PRODUCED WATER TREATMENT USING MICROBIAL DESALINATION CELLS

by

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Approval Signatures

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Dedication

To my loving and caring family…

Abstract

Globally, 250 million barrels of produced water is generated daily for extracting 80 million barrels of oil. Having a highly variable composition and no economic value, produced water presents serious environmental problems. While the treatment of produced water is of paramount concern, existing desalination technologies are highly expensive and energy-intensive leading to great investments by oil industries. Microbial desalination cells (MDC) provide a promising alternative through their potential for negligible energy input, use of low-cost resources, low waste production, and electricity generation. However, MDC is a relatively new technology and its application in industries is limited by its low desalination efficiency and pH instability. This research investigates the effect of various factors on the performance of MDC employing Saccharomyces cerevisiae yeast as electron generating microorganisms. Two mediators, methylene blue, and menadione are used as electron promoters to shuttle the electrons from the yeast cells to the anode electrode. In particular, a two-level partial factorial design is implemented where, MDC desalination efficiency is investigated at two (low/high) levels of three input factors: aeration in anolyte (aerobic/ anaerobic), hydrophilic mediator concentration (0.5– 2 mM), and concentration of Total Dissolved Solids (TDS) in produced water (20– 40 g/l). Acquired experimental data are statistically analyzed using single effect and interaction plots. In addition, several other operating parameters and configurations are investigated in order to achieve optimum conditions for best performance. These include aeration rates in the anode and cathode chambers, the concentration of lipophilic and hydrophilic mediators, the pH of the anolyte solution, the use of activated carbon granules, and the repeated batch operation. Moreover, an MDC unit is operated at the optimized conditions where it resulted in 36% desalination after 72 hours. The study revealed that the operation of repeated batch cycles was the most effective among other parameters in improving desalination efficiency of MDCs. Furthermore, the factorial design study concluded that produced water TDS has the highest single effect on MDC performance and that there is a significant interaction between all three input factors employed in the factorial design.

Keywords: ***Microbial Desalination cell, produced water, methylene blue, mediator.***

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List of Abbreviations

AEM	Anion exchange membrane
AMDC	Air cathode microbial desalination cell
APE	Alkylphenol ethoxylate surfactants
BMDC	Biocathode microbial desalination cell
BOD	Biological oxygen demand
BTEX	Benzene, toluene, ethylbenzene, and xylene
CEM	Cation exchange membrane
DGF	Dissolved gas flotation
DNA	Deoxyribonucleic acid
DOE	Design of experiments
ED	Electrodialysis
IGF	Induced gas flotation
MB	Methylene blue
MCDC	Microbial capacitive desalination cell
MDC	Microbial Desalination Cell
MES	Microbial electrochemical systems
MF	Microfiltration
MFC	Microbial Fuel Cell
MPPE	Macroporous polymer extraction
NF	Nanofiltration
NORM	Naturally occurring radioactive materials
OSMDC	Osmotic microbial desalination cell

PAH	Polycyclic aromatic hydrocarbons
PW	Produced Water
RO	Reverse osmosis
SMDDC	Submerged microbial desalination–denitrification cell
TDS	Total Dissolved Solids
TOC	Total organic carbon
UF	Ultrafiltration
UMDC	Up-flow microbial desalination cell

Chapter 1: Problem Statement and Introduction

This chapter provides an introduction about the necessity and challenges of the subject under study, i.e., produced water treatment. The objectives of the thesis and the problem investigated in this study are then presented, and finally, the organization of the thesis is presented.

1.1. Problem Statement

Fresh water is an essential material for our survival. All living forms and a myriad of residential, agricultural and industrial activities depend on its supply. However, the same activities generate polluted water while population explosion depletes existing fresh water sources. Significant water shortages across the world have raised the demand for desalination of seawater and treatment of wastewater before its discharge into the ocean [1].

The oil and gas industry generates more polluted water than desirable product. Globally, around 250 million barrels of produced water is generated daily compared to 80 million barrels of oil extracted [1, 2]. Produced water accounts for 80% of wastes generated during oil and gas production and it is the largest waste stream by-product of the industry [3]. Moreover, as reservoirs mature and more oil is extracted, the ratio of produced water to oil rises [4].

In 2003, offshore facilities around the world discharged around 667 million metric tons of produced water to the ocean [5]. It is therefore evident that environment-friendly discharge of produced water is imperative for achieving sustainable development in the oil and gas industry. However, there are numerous challenges facing produced water treatment. Produced water composition is complex and can include several thousands of compounds of organic and inorganic chemicals, minerals, heavy metals, and radioactive materials [1]. Such high contamination and complex composition lead to huge investments by industries on expensive treatment equipment. In fact, the cost of operating produced water treatment and disposal facilities determines the profitability of an oil reservoir [1]. Oil wells often shut down when the cost of handling produced water exceeds their revenue [1].

The most common methods for reducing produced water inorganic salt contents include reverse osmosis and electrodialysis. However, these treatment technologies are highly energy intensive and expensive [6, 7]. For example, the most energy efficient reverse osmosis system installed for treating produced water requires 1.8–2.2 kWh/m^3 of energy for its operations, which is higher than the theoretical minimum energy requirement of 1 kWh/m^3 [2, 8, 9]. Moreover, auxiliary processes such as pumping and pre-treatment increase the total energy demand for desalination to 3-4 kWh/m^3 [2, 8, 9]. According to some investigators, further advancements in reverse osmosis technology will, most likely, not be able to reduce energy consumption below 3 kWh/m^3 [7].

Therefore, there is serious demand for more cost-effective treatment methodologies. The microbial desalination cell (MDC) is an emerging technology offering alternative desalination solutions and great promises of negligible energy input, use of low-cost resources, low waste production and subsequent electricity generation. However, MDC technology is still in its infancy. Its widespread commercialization is impeded by numerous challenges including low current output, pH instability, high internal resistances (polarization), and membrane biofouling [9]. There is a multitude of factors that affect MDC performance and operation. In order to address these challenges and investigate the effect of various operating conditions, a scientifically effective experimental design is necessary.

In most research areas, factorial experimental designs are employed to investigate the effect of several factors on certain response variables simultaneously. This technique allows for additional analysis of the interaction of several factors with each other as well as their combined and individual effects on the response variables [10]. Therefore, this approach leads to more informative results and is, thus, favored over experiments where only one factor is varied at a time [10]. It also saves resources in time and money in minimizing the number of needed experimental runs for the same amount of information gained when compared to one factor at a time experimental program [10].

1.2. General Background

Produced water from oil and gas industries is generated from three main sources: 1) formation water which is either fresh water or seawater, that is trapped inside the oil/gas reservoirs, and is released to the ground along with the hydrocarbons during oil exploration, 2) injection water which is pumped into reservoirs along with production chemicals to enhance oil and gas recovery rates, and 3) condensed water which is present in the reservoirs in gas phase and condenses during oil and water separation processes [1, 11, 12].

