

Bench-Scale Investigation of Treatment Technologies for Flowback Fluids from Shale Gas Fracturing

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Abstract: This paper presents the results of the investigation of flowback fluids treatment from shale gas fracturing by bed sorption, reverse osmosis, and electrocoagulation. It was found that the bed sorption experiment with 1:3 ratio of vermiculite:zeolite was effective at improving the quality of the flowback fluid sample with an overall reduction in Na^+ level of 7.50%, EC of 2.40%, and Cl^- of 1.31%. The two membrane in series configuration combined with the ClO_2 pretreatment achieved a 92 % salt rejection concurrent with a 93 and 90% of Cl^- and Na^+ reduction in the permeate. For the flowback sample containing guar in the matrix, electrocoagulation operated in batch mode yielded decrease in turbidity ranging from 43 to 98%, TSS from 54 to 86%, and COD from 61 to 76%. Management options and priority risk index for disposal options were also ascertained.

Key words: hydraulic fracturing, flowback, salinity, reverse osmosis, bed sorption, electrocoagulation

1. Introduction

Hydraulic fracturing, also referred to as fracking, is a well stimulation technique used by Oil and Gas industry to recover natural gas from deep shale or other unconventional formations. Normally, fracking is performed only once in the life of a well. Increase in natural gas extraction around the world is being driven by rising energy demands, mandates for cleaner burning fuels, national security, and the congruence economics of energy use. Shale formations can provide access to very large quantities of natural gas. While considered as both a significant source and reservoir rock for hydrocarbons, shale is a sedimentary rock composed of clay mineral and fine-grained siliciclastic particles deposited over millions of years under variable heat and pressure [1].

Fracking fluids are complex mixtures composed of gelling, foaming stabilizing and iron controlling agents,

corrosion inhibitor, pH adjuster, clay stabilizer, surfactant, binders, breakers and proppant such as sand, silica, quartz [2]. These chemical additive systems may be used in various formations to improve the flow of fluid, kill bacteria that can potential reduce fracturing performance, thicken or thin the fluid matrices. These chemical additives are injected at high volumes and pressure into the deep well to open the fractures in the formation that further triggers the flow of natural gas to the wellbore [3] Once the fracture is completed, the pressure drops and the zone settles down on the proppant but does not close. The thixotropic characteristics of the fluid dissipates and the water flows back to the surface over time [4].

High-volume hydraulic fracturing operations result in two types of waste streams known as flowback and produced water; that is a combination of returned fracture fluids and natural water from the formation. Each waste stream has a distinct chemical composition accompanied by naturally occurring substances, depending upon the location of the well site. Flowback consists of a mixture of chemical additives and natural occurring substances that comeback to surface

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following the hydraulic fracturing operations. Produced water on the other hand, is the combination of the fluid mixtures that return to the ground surface after gas well production and generated throughout the lifespan of the well [4]. Flowback period usually lasts for up to few days to few weeks and the volume is contingent on the geologic formation, and operating procedures. Current estimation states that approximately 10-40% of the fracturing fluid flows back to the surface as flowback and produced water [5].

As hydraulic fracturing activities increase, so are related environmental problems and concerns especially pertaining to management of water streams that are contaminated. Water requirements for typical hydraulic fracture operation may vary widely, but on the average requires several millions of water per well. Obtaining the water necessary for use in shale or unconventional gas development is progressively challenging operators to find new innovative and sustainable ways to secure reliable, affordable, and supplies of water. Besides, significant water volume sourcing, highly saline flowback and produced water cannot be discharged to its original ecosystem because the sourced water once used does not meet the parameter criteria as it relates to the Canadian Council of Ministers of the Environment [6]. The most common method of managing wastewater is storage in enclosed tanks with secondary containment [7] while underground injection of both flowback and produced water in saline aquifers is a common practice [8].

Unconventional gas drilling also requires a massive number of trucks to haul equipment and water to and from drilling sites while drilling trucking costs for water can be one of the biggest expenses. The disposal of the flow back is of great concern since the fracking process contaminates millions of gallons of water used at each drill site with an array of chemicals that may be carcinogenic. Since most of that water is currently hauled away to be injected into deep disposal wells, there is concern that this highly contaminated water will migrate into existing aquifers actively used for

domestic purposes or may discharge in surface water bodies. Given the excessive costs involved in water procurement and management throughout the process of shale gas development, the proposed research investigated potential treatment solutions. The primary aim of this study is to evaluate various treatment methods for treating flowback wastewater fluids that will allow their potential reuse for hydraulic fracturing in tight hydrocarbon formations at various stages of hydraulic fracking operations. More specifically, this will create the potential opportunities to reduce freshwater consumption and therefore act as resource in the quest for achieving operational sustainability.

2. Material and Methods

2.1 Flowback Sources

The two sources of the flowback fluid samples were collected during the final stage of hydraulic fracturing operations conducted in the Montney Formation, NE BC and Central Alberta, the Caroline-area, respectively. The Montney Shale Formation lithology is rich in natural gas, liquids and mainly composed of silt, siltstone, limestone with varying degrees of dolomitization. This brittle composition of the lithology contributes to successful hydraulic fracturing operations. The surface to the top depth of Montney Formation ranges from 500-4500 m that further increases from northeast to southwest [1]. The Duvernay Formation is a stratigraphical unit of Frasnian age in the Western Canadian Sedimentary Basin. It is present in the sub-surface in central Alberta and reaches a maximum thickness of 250 metres east of Lesser Slave Lake [9]. It is composed of laminated bituminous shale calcareous shale and dense argillaceous limestone. Pyrite disseminations are common while calcarenite and coral rich mudstone are also present. A total of 30 L of contaminated hydraulic fracturing fluid samples originated from the Montney Formation were collected in 3 × 10 L HDPE, labelled (Frac MF) and capped with a six cm ID plastic lid. Similarly, 4 × 30 L fluid samples from the Durvernay

Formation were retrieved, identified (Frac DF) and each container was then capped. The Frack DF fluid matrix is marked by the unique variability of elevated concentration of the residual gelling agent guar, a polysaccharide. Guar is an effective fluid loss control additives because of its colloidal property and high molecular weight (Fig. 1). One of the most important characteristics of guar is its ability to develop viscosity in fresh water and brine. It is also integral to the successful cooling of cementing slurries and drilling bits during drilling operation.

The handling of the two sources of the flowback fluid samples was conducted in the same manner. Review of both, the Duvernay and Montney Formations fracking operations indicated that the guar agent was used only in the Duvernay Formation in drilling fluids program.

Samples collected in the field were stored with ice that maintained the cooler temperature around $5^{\circ}\text{C}\pm 2$. The temperature was monitored with an alcohol thermometer placed inside of the cooler. The samples were subsequently transported to the Mount Royal University (MRU) Environmental Science Laboratory in Calgary and stored in the fridge at $4^{\circ}\text{C}\pm 1$. Once in the laboratory, all samples from each respective site were consolidated, labelled and homogenized in a 30 gal HDPE container. The two containers were then stored in a cold room at $6^{\circ}\text{C}\pm 1$. Each container was gently stirred for about three minutes with a PVC rod to allow collection of representative subsamples for the experiment.

