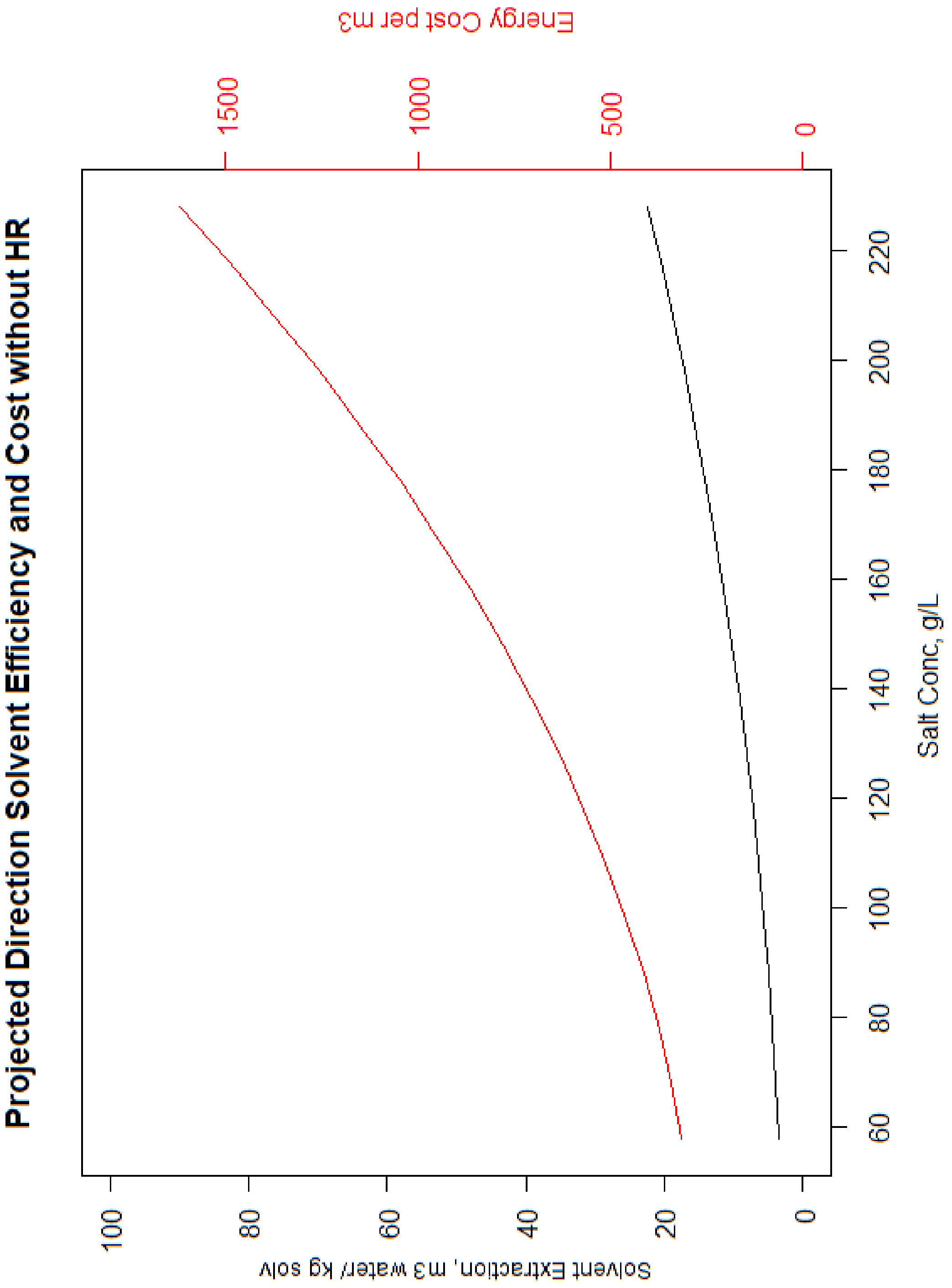

Figure 16: Projected DSE and energy cost (kWh) without HR at 50C dT to create 1 m3 of water