Produced water normally consists of more than a thousand compounds and its composition varies from one production facility or region to another [1]. Its composition depends on the presence of water-soluble components and minerals that exist with the oil and gas in the reservoir, the production chemicals added during oil/gas production and the type of oil and water separation process used [1].

During the oil extraction process, large pressure drop exists between the reservoir and the surface. This pressure drop is used to extract oil and formation water from the reservoir [13]. Various techniques are commonly employed to enhance oil recovery. Among these, water injection methods significantly increase the produced water quantity [13]. Additionally, surfactants are added to the reservoir to reduce the surface tension between oil and water in order to facilitate easy movement [14]. These surfactants and other reservoir contaminants (e.g., salts, metals, radio-isotopes) are present in the injected water as pollutants and later become part of the produced water [14]. If aquifers are used for water encroachment then injected water composition depends on the aquifer composition as well [15].

Oil industries employ various methods to treat produced water to meet discharge requirements before disposing it into the sea, an aquifer, or into a reservoir. Commonly employed produced water treatment technologies for removing inorganic salt contents include filtration and electrodialysis and those for removing oil and grease contents include hydrocyclones, gravity separators and evaporators [2]. Other technologies include ion-exchangers, inclined plate separators, corrugated plate separators, centrifuges, coalescers, gas flotation, solvent extraction, adsorption and combined physical and chemical technologies like C-TOUR [1].

In this thesis, produced water treatment using an emerging technology, i.e., the microbial desalination cell (MDC) technique, will be experimentally investigated. MDC is expected to be capable of addressing the major pain area of the energy-intensive state-of-the-art desalination methods. MDC methodology combines electrodialysis of inorganic salts with the concept of the microbial fuel cell (MFC) which uses microorganic electrochemical reactions to generate electricity [16, 17]. Produced water, whose ionic conductivity is twice that of seawater, significantly enhances current generation which in turn improves desalination of produced water [1]. MDCs can assist existing industrial desalination methods by acting as a pre-treatment step and by supplying power for their operations [18].

1.3. Research Objectives

This study focuses on the use of one type of yeast, i.e., Saccharomyces Cerevisiae, for produced water desalination along with simultaneous electricity generation in a microbial desalination cell assembly. The effects of various factors on desalination efficiency and current output will be experimentally investigated. The specific objectives of the present study are to:

1. Explore the current generation capacity of hydrophilic and lipophilic mediators and their combinations.
2. Study the impacts of different operating conditions in MDCs on the efficiency of produced water desalination.
3. Perform a factorial experimental design for studying the effect of the following three factors on MDC performance: aeration in anolyte (aerobic/ anaerobic), hydrophilic mediator concentration (0.5/– 2 mM), and Total Dissolved Solids concentration in produced water (20/– 40 g/l).
4. Generate regression models that fit the experimental data by using the factorial design analysis approach.
5. Evaluate the properties of anolyte and catholyte solutions before and after produced water desalination.
6. Investigate the performance of one MDC unit when operated for a longer operation time under optimized conditions.

1.4. Thesis Organization

This thesis is structured in five chapters. Chapter One provides a brief introduction to the topic of this research. It also defines the problem statement which underlines the necessity of this study. The main objectives of this thesis are also covered in this chapter.

The first section of Chapter Two illustrates the properties of produced water, the various contaminants present in produced water and their environmental toxicity. The second section includes an extensive literature review about the currently used produced water treatment technologies, their advantages, and disadvantages. The operating principles of microbial desalination cell technology, together with the theory and parameters that govern MDC performance, are delineated in the third section of Chapter Two.

Chapter Three describes the parametric study while addressing its methodology and experimental procedures. It provides details for all the instruments used and materials procured. Furthermore, this chapter extensively discusses the results of the effects of the following parameters on MDC desalination efficiency: aeration rates in anode and cathode chambers, the concentration of lipophilic and hydrophilic mediators, pH of the anolyte solution, use of activated carbon granules, and repeated batch operation. Comparisons are drawn between the results of this research with those of existing publications on MDCs and MFCs.

Chapter Four examines MDC desalination performance through a two-level partial factorial experimental design. It presents a brief theoretical background of factorial designs and illustrates experimental procedures followed in this research. The results of the experiments are discussed using single effect plots and interaction effect plots. Moreover, a regression model is developed for each response variable and model adequacy is verified using normal probability plot of residuals.

Finally, Chapter Five summarizes the findings and conclusions of the thesis and provides recommendations and suggestions for future extensions.

Chapter 2: Literature Review

2.1. Properties of Produced Water

The composition of produced water is as complex as and similar to the composition of oil that co-exists with it in the reservoir [1]. Produced water carries all the water-soluble components from the reservoir in the dissolved form and some oil-soluble compounds in the dispersed or particulate form [19]. Therefore, the kind of compounds and their concentration vary widely based on the geological location of the reservoir, the type of water treatment facilities, the operating conditions and the chemicals added [4].

The major chemical components of produced water may fall in one of the following categories [1]:

a) Inorganic salts

b) Organic compounds

c) Metals

d) Naturally occurring radioactive materials (NORM)

e) Production chemicals

2.1.1. Inorganic salts. Produced water can contain a wide range of salt concentrations from a few to 300 parts per thousand [20]. In view of typical seawater salinity of 32-36 parts per thousand, this implies that direct discharge of produced water into the ocean can have serious toxicological effects on aquatic life [7]. The inorganic ions that contribute to salinity are sourced from formation water and their concentration depends on the reservoir age, location and formation geology [1]. The most commonly present inorganic ions, in decreasing order of their relative abundance, include Na^+, Cl^-, Ca^{+2}, Mg^{+2}, K^+, SO_4^{-2}, Br^-, HCO_3^- and I^- [21].

Ba^{+2} and some other cations in produced water form insoluble precipitates with SO_4^{-2} and S^{-2} ions [6]. Because of this, produced water with high sulfide or sulfate ion concentration (e.g., produced water from sour oil reservoirs) results in a decrease in barium ion concentration [6]. However, the precipitate may cause scaling in production pipes where the cation meets sulfide and sulfate ions [6]. Sometimes, the precipitation causes other elements like radium radioisotopes to precipitate along with the barium scale [1]. High concentration of inorganic ions, therefore, increases density, scale formation, salinity and buffering capacity of the produced water [7]. Having different ionic concentration and higher density than that of seawater increases the aquatic toxicity of produced water [7]. If the produced water is discharged into another water body, a high NH_4^+ concentration can increase toxicity and possibility of eutrophication in the receiving water [22]. Without NH_4^+, the possibility of eutrophication is low because of generally low concentrations of nitrates and phosphates in produced water [8]. Table 2.1 lists the typical composition and characteristics of produced water [2].