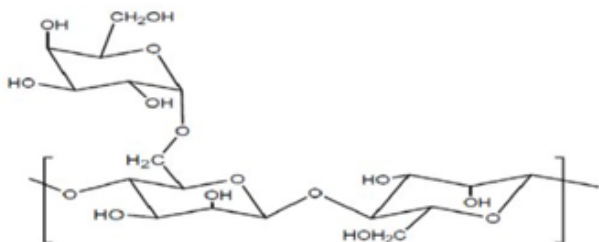


Fig. 1 Basic representative chemical structure of guar gum.

2.2 Analytical Program/Chemicals

All the chemicals used in the study were reagent grade. Each consolidated raw sample was initially characterized for various chemical and physical properties by a commercial laboratory located in Calgary. Target constituents of interest because of strategic environmental concerns are summarized in Table 1 along with the methods and the quality assurance and control (QA/QC) of the testing program. Additionally, QA/QC program included duplicate, method blank, method blank spike and matrix spike. The chemicals of concern as it pertains to the study were TDS, COD, TSS, EC, turbidity, chloride ion, Ca, Mg, Na, K. Reagents to generate ClO_2 as the oxidizer were acquired from Twin Oxide Canada Corporation. It involves using a two component method of acid and chlorite combination according to the following reaction: $5 \text{NaClO}_2 + 4 \text{HCl} \leftrightarrow 4 \text{ClO}_2 + 5 \text{NaCl}$. The TwinOxide system typically generates a ClO_2 solution with a purity of 99%. Chlorine dioxide solutions of 500 ppm were prepared in distilled water, stored in the cold in a dark plastic bottle at 5°C . The solution was used within a few hours of preparation.

2.3 Experimental Treatment Design

Due to the complex nature of flowback fluids, various treatment methods were investigated. These methods were configured within the framework of achieving optimum treatment efficiency. These various methods are briefly narrated in Table 2.

2.3.1 Bed Sorption

This treatment method was used for treating the Frack MF flowback sample. The bed sorption set-up consisted of a clear plexiglass column of 7 cm in ID and 20 cm deep packed with natural vermiculite and zeolite composite as the sorbent materials (Fig. 2). The zeolite was purchased from the Beaver River Zeolite Company, Preston, Idaho, USA, and was used in its natural forms. The vermiculite is commercially marketed by Holliday®. Three different ratios of vermiculite:zeolite (V: Z) consisting of: 1:1, 3:1 and

1:3, respectively. A total of 80 g of sorbents composite of a desired ratio was allowed to equilibrate for 30 minutes with 200 ml of the frack water matrix sample before effluent collection is initiated. Effluent was then collected at various time intervals in a graduated cylinder. Collection of treated effluent was conducted

at 10 minute intervals, corresponding to total running time of 39, 45, and 90 minutes, respectively. Effluent collected for each time interval was labelled and stored in the fridge at 5°C for subsequent analysis. The analysis consisted of Ca²⁺, K⁺, Mg²⁺, Na⁺, EC, and Cl⁻.

Table 1 Summary of parameters QA/QC.

Parameters	Methods	QA/QC
pH	Orion Ag/AgCl glass probe	As specified by manufacturer
EC*	Tracer PockeTester	As specified by manufacturer
TSS**	Photometric	As specified by manufacturer in proceduresmanual for Hach DR/2010
COD***	Nephelometric	As specified by manufacturer in proceduresmanual for Hach Turbidimeter Model 2100 A
Turbidity	Nephelometric	As specified by manufacturer in proceduresmanual for Hach Turbidimeter Model 2100 A
TDS****	Tracer PockeTester	Accuracy check as specified by manufacturer
SO ₄ ²⁻	Turbidimetric	Accuracy check as specified in proceduresmanual for Hach DR/2010
Ca	Atomic absorption	Accuracy check as specified by Perkin Elmer in User's Guide manual for Model 3110
Mg	Atomic absorption	Accuracy check as specified by Perkin Elmer in User's Guide manual for Model 3110
K	Atomic absorption	Accuracy check as specified by Perkin Elmer in User's Guide manual for Model 3110
Na	Atomic absorption	Accuracy check as specified by Perkin Elmer in User's Guide manual for Model 3110

*EC, electrical conductivity; **TSS, total suspended solids; ***COD, chemical oxygen demand; ****TDS, total suspended solids

Table 2 Summary description of treatment methods used in the study.

<p>Bed Sorption: It involves a packed bed sorption column whereby dissolved contaminants are transferred from the liquid phase of contaminated water on a solid sorbent material with high surface area and sorbing capacity. Generally, the feed is pumped counterflow into the packing bed to minimize preferential flow. Alternatively, the feed may be introduced at the top of the contact bed with effluent flow controlled by a valve. As contaminated effluent flows through, contaminants are partitioned on the packed bed and removed from the effluent. A breakthrough concentration is reached as either the minimum detectable or maximum allowable concentration in the effluent from the bed.</p>
<p>Oxidative: As an oxidizer, chlorine dioxide (ClO₂) was used because it is a relatively strong, watersoluble oxidant, works well over a broad pH-range from 4-10. Additionally, it does not hydrolyze in water and does not appear to react favorably with natural humic material like in the case of chlorine. The later produces trihalo methanes in conjunction with some other harmful chemical by-products. By-products such as quinones and sulfonic acids may be potentially created by ClO₂. For practical considerations, quantity and types of by-products are generally dictated by concentration and type of humic material and concentration of ClO₂.</p>
<p>Electrocoagulation: It uses an electrical current connected to parallel electrodes and thereby produces ions into the water matrix. Oxidation leads to destruction of contaminants or reduce them to less toxic species. This process creates a combination of mechanisms operating synergistically to treat the contaminated water. The ions produced induce flocculation of dispersed contaminants in the matrix by zeta potential reduction. In addition, the hydrogen gas bubbles carry by adhesion colloidal pollutants to the top of the water. Suspended particles increase in size to form larger aggregates. These macroflocs will rapidly continue to grow in size to settle at the bottom or be removed from the treated water matrix by filtration. Choices of filter could be of any type.</p>
<p>Reverse Osmosis: In very simple terms, reverse osmosis (RO) uses a high pressure pump on the contaminated water side. The water molecules are forced through a semi-permeable membrane. The dissolved contaminants in the form of salts, heavy metals, organics, bacteria and pyrogens are not allowed through and are discharged through the concentrate stream. However, the water stream that was pushed through the membrane typically referred to as the permeate, contains very little contaminants and around 98% of the dissolved salts removed from its matrix. Reverse osmosis is one of the pioneer desalination technology and has emerged as one of the most prevalent seawater and brackish water desalination process.</p>

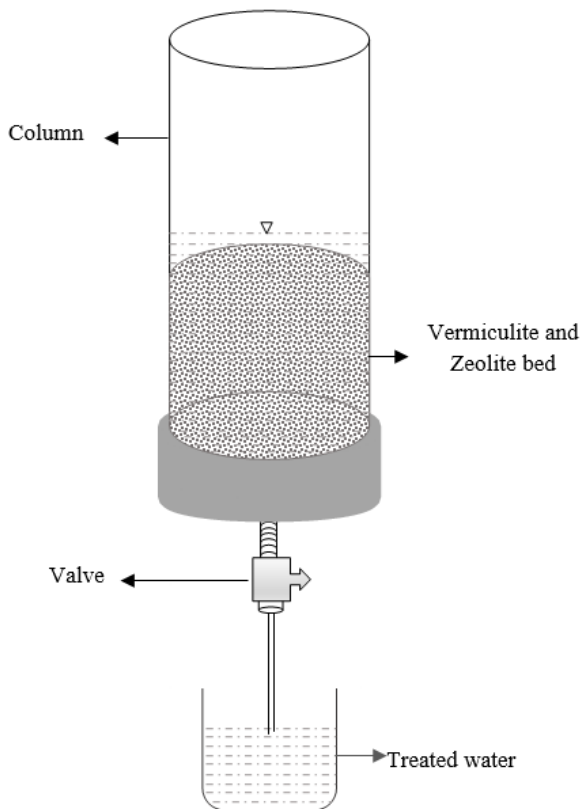


Fig. 2 Schematic diagram for vermiculite and zeolite bed sorption treatment (NTS).