***Table 10**: Projected treatment cost per unit volume*

Management option	**Min Cost ($/bbl)**		**Max Cost ($/bbl)**
Disposal	0.30		22.00
Reuse or recycle	0.05		26.25
Chemical treatment	0.02		2.30
Membrane treatment	2.50		3.50
Thermal technologies	0.10		105.00
Biological treatment	0.01		2.00
	ΔT 40 C	**ΔT 50 C**	**ΔT 60 C**
Fe (VI) [5 mg/L] + DSE, 1 M, 80% HR	0.76	0.84	0.92
Fe (VI) [5 mg/L] + DSE, 1 M, 90% HR	0.39	0.43	0.47
Fe (VI) [5 mg/L] + DSE, 1 M, 95% HR	0.20	0.22	0.24
Fe (VI) [5 mg/L] + DSE, 2 M, 80% HR	1.38	1.35	1.62
Fe (VI) [5 mg/L] + DSE, 2 M, 90% HR	0.70	0.68	0.82
Fe (VI) [5 mg/L] + DSE, 2 M, 95% HR	0.36	0.35	0.42
Fe (VI) [5 mg/L] + DSE, 4 M, 80% HR	8.63	5.80	4.87
Fe (VI) [5 mg/L] + DSE, 4 M, 90% HR	4.32	2.91	2.44
Fe (VI) [5 mg/L] + DSE, 4 M, 95% HR	2.17	1.46	1.23
Fe (VI) [5 mg/L] + DSE, 1 M, No HR	3.72	4.14	4.53
Fe (VI) [5 mg/L] + DSE, 2 M, No HR	6.83	6.68	8.05
Fe (VI) [5 mg/L] + DSE, 4 M, No HR	43.11	28.95	24.29

As noted in **Table 2** and **Table 10**, the costs for treatment, including this proposed process, range quite extensively. To be better visualize the possible niche where ferrate (VI) and DSE compete with, a plot of possible values was created using sources from the literature (Figure 17). Currently, DSE occupies in many of the same ranges of TDS that other technologies do, but some notable advantage can be had with better solvent selection and process design. Some of these competing technologies are well established but cannot tolerate the higher salinities or various other constituents that produced water comes with. Other technologies may be relegated to a zero-liquid discharge role and may come with exorbitant energy costs. Finally, some technologies like DSE may still be in the conceptual role, and not quite ready for implementation.