Table 2.1: Typical composition of Produced Water [2]

Parameter	**Values**	**Metal/ Heavy metal**	**Values (mg/l)**
Density (kg/m^3)	1014-1140	**Calcium**	13-25,800
Surface tension (dynes/cm)	43-78	**Sodium**	132-97,000
TOC (mg/l)	0-1500	**Potassium**	24-4,300
COD (mg/l)	1220	**Magnesium**	8-6,000
TSS (mg/l)	1.2-1000	**Iron**	<0.1-100
pH	4.3-10	**Aluminium**	310-410
Total oil (mg/l)	2-565	**Boron**	5-95
Volatile components (mg/l)	0.39-35	**Barium**	1.3-650
Total non-volatile oil and grease components (g/l)	275	**Cadmium**	<0.005-0.2
Chloride (mg/l)	80-200,000	**Chromium**	0.02-1.1
Bicarbonate (mg/l)	77-3990	**Copper**	<0.002-1.5
Sulphate (mg/l)	<2 – 1650	**Lithium**	3-50
Ammonical nitrogen (mg/l)	10-300	**Manganese**	<0.004-175
Sulphite (mg/l)	10	**Lead**	0.002-8.8
Total polar (mg/l)	9.7-600	**Strontium**	0.002-1000
Higher acids (mg/l)	<1 – 63	**Titanium**	<0.01-0.7
Phenols (mg/l)	0.009-23	**Zinc**	0.01-35
Volatile fatty acids (mg/l)	2-4900	**Arsenic**	<0.005-0.3

2.1.2. Organic compounds. Organic compounds are present in produced water in dissolved as well as dispersed form depending on the original source [4]. These compounds include organic acids and petroleum hydrocarbons such as BTEX (benzene, toluene, ethylbenzene, and xylene), PAH (polycyclic aromatic hydrocarbons) and phenols [1]. The organic content of produced water is identified using TOC (total organic carbon) concentration which can vary from 0.1 mg/L to more than 11,000 mg/L [11]. Oil and grease exist in produced water in the following forms [4]:

- free oil in the form of large droplets that are easy to remove from produced water,
- dispersed oil in the form of small droplets,
- dissolved oil that is the most challenging to treat.

2.1.2.1. Organic acids. Organic acids found in produced water are either aliphatic or aromatic hydrocarbons containing one or two carboxylic groups [11]. Organic acids having fewer carbon atoms are relatively more abundant than those with higher carbon atoms because of lower molecular weight and higher solubility in water [12]. Among these, formic acid and acetic acid are the most abundant in produced water [12]. The low molecular weight organic acids have a lower harmful effect on aquatic life since they are easily biodegradable by microorganisms, plants, zooplanktons, and phytoplanktons [14]. However, organic acids corrode production pipes in treatment facilities as they increase acidity [23]. The concentration of organic acids depends on the type of oil, its pH, and pressure and temperature of the reservoir [1]. At the right environmental conditions, hydrocarbons in the reservoir may undergo microbial degradation or hydrous pyrolysis to produce many of these organic acids [14]. Sometimes, these processes produce naphthenic acids when the aromatic hydrocarbons are anaerobically degraded. Because of their low solubility, however, they are only present in produced water in small amounts [14]. Aromatic acids increase the toxicity of produced water since they adversely affect growth and reproduction of some aquatic species [23, 24]. Only small concentrations of aromatic acids are found in produced water [14].

2.1.2.2. Petroleum hydrocarbons. As with organic acids, petroleum hydrocarbons are sourced from the associated oil reservoir where its water-soluble components are present in produced water in greater quantity [1]. The aliphatic and aromatic hydrocarbons having lower molecular weight are present in produced water in dissolved form. Whereas, the higher molecular weight hydrocarbons, being less water-soluble because of higher carbons, are present in the dispersed form [19]. Hydrocarbons are difficult to separate from water completely [14]. Therefore, treated water that is discharged into a water body still contains some dissolved low molecular weight aromatic hydrocarbons and smaller oil droplets of size between 1 and 10 micrometers [8]. The commonly present petroleum hydrocarbons are BTEX, PAH, and phenols [1].

The monocyclic aromatic hydrocarbons also termed BTEX are among the most abundant group of chemicals in produced water [1]. Besides these, produced water can have small amounts of alkyl benzenes with 3 or 4 carbons in the alkyl group [25, 26]. Higher alkylation of a hydrocarbon compound decreases its solubility in water and consequently, decreases its concentration in produced water [27]. BTEX, however, are easy to separate from water because of their relatively high volatility. Even if they are not separated by means like air stripping, they will evaporate in the receiving water body also [27].

PAH (Polycyclic aromatic hydrocarbons) are the aromatic hydrocarbons that have more than one fused rings [1]. PAHs with 2 or 3 rings are more abundantly present in produced water in the dissolved form [26]. The PAHs with 4 to 6 rings are rarely found in produced water but if present they exist as dispersed oil droplets [19]. They are highly persistent and toxic to the receiving water body and are, thus, of the greatest concern [28].

The alkyl phenols present in produced water, in decreasing order of their relative abundance, include phenol, methyl-phenol, dimethyl-phenol, and those with more carbons in the alkyl group [29]. The most toxic among these are the highly alkylated phenols, but fortunately, their presence is rare [1]. However, surfactants, like alkylphenol ethoxylate surfactants (APE) which are used as production chemicals for extracting viscous oils out of the reservoir, may degrade to soluble species in produced water as highly alkylated phenols [30]. Because their highly toxic nature, however, they are usually replaced with safer surfactants [30].

2.1.3. Metals. The metals may be present in dissolved form or as micro-particulates [1]. Some of them are commonly found in produced water at concentrations that are substantially more elevated than in the surrounding seawater [1]. These metals include barium, mercury, zinc, iron, and manganese [28]. Metal concentration and molecular nature in produced water depend on the reservoir age, reservoir geology, and inorganic composition of injection water [21]. Formation waters are mostly anoxic i.e., devoid of dissolved oxygen [1]. Therefore, when these waters are brought to the surface, previously high concentrations of iron and manganese precipitate as oxyhydroxides [31]. This may also bring about co-precipitation of some other metals. Sometimes other metals may form complexes or be absorbed on solid hydrous iron and magnesium oxides in the water [29, 30]. Steel structures that contact with the oil and produced water at the excavation or process unit may impart zinc and lead to the produced water [1]. Heavy metals are highly toxic to aquatic life when present above their threshold concentrations [32, 33]. They can bio-accumulate in certain species, cause damage to tissues and DNA, and inhibit growth and regeneration [33]. Therefore, removal of heavy metals from produced water is of paramount importance for increased environmental safety.