2.3.2 Reverse Osmosis

(1) Single Crossflow Membrane Filtration

The DOW FILMTEC™ Brackish water membranes, model BW30-2540 used in the single membrane experiment, is manufactured by Dow® and commercially available. It has the following dimensions 2.5”×40” with 600 GPD capacity and operate at low pressure. The frack water stream was passed through the pristine column at a fixed pressure of 10, 12 15, 20, 23, 25, and 28 bar pressure and backwashed as per manufacturer specifications. Based on the tested operational flow rate, optimal flow rate could then be assessed. Both permeate and condensate were then collected for each run and analyzed for EC. Based upon EC reduction in permeate, 12 and 15 bar pressure were used for the final experimental set-up as shown in Fig. 3. A total of 7 and 10 L of saline water was treated at flow rates of 0.45 L/min (FR 1) and 0.7 L/min (FR 2) respectively. The condensate was collected and recycled as feed water for treatment.

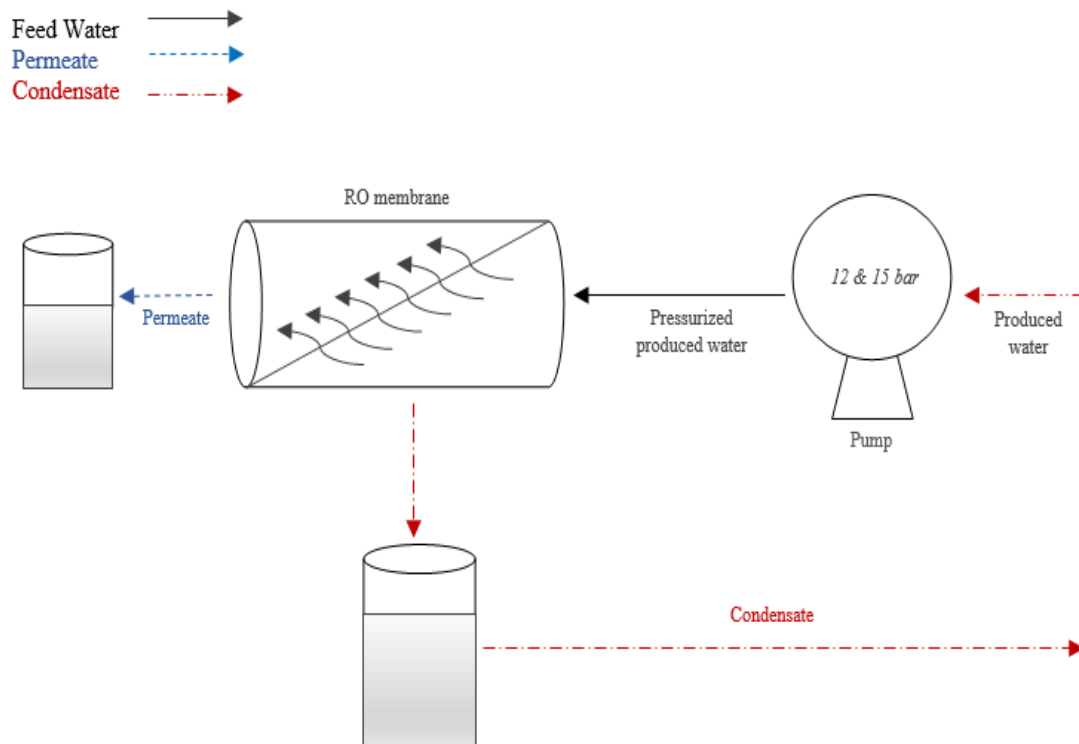


Fig. 3 Schematic diagram for reverse osmosis treatment using a single membrane (NTS).

(2) Crossflow Membrane Filtration in Series

DOW FILMTEC™ Brackish Water Membrane model LE-4040 is manufactured by Dow® and commercially available. The LE-4040 was 4"×40" with 2500 GPD capacity. Both membranes were configured in series and operated as low pressure membranes resulting in less energy usage and lower costs. Pre-treated frack water was passed through the membrane train at a single flow rate of 0.45 L/min and 12 bar pressure as shown in Fig. 4. Condensate collected from membrane 2 was recirculated as feed water through the system for treatment. Permeate from membrane 2 and condensate collected from both membranes 1 and 2 were analysed for pH, EC, TDS and Cl⁻, respectively.

The percent of salt rejection and recovery calculations for both single membrane and two-membrane treatments was calculated using the EC of permeate and original flowback water according to Eqs. (1) and (2), respectively:

$$\text{Salt rejection}\% = \frac{\text{EC of original sample} - \text{EC of permeate}}{\text{EC of original sample}} \times 100 \quad (1)$$

$$\text{Recovery}\% = \frac{\text{Permeate volume}}{\text{Total volume}} \times 100 \quad (2)$$

(3) Pre-Treatment of Flowback Fluid with ClO₂

RO technology faces a major challenge in form of membrane fouling as biological, crystalline, colloidal and organic can lead to a significant decrease in salt rejection and performance efficiency of the membrane. A suitable pre-treatment strategy was established for the Frack MF sample with objectives of controlling biofouling and maximizing efficiency in terms of permeate volume recovery, bacterial cell count reduction along with longevity of the membrane. Based on a literature review ClO₂ was found to be an effective inhibition of biofilm formation around 0.2 to 1 ppm residual concentration in the fluid matrix [10]. For the purpose of the experiment, 10 L of the Frack MF flowback fluid was pretreated overnight with a residual concentration of 5 mg/L ClO₂.

(4) Electrocoagulation Treatment

The 110 Volt electrocoagulation treatment unit is depicted in Fig. 5. It was used as a main technique for testing its feasibility at removing guar polymer and its derivatives from the Frack DF flowback fluid. The electrocoagulation treatment cell has a 0.50 L empty capacity and can accommodate a total of nine metal electrodes. Sacrificial anode and cathode were made of the same aluminum elemental metal. Each electrode has the following dimensions 3 cm wide × 36 cm long × 0.3 cm thick and fits in a 0.5 × 30 cm slot having 0.40 cm groove carved in the treatment cell. Electrode material strongly influences the nature of electrochemical reactions occurring in an electrocoagulation system. It is generally found that aluminum yields a higher level of treatment effectiveness [11]. All treatments in the reactor chamber were conducted with two aluminum electrodes configured in parallel. The gap between the two electrodes was 4 cm. Such gap allows to minimize significant ohmic change and the electrode overpotentials which may result in the fluid and the electrodes being over heated. In electrocoagulation, increase in temperature is directly proportional to the electrical power consumed.