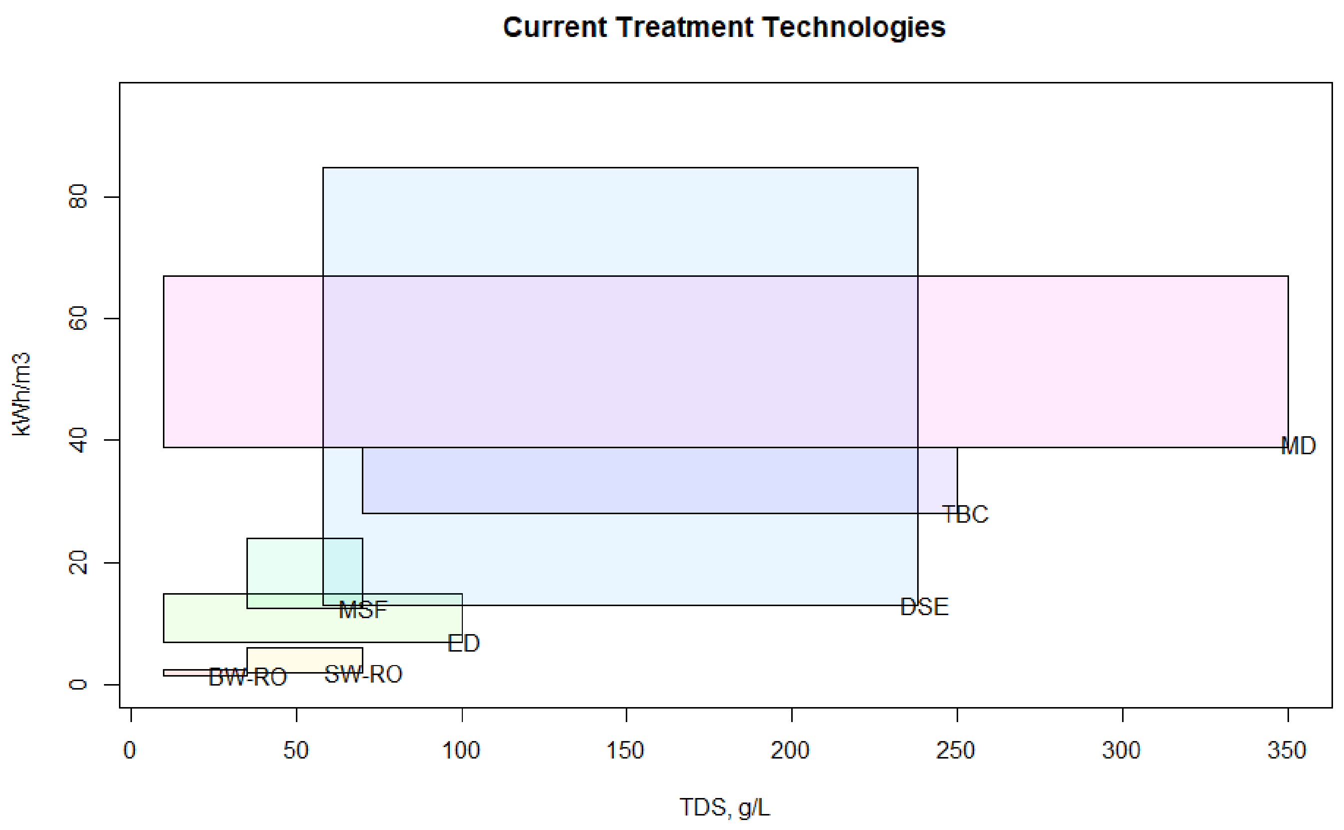

Figure 17: Comparison of emerging, currently used, and experimental technologies for treating salt waster at a range of TDS values

BW-RO: Brackish Reverse Osmosis (RO)   SW-RO: Seawater RO

MSF: Multistage Flash   ED: Electrodialysis

DSE: Directional Solvent Extraction   TBC: Thermal Brine Crystallizer

MD: Membrane Distillation

LIMITATIONS OF STUDY

Composition of SPW were limited to a number of constituents for a variety of reasons. As noted before, it is impossible to test the full range of probable compositions that produced water could contain. Therefore, study was limited to a reasonable range of values that would presumably be encountered based on published literature.

Order of treatment processes

It is currently theorized that the order of the current treatment regime (i.e.: ferrate (VI) then solvent) is the only route that mitigates the constituents of concern. Of greatest importance, the (chosen) oil phase is soluble in the solvent and it is currently unknown how it affects the solvent's performance for water extraction in the long-term. The oil phase could feasibly be removed from the solvent using a (later) fractional distillation separation, but it remains equally unexplored in this particular context. Usage of the solvent first would also presumably help in reducing the overall salinity and organic loading of the water to be treated by ferrate, but there are other concerns. The solvent is more susceptible to reduction/ oxidation reactions from the ferrate (VI) rather than the oil phase and would form a variety of compounds if the ferrate (VI) were not fully neutralized. This reaction would not only form potentially toxic water-soluble compounds but would also reduce the available volume of solvent for water extraction on the next cooling-heating cycle, which would defeat the initial premise of the directional solvent extraction process.

Ferrate dosage

The currently used methodology of measuring the concentration of the ferrate solution has several issues to overcome. When dissolving the dry ferrate salts into water, incomplete dissolution is a common outcome. Common techniques for improving saturation of a solution such as more vigorous stirring, raising the solute temperature, increasing volume of solute all work against the preparation of the ferrate stock solution. When more vigorous stirring occurs, the ferrate will start to prematurely decompose to iron hydroxide, probably due to introduction of atmospheric oxygen being incorporated and reacted with. Raising the temperature of the solute will also initiate premature decomposition, while adding more solute merely lowers the concentration of the dosage.

With respects to the dosage to be added into the SPW, it is important to consider the underlying parameters for application. Within this study, it was not investigated to determine the upper range of concentrations that can be dissolved into solution from a dried ferrate (VI) preparation. As with the determination of initial concentration of the stock solution, other methods of preparation of the ferrate salts (Ciampi & Daly, 2009) may similarly yield better results for purity and volumes.