2.1.4. NORM (naturally occurring radioactive materials). Radioactive materials that occur most plentifully in produced water are Radium-226 (^{226}Ra) and Radium-228 (^{228}Ra) [34]. Radium is formed when Uranium-238 and Thorium-232 decay in the rocks associated with oil reservoirs [34]. The ^{226}Ra and ^{228}Ra concentration in produced water from some production facilities may reach up to ten thousand picocuries per liter [28]. This is to be contrasted to surface ocean waters which naturally contain 0.027-0.04 picocuries per liter of ^{226}Ra and 0.005-0.012 picocuries per liter of ^{228}Ra [24]. Such elevated concentrations of radioactive materials have a high potential for harmful biological effects, although their exact impact on marine life is still unclear due to lack of baseline data on benthic biology [25]. Radioactive materials sometimes co-precipitate from produced water along with Barium salts and thus, appear in scales [6].

2.1.5. Production chemicals. Production chemicals are additives that are used in oil and gas production activities for various reasons including enhancement of oil recovery, protection of system from corrosion by oil well contaminants, separation of water, oil and gas, and prevention of methane hydrate formation [1]. These production chemicals include gas-treating chemicals, biocides, emulsion-breakers, scale inhibitors, hydrate inhibitors and other solvents [8]. Many of these chemicals can act as genotoxicants or cytotoxicants even if they are present below detection limits [35]. The chemicals having highest toxicit towards marine life include corrosion inhibitors, biocides, and reverse emulsion breakers [35]. However, their toxicity may get eliminated or reduced if high-risk chemicals undergo reactions during the production activities before being discharged into the ocean [35].

Most of the production chemicals are less water-soluble and are not found in produced water [36]. Others that are water-soluble are present in produced water but are removed during treatment in industries [8]. However, the concentration of production chemicals in produced water increases when their demand rises due to the aging of oil fields since they help maintain the efficacy of production activities [37].

Since treatment chemicals are used to solve specific operational problems, they are not added if there is no demonstrated need [1]. However, excessive use of biocides and corrosion inhibitors can raise environmental concerns. Such environmental problems can be mitigated through best management practices available for industries. These practices include the Offshore Chemical Selection System (OCSS) and calculation of the Environmental Impact Factor (EIF) for each chemical [1]. Therefore, less toxic alternatives can be used to replace the toxic production chemicals having high EIF [1].

2.2. Treatment of Produced Water

Treatment of produced water is important for industries to meet waste stream discharge standards. It also allows produced water to be considered a valuable by-product rather than a harmful waste. With suitable treatment methods, produced water has a wide range of possible applications for re-use. It can be re-injected into an underground reservoir for maintaining the reservoir pressure provided that the water is free from excessive solids, corrosive chemicals, and microbes to prevent plugging and equipment damage inside the reservoir [1]. Produced water can also be injected into a shallow aquifer for future use or it can be used for irrigation in agriculture [38]. However, these two applications require adequate salinity removal from produced water. Treated produced water can also be reused in industrial processes such as hydraulic fracturing during drilling operations and as a utility cooling water in power plants [38]. Produced water, therefore, can be treated for various objectives such as removal of soluble organics, disinfection, removal of suspended solids, softening, desalination, de-oiling and removing NORM [39]. This section lists the existing technologies based on physical, chemical, biological and combined principles that are available for produced water treatment.

2.2.1. Membrane technologies. Membrane processes are the most commonly used treatment technology for removing inorganic salts, as well as oil content, from produced water [1]. The advantage of membranes is that they don't use toxic chemicals, they require lower costs, and use less space for installation as compared to other chemical and biological treatment methods [2]. Their main disadvantage is membrane fouling and scale formation that adds to maintenance costs. Methods based on membranes can also be energy intensive [2]. The most popular membrane technologies used in industries for produced water treatment are filtration and electrodialysis.

2.2.1.1. Filtration. The various categories of filtration, in the order of largest to smallest membrane pore size, include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [1]. MF is mainly used to remove suspended solids, UF for removal of macromolecules, NF for removal of multivalent ions, and RO is used to separate dissolved and ionic components [40]. RO membranes are capable of filtering away all contaminants from water except for dissolved gases and certain organic compounds of low-molecular weight [41]. Within the filtration categories, ceramic membranes are preferred over polymeric membranes because they are more effective in handling high-temperature treatment processes and produced water with high oil content, foulants, and strong cleaning agents that are typically existing in produced water [42].

MF using low-pressure-driven membranes of pore size range 0.1 - 5 µm and UF using membrane pore size less than 0.1 µm or their various combinations are applied for removing oil content from produced water [42]. However, as the membrane pore size decreases, higher energy is required to push the water solution through the membrane and the potential for membrane fouling increases [1]. Hence, membrane filtration processes, in general, require pretreatment to remove sand and other larger constituents before they reach the membranes [1].

Cost-effective use of membranes in produced water treatment faces some important challenges including uncertain membrane life, flux degradation, low average flux rate, and sensitivity to variation in pre-treatment and flow [43]. Zeolite membranes help address some of these challenges because of their high chemical, mechanical, and thermal stability [44]. Bentonite clay membranes can also be used for produced water treatment as long as the produced water doesn't contain high Total Dissolved Solids (TDS) concentration [44].

2.2.1.2. Electrodialysis (ED). Electrodialysis relies on an external power supply to generate an electrical potential difference between its anode and cathode electrodes [45]. The potential difference acts as a driving force for moving salt ions out of the wastewater and into the electrode chambers [45]. The electrode chambers are connected to the compartment containing wastewater by ion-selective membranes. As is shown in Figure 2.1, when electrical current is applied and water is allowed to pass through the membranes, the cations migrate towards the cathode which is the negatively charged electrode [45].

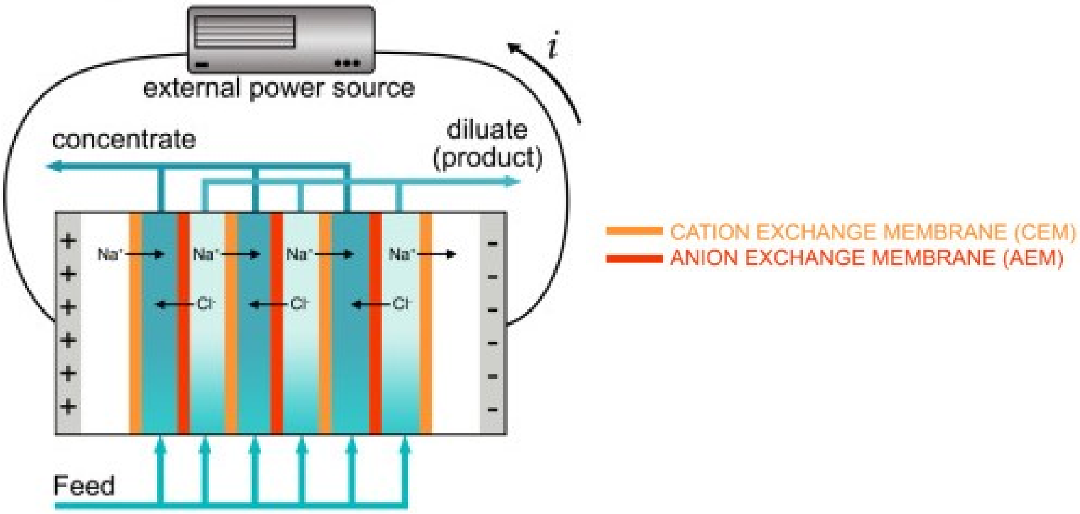


Figure 2.1: Schematic of Electrodialysis cell for desalination of seawater [46]