The electrocoagulation cell was filled with a fix volume of 0.45 L of the flowback fluid Frack DF sample and batch treated by passing current across the metal electrodes. Since the treatments were batch operated, the batch reactor has neither inflow nor outflow of effluent during the treatment process. Noteworthy, the system can also be operated in continuous mode. In this study aluminum electrodes only were used, and the liquid waste has a pH of 6.5. These consequently favor the formation of aluminum hydroxide i.e., Al(OH)₃ as the coagulant. All the treatments under the operational conditions and listed in Table 3. Following the electrolysis time in the electrocoagulation reactor, the treated sample was directly transferred in a 2 L glass beaker, covered with parafilm and stored overnight, allowing the foam formed to coagulate at the bottom. The clear liquid was

then carefully transferred in a 2 L Erlenmeyer flask with a 60 m plastic syringe, parafilm and kept

refrigerated before being analyzed. All analyses were performed in duplicate and reported as average values.

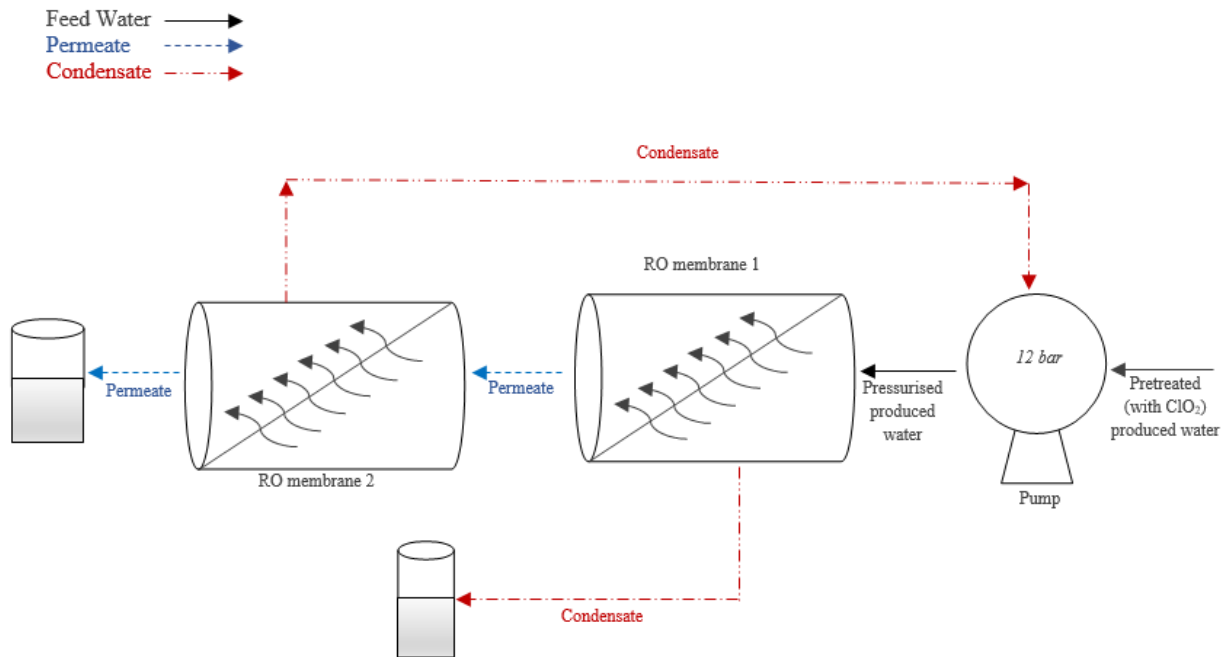


Fig. 4 Schematic diagram for reverse osmosis treatment in series configuration (NTS).

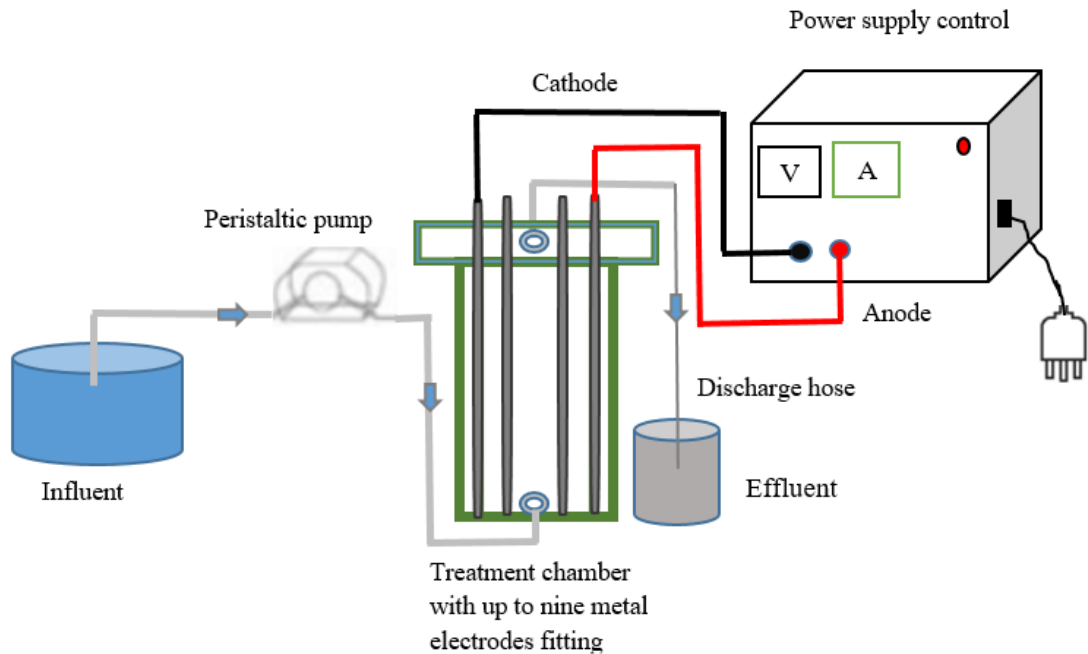


Fig. 5 Schematic diagram of the laboratory scale setup of the electrocoagulation unit (NTS).

Table 3 Treatment design for the electrocoagulation tests.

Variables	
Voltage (V)	Duration (Sec.)
5	15
	30
	45

10	15
	30
	45
18	15
	30
	45

3. Results and Discussions

3.1 Bed Sorption

Due to their high cation exchange properties, zeolite and vermiculite have been widely used adsorbents for wastewater management. In particular, zeolite is one of the adsorbent materials for separation and purification of wastewater [12] and to treat oilsands tailing pond wastewater, both in its natural and modified forms [13]. The bed sorption experiment primary goal was to evaluate its potential at decreasing the salinity level in the Frac MF sample. A total of nine effluent samples were collected for each run for the various treatments of vermiculite: zeolite (V:Z) composite ratios which resulted in at least 45% recovery of the influent. The

1:1 (V:Z) consisted of a total mixture of 80 g that was constituted of 40 g vermiculite and 40 g of zeolite. On the other hand 3:1 (V:Z) was 120 g vermiculite and 40 g zeolite while the 1:3 (V:Z) consisted of 40 g vermiculite and 120 g of zeolite. The removal of the main soluble salts for the various treatments are summarized through Tables 4-6, respectively.

The amount of treated effluent recovered from the performed treatments ranged from 35% for the 3:1 ratio to 55% for the 1:3 ratio while a 45% effluent recovery was obtained in the case of the 1:1 ratio. As shown through Tables 4-6, the results for the three ratios of vermiculite: zeolite treatments yielded significant variations as to the measured inorganic parameters Ca^{+2} , K^{+} , Mg^{+2} , and Na^{+} as well as in EC and Cl^{-} . The

Table 4 Effluents characteristics of 1:1 vermiculite:zeolite treatment.