Next, as this study is functionally a small volume, batch reactor and not continuous flow implementation, the volume of ferrate relative to the volume of solute (and perhaps the buffer concentration) needs to be considered. With the relatively small volumes (e.g.: 300 mL) for the SPW in conjunction with (potentially) higher concentrations of ferrate, the volumetric amount of the dissolved ferrate dosage will have a profound impact on the initial salinity and turbidity. More simply, the SPW would be watered down. This additional volume of solute (nominally water) would need to be accounted for as it would influence the second half of the treatment process. Work by Boo et al. (2019) has suggested that the solvent has higher recovery volumes of water at lower salinities but in this case may require a greater volume of solvent to be needed (as the presumption is that equal molar proportions are used between brine and solvent). As an example, in an early set of the trials a 300 mL SPW brine was used. In order to deliver a 12 mg/L as Fe dose, 100 mL of concentrated ferrate stock solution would need to be added to correctly dilute down the ferrate. This would effectively reduce the initial salinities from 1 M, 2 M, and 4 M to 0.75 M, 1.5 M, and 3 M brines. This additional volume of water has profound impacts on the efficacies for usage of ferrate for oxidation and coagulation, but also the performance of the solvent. Both are affected by the initial salinity and turbidity present, and it is difficult to truly separate out the effects of a (relatively) large addition of solute volume when total volumes are low. While not used here, we would propose that ferrate (VI) is either synthesized on-site using the preferred wet oxidation methodology, and concentrations determined by ABTS absorbance suggested by Lee et al. (2004).

Solvent and constituent interactions

At this time, it is not fully understood the interactions between some of the constituents and the solvents, and the long-term effects on the performance of the solvent. Of primary concern, the oil phase’s preference to being adsorbed into the solvent (rather than the water) proves to be both an experimental and operational concern. If the ferrate pretreatment does not fully remove the oil phase from the water (both surface oil as well as suspended microparticles), the solvent will adsorb the oil and retain it. To fully separate out such a mixture, a fractional distillation removal may be needed. No interaction is expected between the solids (e.g.: clay, sand) phase of the SPW and solvent.

CHAPTER VI: CONCLUSIONS

Assessment of ferrate (VI) efficacy

Ferrate (VI)'s usage in this waste stream appears to be justified given the removal efficiency and low treatment cost per volume. The by-product produced is easily removed through conventional filtration and does not affect subsequent processes. Additionally, when properly applied the ferrate (VI) breaks suspensions that would potentially affect the DSE portion of treatment. Ferrate (VI) application in this limited set of trials demonstrated high removals of turbidity at affordable doses.

Assessment of DSE using DIPA

DIPA presents a good candidate for DSE for hypersaline solutions, and results align with relevant research within the DSE field for desalination. Of note, under improved and differentiated operating conditions DIPA showed improved salt rejection rates and higher water recovery rates. DSE has the potential to fill a treatment void where in addition to water recovery from produced water, conventional treatments for desalination, zero liquid discharge, and environmental remediation are not entirely viable due to energetic costs.

Economic justification of combined treatment process

This combined treatment pathway shows promise in being a viable treatment technology. When compared to other treatment technologies, the cost per treatment volume does appear to compete against (and displace) established processes. In some cases, the treatment cost is not entirely competitive, but we feel that as the perception towards water usage and waste stream production management within this industry shifts, this has strong potential to be a flexible option given the relative simplicity. We acknowledge that not all aspects of the combined process have been fully examined, namely the full influence of ferrate (VI) dosage on constituents or energetic costs for DSE, but this study presents a preliminary examination for future work.

Recommendations for future work

For future research, more examination is needed in both treatment processes. While well-established within the literature for municipal and emerging contaminants, there is little work in assessing ferrate (VI)'s ability to oxidize under the highly saline conditions or target the extensive list of contaminants that produced water contains. Of interest, reduction in the radionuclides, heavy metals, and non-alkane hydrocarbons are suitable targets for ferrate (VI), especially when considering dosage. Additionally, the interaction between ferrate (VI) and solvent needs to be addressed to optimize treatment pathways; ferrate (VI) may present as an ideal candidate to remove residual solvent present with product water, if end-products are safe for consumption. While the cost of ferrate (VI) remains a high barrier to adoption, further work justifying ferrate (VI)'s usage will incentive researchers in developing novel solutions for synthesis and delivery.

Solvent choice and treatment parameters also seem like likely targets for optimization given the disparate influence they have on cost per treatment. As noted, many groups are working on selection of a solvent that produces water at high volumes with low salinity and at a low energetic cost. Amine- based solvents seem to be able to support this, but further work into the molecular movement of salts and solutes into the solvent layer present equally interesting questions to be answered. Further research is also needed as to the determination of movement of hydrocarbons into the solvent layer and how that affects long-term efficacy.

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