Similarly, the anions migrate towards the anode which is the positively charged electrode. This allows separation of inorganic salts or ions from the wastewater [45]. When multiple compartments are placed between the anode and cathode chambers, the ion-selective membranes are placed such that solutions in the even compartments are desalinated and get concentrated in the odd compartments (Figure 2.1) [45]. One advantage of electrodialysis is that it needs lower pressure than RO and, thus, has lower energy requirements [47]. This method is suitable for produced water that contains low TDS. When using produced water having high TDS, the solution's internal resistance to current flow is high causing the power demand and costs to be high [48].

2.2.2. Ion exchange. In this water treatment technology the dissolved salts and minerals, which are existing in an ionized form are removed by exchanging ions with ion-exchange resins, as shown in Figure 2.2 [48, 49]. The produced water passes through a column that is packed with ion-exchanger materials where the inorganic salt and mineral ions, like sodium ions, are exchanged with the hydrogen ions on the resin's exchange sites [1]. Ion exchange, therefore, causes the pH of the water to drop because of the addition of more hydrogen ions coming from the resin. Generally, the pH is then raised by using calcium carbonate [1].

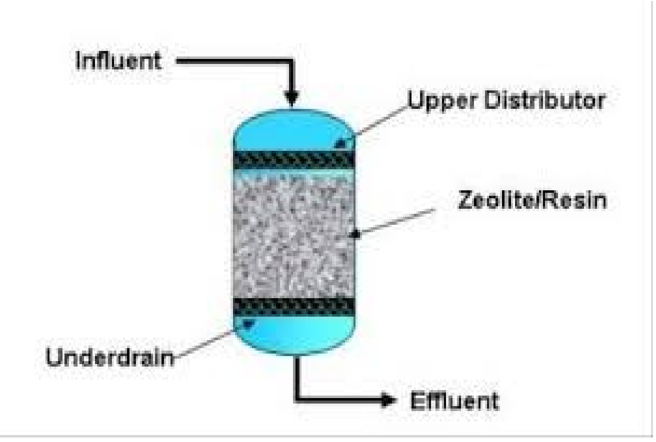


Figure 2.2: Schematic of a column using ion-exchange resins [51]

The method has various advantages like low energy requirement, continuous regeneration of resin, high efficiency, and possible mobile treatment [2]. Ion exchange technologies require comparatively less pre-treatment than other membrane technologies [2]. The disadvantages of ion-exchange resins include high effluent concentrate and post-treatment [2]. Its waste stream has regeneration chemicals like concentrated brine and other salts. The most commonly used resins as ion exchangers are zeolites [2]. For example, hydrophobic zeolite pellets were used in a fixed bed to remove soluble organic compounds in produced water [46, 47].

2.2.3. Evaporation. Some evaporation technologies such as vapor compression, falling film, and vertical tube evaporators are very effective in produced water treatment [52]. Figure 2.3 shows the schematic diagram of a multi-effect evaporator. Advantages of evaporators include lower costs for handling waste because no chemical sludge is produced and lower maintenance costs for materials and labor [52].

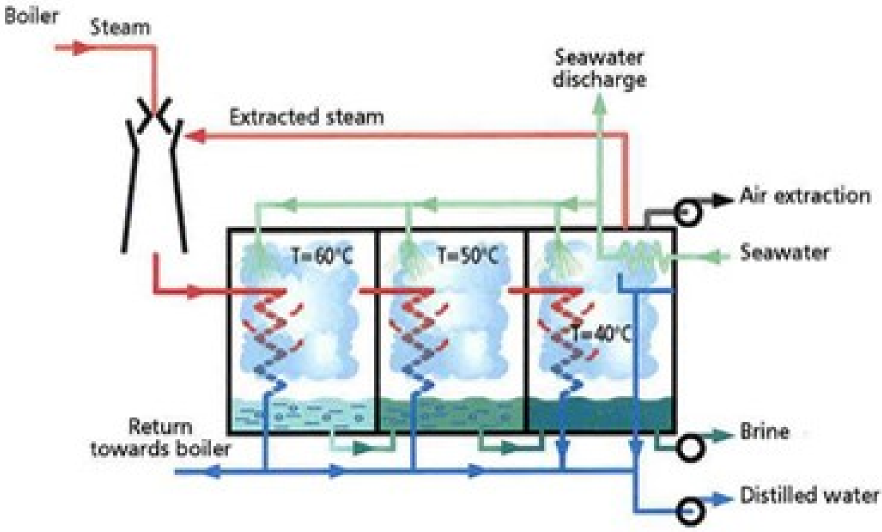


Figure 2.3: Schematic of multi-effect distillation design [53]

Evaporation technologies have traditionally suffered from high energy requirement. However, there have been some attempts to alleviate this problem utilizing better engineering designs [54]. A major disadvantage of evaporation technologies is the scaling and corrosion of heating elements inside distillation columns due to precipitation of oversaturated salts [52].

2.2.4. Gravity separators. For removing oil and grease from produced water, produced water is firstly passed through physical separators whose operation relies on gravity, centrifugal force, or pore-size trapping [1]. Gravity separators rely on the principle that the velocity of oil as it rises depends on droplet diameter and the fluid viscosity. Additionally, the total rising path of the oil droplets can be reduced by using inclined or corrugated plates [1]. Gravity separators with additional internal plate structures are called advanced gravity separators. Figure 2.4 shows the schematic diagram of a type of advanced gravity separator. The advantage of advanced separators over conventional separators is that the former can collect oil droplets of even smaller size. In conventional separators, the oil droplets take much longer to reach the surface and thus, may not get separated [1]. Advantages of gravity separators include very low energy requirements, low installation and operating costs, high efficiency for removal of bulk oil and suspended solids, no moving parts, and robust technology that is resistant to breakdowns in the field [39]. Disadvantages of gravity separators include incapability to separate fine oil particles and high retention time. Moreover, the waste stream of such separators contains suspended particles slurry [39].