Effluent ID	Volume collected (ml)	Cumulative time (min)	Ca	K	Mg	Na	Cl^{-}	EC
			mg/L					$\mu\text{S } 10^3$
V0	0	0	3570	1100	426	32100	64000	176
V1	10	1:46	3670	936	970	31695	64000	173
V2	10	4:35	4085	1123	1722	34919	80000	172
V3	10	8:50	3859	1054	1445	32193	56000	174
V4	10	15:54	3841	1075	1738	31674	65333	183
V5	10	33:51	3968	1148	1994	31624	68000	174
V6	10	48:15	4080	1147	2001	30837	68000	173
V7	10	67	4097	1158	2000	30094	80000	169
V8	10	72	4854	1461	2000	33363	66476	174
V9	10	90	4471	1348	1999	29612		

Table 5 Effluents characteristics of 1:3 vermiculite:zeolite treatment.

Effluent ID	Volume collected (ml)	Cumulative time (min)	Ca	K	Mg	Na	Cl^{-}	EC
			mg/L					$\mu\text{S } 10^3$
V0	0	0	3570	1100	426	32100	64000	176
V1	10	2:15	5189	2846	798	30315	80000	178
V2	10	4:45	5988	3427	682	31403	76000	174
V3	10	7:20	5336	2828	594	28248	88000	176
V4	10	10:15	5151	2771	574	28736	56000	172
V5	10	13.25	5002	2631	568	28639	64000	168
V6	10	17.00	4750	2387	548	27625	60000	166
V7	10	20.33	4653	2340	592	29565	56000	173
V8	10	24.11	4445	2169	623	29081	52000	166
V9	10	28	4904	2429	764	31981	40000	172
V10		32.30	4667	1986	784	30180	32000	172

Table 6 Effluents characteristics of 3:1 vermiculite:zeolite treatment.

Effluent ID	Volume collected (ml)	Cumulative time (min)	Ca	K	Mg	Na	Cl ⁻	EC
			mg/L					
V0	0	0	3570	1100	426	32100	64000	176
V1	10	1.06	3374	694	960	31827	56000	172
V2	10	2.41	3466	682	1055	32330	60000	172
V3	10	4.30	3756	735	1626	35098	56000	176
V4	10	6.34	3526	693	1369	32398	60000	175
V5	10	9.02	3966	795	1994	36761	60000	172
V6	10	29.46	3503	712	2000	30672	64000	173

concentrations of Mg⁺² in the effluent increased relative to the initial concentration in all of the three treatment ratios. Notably, Na⁺ concentrations were reduced markedly in the 1:3 ratio. On the other hand, concentrations of K⁺ in the effluents progressively decreased in the 3:1 ratio treatment but seemed to increase above the initial concentration observed in the original sample matrix for the 1:1 and 1:3 ratios, respectively. Contrary, Ca⁺² concentrations showed an increasing trend in all of the three ratios with a greater dip and rise in the 1:3 treatment ratio.

With the 1:1 ratio treatment, Na⁺ and EC were overall reduced by 1% and 1.13%, respectively, while Cl⁻ increased by 8.60% in the total effluent collected. Regarding the 3:1 ratio treatment, both EC and Cl⁻ were lowered by 1.40% and 3.05%, respectively, whereas Na⁺ by 4.40%. The data for the 1:3 ratio treatment shows an overall reduction in Na⁺ level of 7.50%, EC of 2.40%, and Cl⁻ of 1.31%. From a performance standpoint, it appears that the 1:3 ratio of vermiculite:zeolite provides a better treatment combination for improving the quality of the flowback Frac MF sample with respect of decreasing the level of the soluble salts Na⁺ and Cl⁻ as well as EC as a general indicator of the treated matrix salinity.

The variations observed in the measured inorganic parameters Ca⁺², Mg⁺², Na⁺, and Cl⁻ present in the collected effluents could be best attributed to a combination of factors. The later while are undoubtedly interactive may be take place concurrently rather than independently. Such factors may include

and may not be limited to competition for sorbing sites, charge and radius of hydration of an ion, adhesion followed by diffusion of the sorbate ions into the sorbents vermiculite and zeolite, rate of equilibrium between sorption/desorption, affinity of some ions vis-à-vis the sorbents, and mass action effect of an ion. The greatest reduction overall in a treated effluent salinity was achieved with the 1:3 ratio with an EC reduction of 2.40% for the total volume collected.

3.2 Reverse Osmosis Membrane

The results for the single crossflow membrane filtration for salt rejection % and volume recovery % are reported in Tables 7 and 8, respectively. Fraction 1 had a higher salt rejection at 77.10 % compared to fraction 2 at 68.40%. Recovery % was the highest with fraction 2 by 6% in comparison to fraction 1 (Table 8). Additionally, Cl⁻ was reduced by 69% in fraction 1 and 64% in fraction 2, respectively, while Na⁺ level was lowered in both fractions by 66%. The permeate and condensate fractions were both tested for NO₃⁻ as a parameter of interest and was not detected in any of the matrices. The results pertaining to the crossflow membrane filtration in series are highlighted in Tables 9 and 10, respectively. The flowback fluid was initially pretreated with a 5 mgL⁻¹ of ClO₂. The benefits of such pretreatment are a reduction in the wastewater turbidity and membrane biofouling during operation and long-term storage. Biofouling typically results in a decrease of membrane performance efficiency and longevity. Interestingly as a result of the ClO₂

pretreatment, condensate collected from both membranes had demonstrated considerable salt rejection. Nonetheless, the same level of salt reduction was achieved in the condensate and permeate originating from membrane 2. Overall, the two membrane train configuration combined with ClO₂ pretreatment of the fluid has resulted in substantial salt reduction (Table 10). Membrane 1 condensate salt

rejection was nearly 91% whereas both condensate and permeate from membrane 2 yielded a 92% salt rejection in comparison to the original wastewater matrix. However, a significant decrease in % recovery as permeate was observed and was calculated to be 5%. Furthermore, Cl⁻ and Na⁺ levels were reduced in the permeate by 93 and 90%, respectively.

Table 7 Salt rejection using a single RO membrane.

Parameter	Original wastewater	Fraction 1*		Fraction 2**	
		Condensate	Permeate	Condensate	Permeate
EC (μS)	176,000	53,000	40,300	40,300	55,600
Salt rejection (%)		69.89	77.10	66.88	68.41

*Fraction 1: flow setting at 0.45 L/min and 12 bar pressure using Masterflex I/P Easy-Load Pump

**Fraction 2: flow setting at 0.70 L/min and 15 bar pressure using Masterflex I/P Easy-Load Pump

Table 8 Recovery % of RO single membrane treatment.

	Total	Fraction 1		Total	Fraction 2	
		Condensate	Permeate		Condensate	Permeate
		Fraction-1C	Fraction-1P		Fraction-2C	Fraction-2P
Volume (L)	7 L	1.0	4.50	10	1.5	7.0
Recovery (%)			64			70

Table 9 Overall salt rejection% in two membrane RO train system.

	Unit	Original wastewater	Membrane 1	Membrane 2	
			Condensate	Condensate	Permeate
EC	μS	176000	16000	14000	14000
Salt rejection	%		91	92	92

Table 10 Total salt rejection % with ClO₂ pretreatment in two membrane RO train system.

	Unit	ClO ₂ treated	Membrane 1	Membrane 2	
			Condensate	Condensate	Permeate
EC	μS	61800	16000	14000	14000
Salt rejection	%		74.11	77.35	77.35

3.3 Electrocoagulation Treatment

This method has become a rapidly growing area of wastewater treatment. It is due to its ability to destroy or remove organic or inorganic contaminants that are typically difficult to treat by chemical treatment systems or remove by filtration. The electrocoagulation technique was applied to the Durvernay Formation frack wastewater source. The significant amount of guar used in this drilling program made this method

attractive. The initial characteristics of the flowback Frack DF fluid used are presented in Table 11. The effects of operating time and voltage changes with respect to removal efficiency (RE%) for turbidity, COD, and TSS, respectively, was obtained using Eq. (3):

$$\%RE = \frac{C_o - C_f}{C_o} \times 100 \quad (3)$$

where C_o and C_f represent the initial and final concentration, respectively.

Table 11 Initial characteristics of frack DF sample.

Parameter	Units	Value
pH		7.64
Turbidity	NTU	780
TDS	g/L	71.5
EC	mS	102
COD	mg/L	7000
TSS	mg/L	608

The results show that electrocoagulation has been effective at decreasing turbidity, COD and TSS in the treated fluid matrix. Guar was removed from the fluid as a whitish gelatinous precipitate. The efficiency increases with increasing voltage with treatment duration seemingly having the greatest effect on removal efficiency. This is likely due to a mass action effect of a continuous supply of electrons as the limiting agent required to exhaust the constituents in the matrix. Two main phenomena are known to occur in such instance. Formation of gas bubbles that entrain the colloidal constituents to the top of the wastewater liquid. These floating particles can then be removed from the top. Additionally, dissolution of the sacrificial anodes acting as a supply of metal hydroxide. Metallic ions react with OH^- generated at the cathode as a strong coagulant. The continuous evolution of insoluble hydroxides as a strong coagulant destabilizes and amasses particle constituents and this combined interaction makes electrocoagulation such an efficient technique. The overall reaction of adsorption of hydroxide on mineral surfaces is typically 100 fold greater on in-situ compared to precipitated hydroxides when metal hydroxides are used as the coagulant. As a final outcome, the process leads to the significant adsorption and removal of contaminants by precipitation out of the solution matrix. The dissolution rate of aluminum electrode at the anode and cathode is illustrated through the following reactions. The anodic oxidation reactions taking place at the anode: $2 \text{Al} \rightarrow 2 \text{Al}^{+3} + 6\text{e}^-$ while the cathodic reduction reaction occurring at the cathode: $6\text{H}_2\text{O} + 6\text{e}^- \rightarrow 3\text{H}_2 + 6\text{OH}^-$ resulting in $2\text{Al}^{+3} + 6\text{OH}^- \rightarrow 2\text{Al}(\text{OH})_3$. Expressing the

overall reaction according to Faraday's law: $\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3/2\text{H}_2$. Since the cathodic reduction reaction induces the hydrolysis of water, OH^- anions are released into the solution matrix with the potential of causing a pH increase and may help balance the pH to more alkaline levels.

Decrease in the various parameters is expressed in % RE in relation to the various treatments are depicted in Figs. 6-8. Turbidity, TSS, and COD generally decreased as voltage level and current duration increased. Decrease in turbidity ranges from 43 to 98%, TSS from 54 to 86%, and COD from 61 to 75%. Similar trends have been reported elsewhere [14-16]. Changes in the treated solutions pH were investigated. For the 5 V input of energy for the three treatment duration time, the average pH was 7.62 ± 0.026 ; at 10 V, the average pH was 7.32 ± 0.04 ; and at 18 V, it was an average of 7.35 ± 0.006 . However, an insignificant drop in the pH value was then observed with an increase in voltage which ranged from 0.12 ± 0.016 to 0.20 ± 0.009 . This may indicate a greater presence of H^+ in the solution relative to an increasing removal of OH^- and formation of organic acidic substances from the decomposition of guar in reactor. The greatest removal efficiency was observed under higher voltage and longer time.

Cost analysis plays an important role as a wastewater treatment technique should be cost attractive. The energy consumption of a treatment process can be calculated per m^3 of wastewater. The power consumption, P , (Wh/m^3) can be calculated using Eq. (4):

$$P = \frac{EIt}{V} \quad (4)$$

where E represents the cell voltage (V), I describes the ampere (A), t is the time of electrocoagulation in hour (h), and V is the volume of wastewater in cubic meter (m^3). The current density, C_d , (A/cm^2) was calculated for each treatment according to Eq. (5):