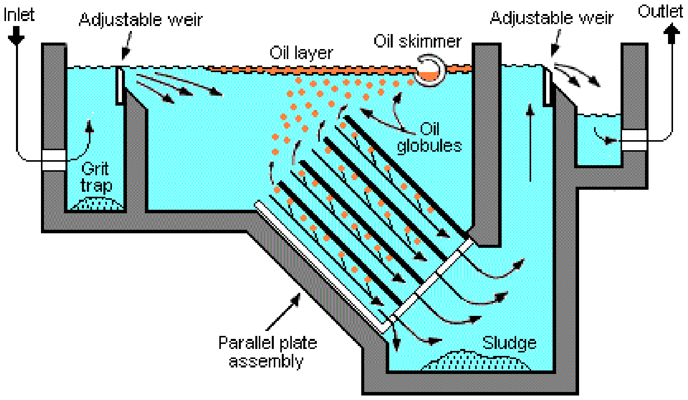


Figure 2.4: Schematic of gravity plate separator [55]

2.2.5. Hydrocyclone separators. Like gravity separators, hydrocyclones separate liquids based on their differences in density. However, they use centrifugal force instead of gravity, as shown in Figure 2.5 [1]. Hydrocyclones have been used since decades for de-sanding and de-oiling wastewater. The liquid/liquid type of hydrocyclone is used for produced water treatment [1]. Hydrocyclones capable of separating solids, oil, as well as water, at high efficiency, and sometimes with novelty, are currently in place [51, 52]. Van den Broek and Van der Zande ranked oil removal efficiencies of physical separators from highest to lowest performance in the following order: centrifuges, hydrocyclones, and plate separators [53, 54]. Advantages of hydrocyclones include compact modules, higher efficiency, and throughput for smaller oil particles [39]. Therefore, hydrocyclones are preferred in off-shore oil production facilities where space availability is at a premium [2]. Their disadvantages include high energy requirements to pressurize inlet streams, no separation of hazardous components, fouling, and higher maintenance cost [39].

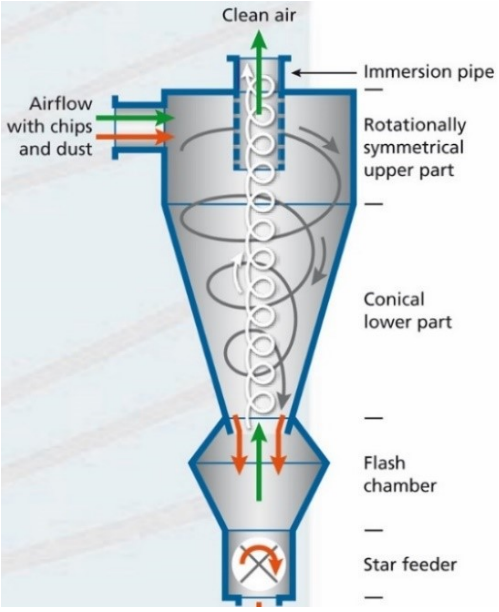


Figure 2.5: Schematic of hydrocyclone separator [59]

2.2.6. Centrifuges. Hydrocyclones and centrifuges both use centrifugal force for oil and water separation except that centrifuges generate much higher forces and can remove even smaller oil droplets [1]. Figure 2.6 illustrates the schematic of a typical centrifuge apparatus. Consequently, they have higher energy and cost requirements than hydrocyclones [2].

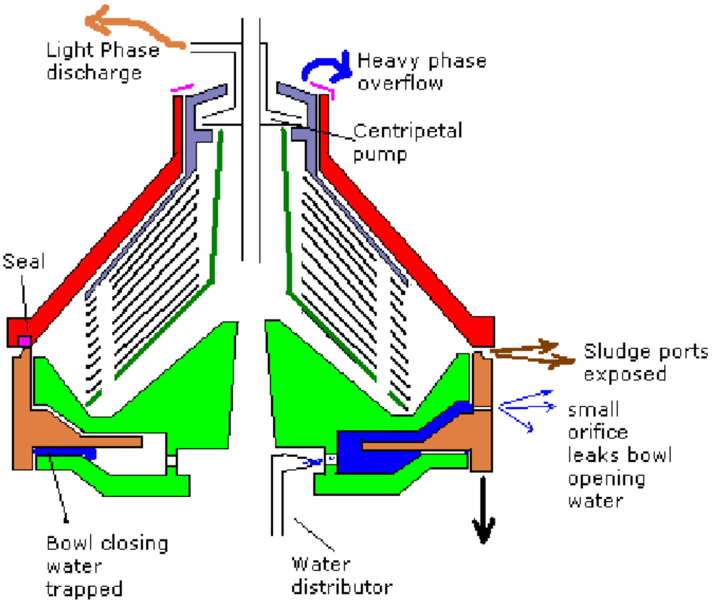


Figure 2.6: Schematic of a centrifuge [60]

Their advantages include efficient removal of smaller oil particles and suspended solids, and lesser retention time [39]. Their disadvantages include high energy requirement for spinning and high maintenance costs. Moreover, the waste stream is a rich suspended particles slurry [39].

2.2.7. Coalescence. Coalescing technologies are also used to remove oil content from produced water by providing additional surfaces to congregate and merge the oil droplets, as shown in Figure 2.7 [1]. Fiberglass, polyester, metal, or Teflon R media are commonly used in coalescers [1]. They can be arranged in either mesh, co-knit, or irregular 'wool' format [1]. While finer meshed media can efficiently coalesce smaller droplets, they are more vulnerable to fouling [39]. Therefore, they require pre-treatment for filtering out some solids before they reach the coalescer [39].

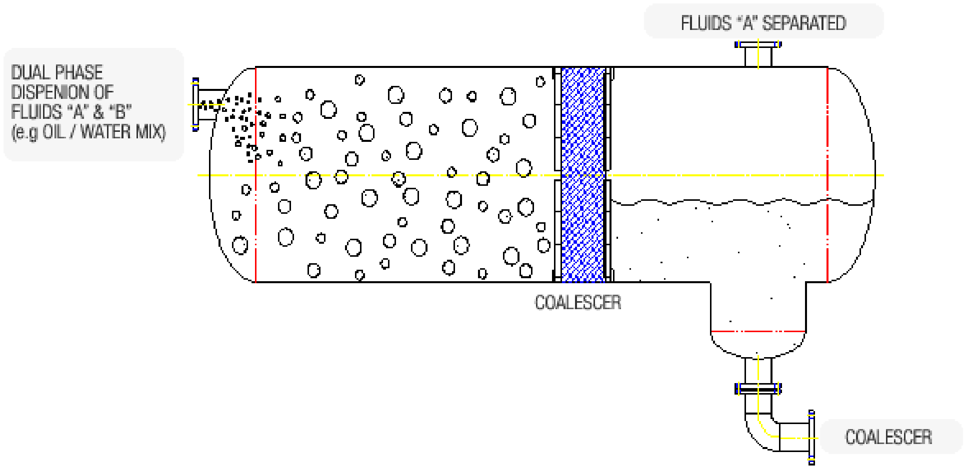


Figure 2.7: Schematic diagram of a coalescer [65]

Another type of coalescers contains a bundle of oleophilic polypropylene fibers which allows rapid coalescence when positioned in the direction of flow of produced water [61]. A recently developed process technology termed as Total Oil Remediation and Recovery can remove dispersed oil particles of diameter greater than 2 μm with a maximum efficiency of 99%. [62] This technology employs filtration, coalescence, gravity separation, multiple stages of adsorption and separation [54, 55]. Another recently developed technology, PECT-U, employs ultrasound for coalescence for primary treatment stage of produced water [57, 58].