$$C_d = \frac{A}{E_a} \quad (5)$$

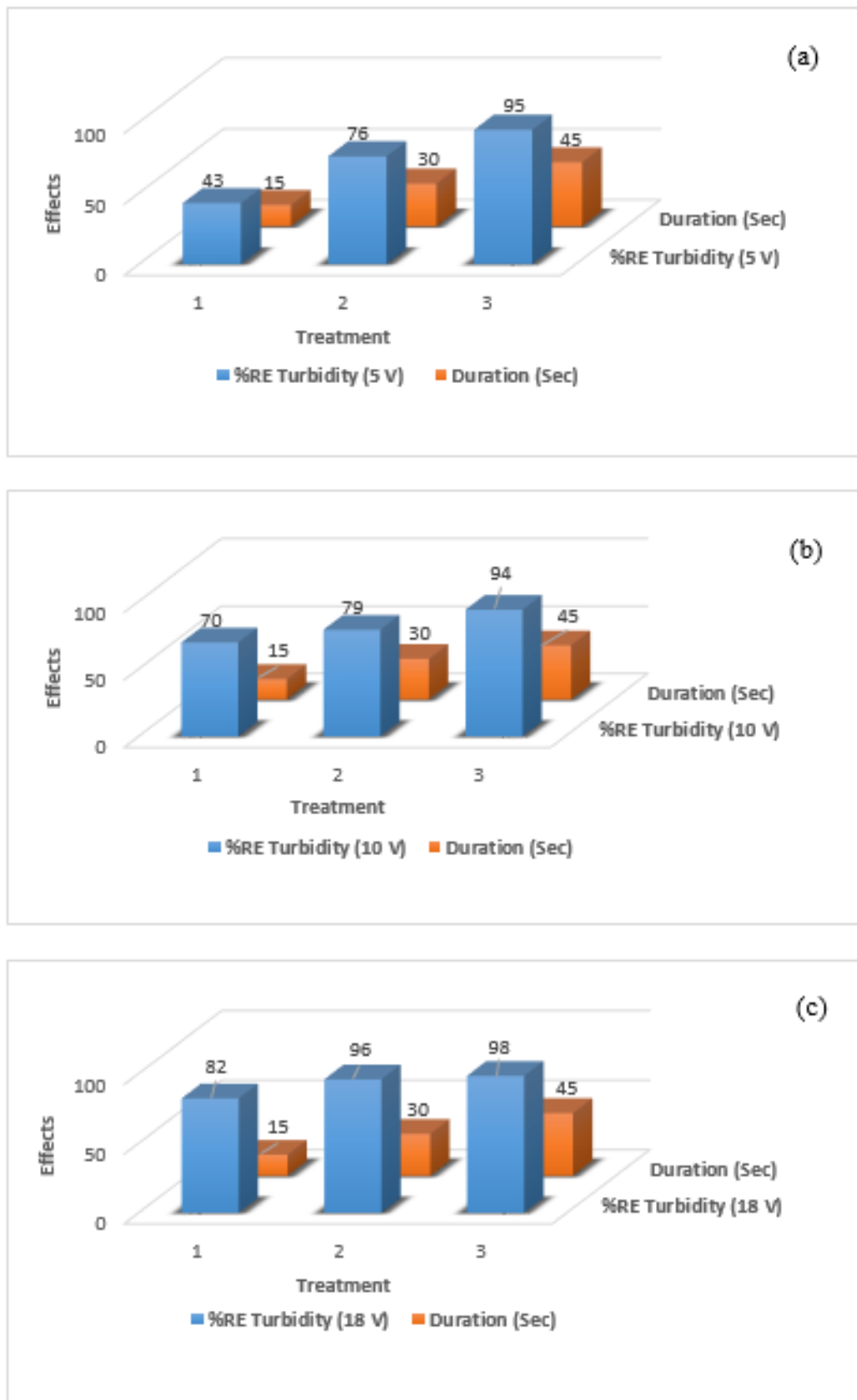


Fig. 6 Decrease in turbidity as related to voltage level and duration (a) (b) and (c).

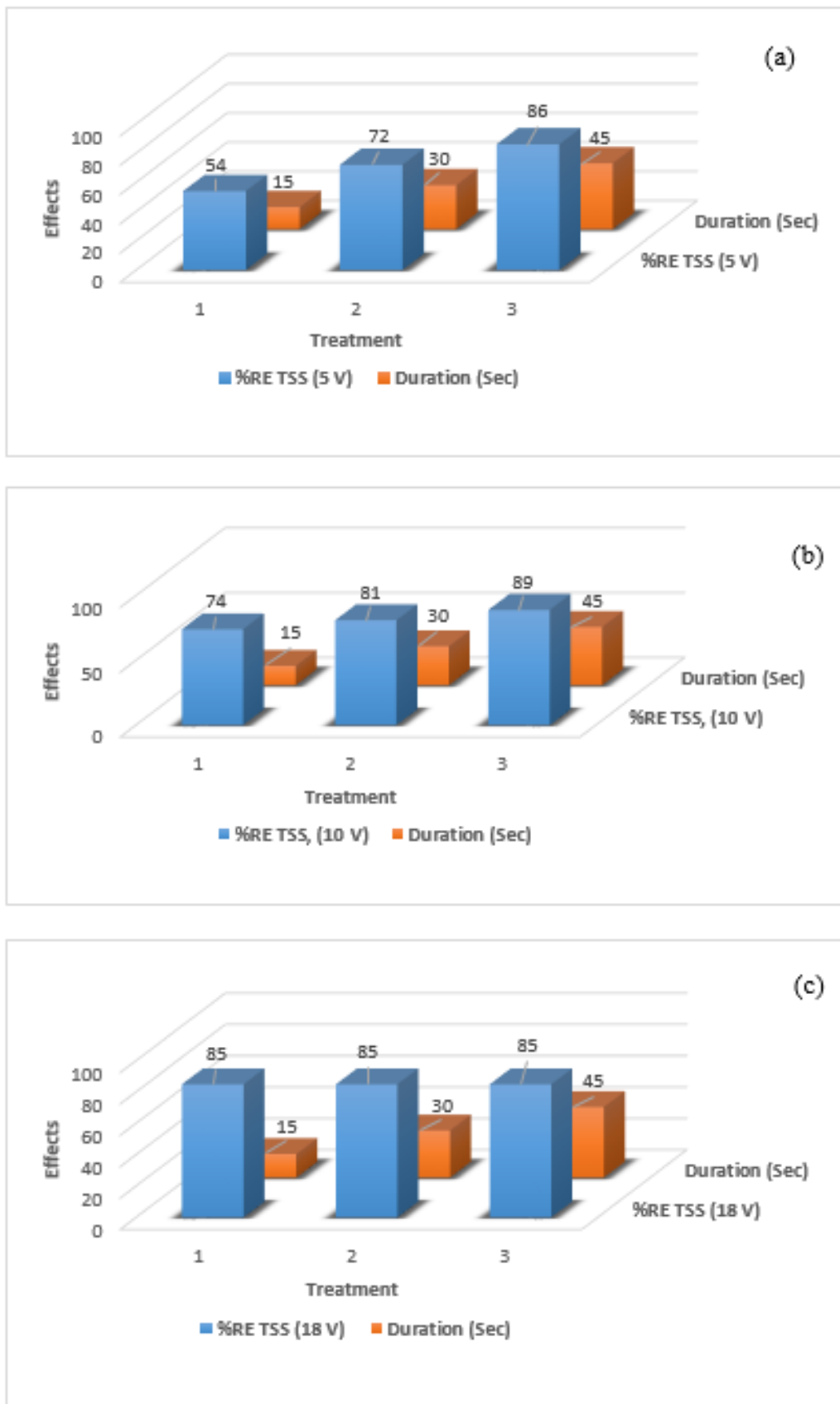


Fig. 7 Decrease in TSS as related to voltage level and duration (a) (b) and (c).

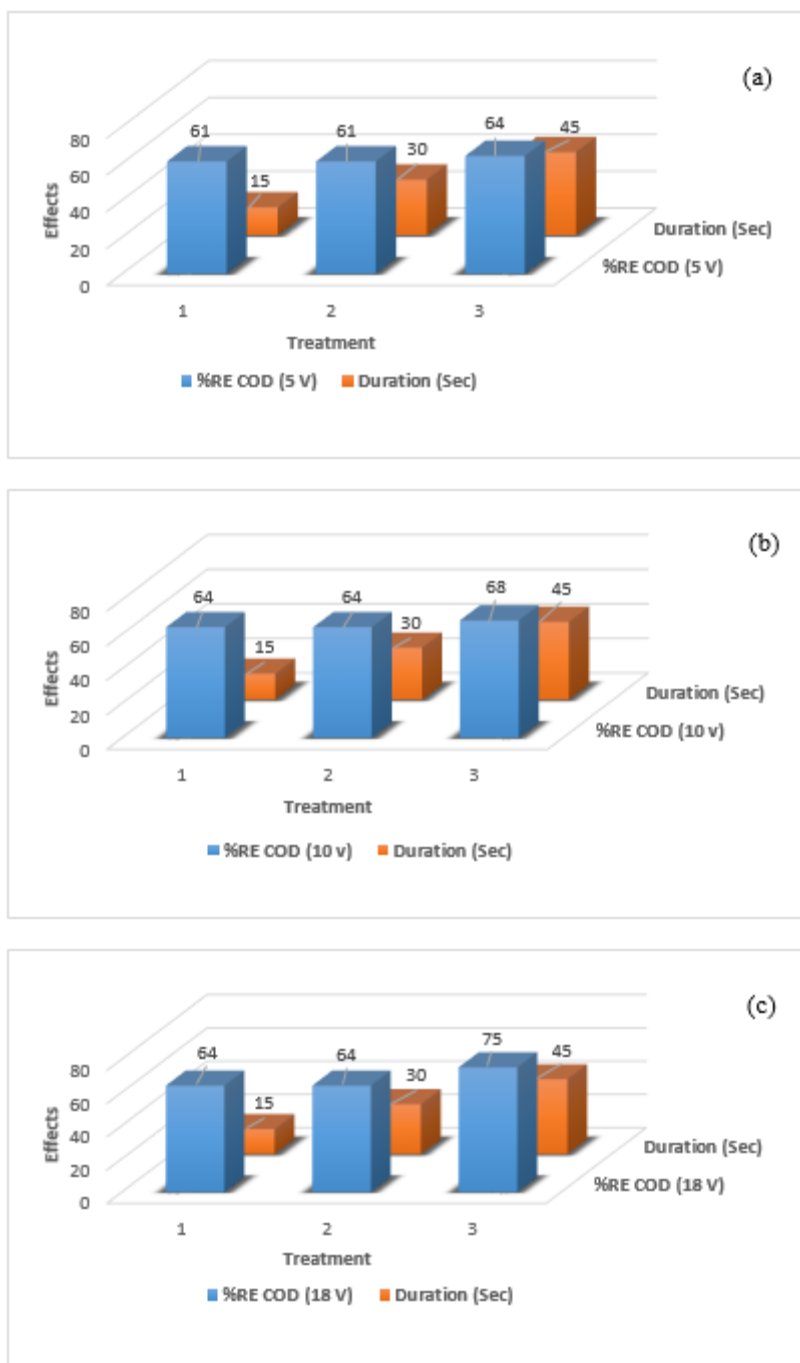


Fig. 8 Decrease in COD as related to voltage level and duration (a) (b) and (c).

where A is the cell current (Amps), E_a represents the electrodes area in the reactor (cm^2) calculated at $216 cm^2$. The results of ratio of % removal efficiency/power consumption as well as the current density for a given treatment are presented in Table 12. For electric current to flow in a solution, a minimum conductivity is required. In electrolysis, conductivity

of the solution is a very important parameter as it will directly affects removal efficiency of the contaminant and operating cost. As shown in Table 11, the sample has a high measured conductivity value. However in situations of low-conductivity of a wastewater, soluble salts such as NaCl or Na_2SO_4 is added to adjust the conductivity. Increase in wastewater conductivity is

accompanied by a decrease in energy consumption [19, 20]. It is clear that according to Table 12, under the batch mode operation of the electrocoagulation reactor, best operating conditions yielding most economical and efficient decrease in TSS, turbidity, and COD were when operational parameters are set at 5 volts and

retention time occurring between 15 and 30 s. The combination of intermolecular forces such as hydrogen bonding and dipole-dipole interactions in the guar and other contaminants were effectively broken apart under the extensive energy into their simplest form and mediated their removal in a precipitate form.

Table 12 Ratio of % RE and power consumption for the various treatments.

				% RE/power consumption		
Treatments		P.C.* (KWh/m ³)	C _d ** (A/cm ²)	Parameters		
Volt	Duration			TSS	Turbidity	COD
10	15	0.65	0.032	1.14	1.08	0.99
10	30	1.34	0.032	0.60	0.59	0.48
10	45	2.00	0.034	0.45	0.47	0.34
18	15	1.71	0.047	0.50	0.48	0.37
18	30	3.41	0.047	0.25	0.28	0.19
18	45	5.24	0.048	0.16	0.18	0.14
5	15	0.21	0.021	2.57	2.00	2.90
5	30	0.41	0.021	1.76	1.85	1.49
5	45	0.69	0.023	1.25	1.38	0.93

*P.C., power consumption; **C_d, current density

4. Risk Assessment of Disposal Options

For the purpose of this study, prevalent wastewater management options were ascertained in light of their potential environmental, social, and economic impacts. A description of the various probability levels are outlined in Table 13. Subsequently, a probability and severity consequence outcome was created to provide a priority risk index (Fig. 9). The interface of environmental, social and economic uncertainty associated with the high volumes of frack water management were systematically evaluated. Associated risks for most common disposal methods are summarized in Table 14 in relation to the comprehensive understanding of probability and severity.

Noteworthy, Table 14 as reported in this study, doesn't provide a dynamic model of varying levels of maturity and external complexities during the life cycle management of frack water. As such, the Table should

Table 13 Probability levels and descriptions for wastewater disposal options.

Probability	Description
Low	Lower environmental, social, and economic effects and mitigation costs
Medium	Serious environmental, social, and economic effects and comparatively more mitigation costs
High	Severe environmental, social, and economic effects and greater mitigation effects

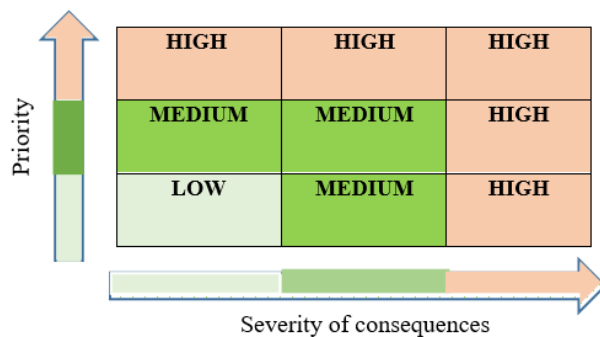


Fig. 9 Priority risk index for wastewater disposal options.

Table 14 Management options and potential environmental, social, and economic consequences.

Management options	Impact	Environmental, social, and economic consequences
Onsite reuse	Low	*Reduce fresh and groundwater consumption *Minor underground leaching risk *No disposal and liability costs *No transportation risks
Storage pond	Medium	*Significant odor risk *Risk for pathogens *Long term liability *Moderate to low potential clean-up cost *Temporal impact *Leaks and underground leaching risk causing surface and groundwater contamination
Storage tanks	Low	*Risk for leaks and releases *Increased underground leaching risk *Odor risk likelihood *Chances of spills during the loading or unloading processes *Clean-up cost potential
Deep well injection	Medium	*Increase underground leaching risk *Greater potential for freshwater aquatic contamination *Off site transportation risk *Higher disposal cost and long term liability *Subsurface impacts uncertainty

be viewed as a predictive guide, static, and where applicable, a functional tool. Additional considerations not explicitly considered in the study are factors governed by site specific conditions and type of contaminants in the flowback. In this regard, may change the nature and severity of impact as to their environmental, social, and economic consequences.

5. Conclusions

Bed sorption, semi-permeable membrane, ClO₂ oxidizer, and electrocoagulation were investigated as a possible technique for the reduction of salinity, COD, TSS, turbidity in flowback fluids were investigated. The results for the bed sorption experiment indicate that the 1:3 ratio of vermiculite:zeolite was more

effective at improving the quality of the flowback fluid sample by reducing the salinity level. An overall reduction in Na⁺ level of 7.50%, EC of 2.40%, and Cl⁻ of 1.31% was achieved. The two membrane in series configuration combined with the ClO₂ pretreatment yielded a 92 % salt rejection concurrent with a 93 and 90% of Cl⁻ and Na⁺ reduction in the permeate. However, when compared the permeate recovery for the single and the two membranes treatment, the permeate recovery for the two membrane was 5% less. Electrocoagulation was an effective technique for the reduction of COD, turbidity, and TSS. Under the batch mode operational conditions, decrease in turbidity ranged from 43 to 98%, TSS from 54 to 86%, and COD from 61 to 76%. Best operating conditions yielding most economical and efficient decrease in TSS, turbidity, and COD were when the system operates at 5 volts with a retention time between 15 and 30 s.

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