2.2.8. Flotation. Gas flotation technologies treat produced water by allowing gas bubbles to rise through a sealed tank as they carry oil droplets and other contaminants along with them to the surface [1]. These contaminants can then be skimmed off from the water. Gas flotation technology is subdivided into dissolved gas flotation (DGF) and induced gas flotation (IGF) [1].

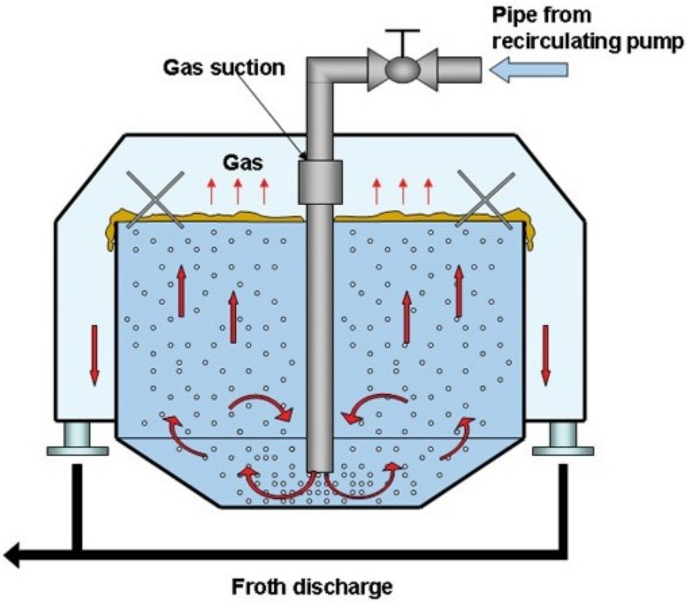


Figure 2.8: Schematic diagram for induced gas flotation [66]

The working of an IGF unit is illustrated in Figure 2.8. Typical IGF units inject fine gas bubbles into the incoming water stream by recirculating clean water from the IGF vessel outlet and pumping this back through an Eductor [67]. The high velocity through the Eductor induces gas into the recycle water stream [67]. On the other hand, DGF units use a dual-sided impeller. One side performs recirculation of liquid while the other side is used to draw vapor into the pump and mix it with the liquid [67].

The difference between DGF and IGF is that DGF units create smaller gas bubbles but require greater space and higher operational and maintenance oversight [1]. Because offshore oil production facilities have serious space constraints, IGFs are most commonly employed there [1]. Chemicals are often added in gas flotation systems to aid the process by breaking emulsions and improving aggregation of particles. For example, in one study ferric chloride was used in dissolved air flotation of produced water as a chemical coagulant, and organoclay was used as adsorbent [68] where 93% removal of the dispersed oil content was achieved [68].

The major advantage of gas flotation is the removal of particles having a diameter of 3 mm or greater with the help of pretreatment and no chemical addition [39]. Gas flotation is capable of efficient removal of oil and grease, small particles, and volatile and other organic components [69]. Disadvantages of gas flotation include incapability to remove dissolved oil contents efficiently, dependency on chemical coagulants for specific removal of target contaminants, and generation of solid sludge [39]. Flotation treatment can cost approximately 0.60$ per cubic meter of produced water [70].

2.2.9. Solvent extraction. Macroporous polymer extraction (MPPE) is a liquid-liquid extraction technology that is commonly used for treating produced water [71]. The process flow diagram of a typical MPPE system is depicted in Figure 2.9. In liquid-liquid extraction, a solvent, also called extraction liquid, is dispersed into the wastewater in order to extract the contaminated chemicals from the wastewater [72]. In MPPE, the extraction liquid is immobilized inside the pores of macroporous polymer particles [71]. Produced water is cleared of hydrocarbons as it passes through the column because of the extraction liquid [71].

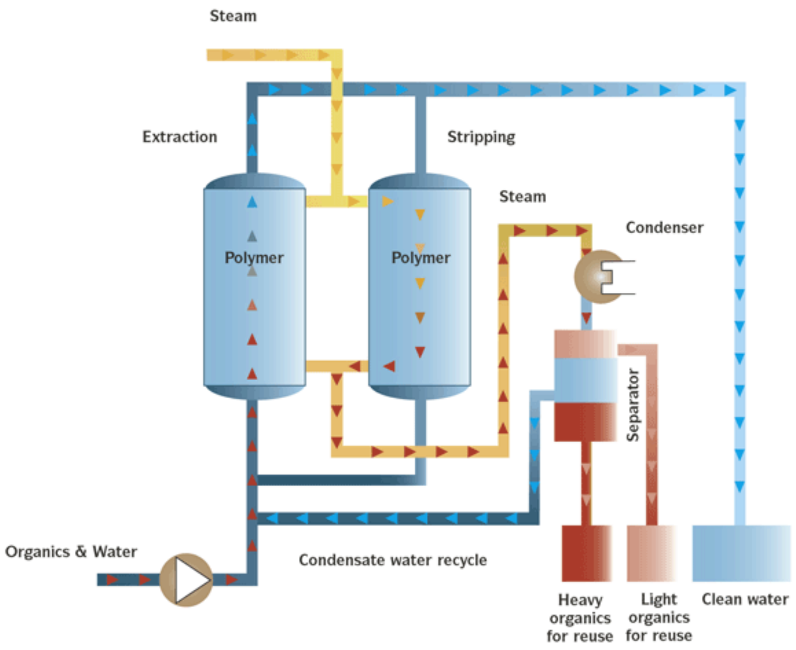


Figure 2.9: Process flow diagram for MPPE technology [73]

MPPE technology removes salt, glycols, heavy metals, and production chemicals like demulsifiers, corrosion inhibitors, and scale inhibitors [71]. The advantages of this technique include low energy requirement, easy operation, and removal of dissolved oil [1]. Its disadvantages include the high cost of installation and maintenance, regeneration of solvent and requirement for pretreatment for removal of oil content. The waste stream in this technique contains solvent regeneration waste [1].

2.2.10. Adsorption. Adsorption is a highly effective technique for organic component removal from produced water [1]. However, it is usually used as a tertiary treatment stage because it cannot handle high contaminant concentrations as they overload the media used for adsorption [1]. The process flow diagram of an adsorption system is depicted in Figure 2.10. The most commonly used adsorption media include organoclay, activated carbon, and zeolite [2]. Organoclay mixtures are capable of adsorbing a large variety of hydrocarbons and organic compounds [74]. Advantages of organoclay cartridges include the elimination of addition of other chemicals, high performance that is unaffected by the size of oil droplets, low energy requirements, and high oil recovery [1]. Advantages of adsorption include compact packed bed modules, low installation and operational cost and high efficiency [39]. Their disadvantages include high retention time and lower efficiency with higher feed contamination. Moreover, their waste streams can contain used adsorbent media and regeneration waste [39].

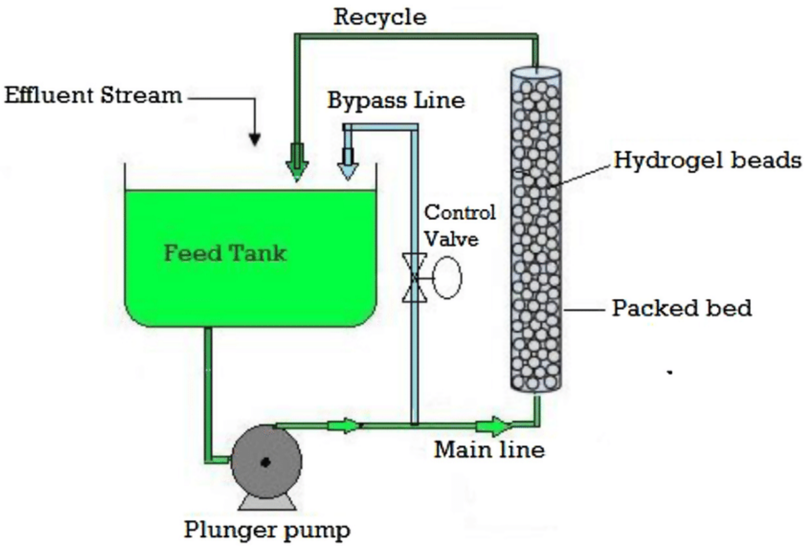


Figure 2.10: Process flow diagram for adsorption [75]

As contaminant concentration increases, cost of treatment increases, and a different level of organoclay is required [1]. One major disadvantage of organoclays is that there isn't any effective methodology available to re-use the fully loaded cartridges and they have to be disposed of instead [49]. The disadvantage of adsorption as a purification technique for produced water is that the adsorbent media gets plugged by the presence of suspended solids and efficiency is reduced. Also, a lot of chemical wastes are generated [76].

2.3. Microbial Desalination Cells (MDC)

2.3.1. Introduction. Microbial desalination cells belong to a subcategory of microbial electrochemical systems (MES) which use biodegradation of materials for directly generating electricity and useful chemicals. Microorganisms, with or without the help of mediators, are employed to degrade organic and/or inorganic substrates (such as those typically existing in wastewater) while their metabolism results in the release of electrons to an external circuit [77]. Thus, MES has the potential to integrate waste reclamation with bio-electricity generation, chemical production, and desalination. Although other technologies like anaerobic digestion are capable of generating biogas which can be further utilized to generate electricity, MES offers a major advantage of the direct generation of electricity from wastes along with negligible external energy requirement.

2.3.2. Operating principle. A typical microbial desalination cell consists of three chambers; anode, cathode and desalination chamber, as shown in Figure 2.11. The chambers are separated from each other using ion-exchange membranes. Anion exchange membrane (AEM) is placed between the anode and desalination chamber while the cation exchange membrane (CEM) is placed between the cathode and desalination chamber. The purpose of the AEM is to only allow passage of anions between chambers through its property of selective permeability, whereas the CEM only allows cations to pass through. Typical electrodes used in the anode and cathode chambers for all MES are carbon or graphite rods, brushes, and cloths [9]. Other materials for electrodes that were recently reported in the literature involved using nickel nanoparticles, phenol-melamine polymers and carbon nanofibres [78]. The anode electrode or the negative electrode is placed in the anode chamber and in contact with the anolyte solution. Similarly, the cathode electrode or positive electrode is placed in the cathode chamber and in contact with the catholyte solution [16].

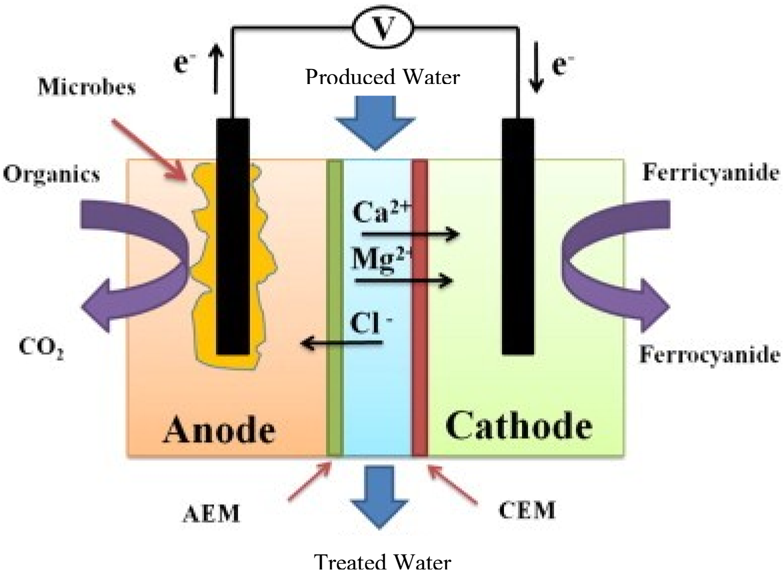


Figure 2.11: Microbial Desalination Cell design [79]

Microorganisms present in the anode chamber release electrons to the anode electrode while simultaneously generating H^+ ions inside the anolyte solution. These positively charged species are prevented from leaving the anode chamber with the help of AEM [80]. As a result, there is an accumulation of positive charge (or H^+ ions) in the anolyte solution and anions travel from the desalination chamber to the anode chamber in order to maintain charge neutrality in the anolyte [16]. Inside the cathode chamber, electrons are consumed by electron acceptors such as oxygen and potassium ferricyanide. The electron acceptors get reduced while consuming H^+ ions, creating a depletion of positive charge in the catholyte [80]. Therefore, the charge is balanced by the transfer of cations from the desalination chamber to the cathode chamber by passing through the CEM. As a consequence of these two charge-transfer processes, salt ions leave the wastewater in the middle chamber allowing the wastewater to be desalinated [16]. Therefore, the driving force for desalination is the charge difference created as a result of electron flow, proton accumulation in anolyte, and proton depletion in catholyte solutions. The driving force for current that flows through the external circuit is the electromotive force i.e. higher electron concentration in anolyte compared to the catholyte solution [81]. Therefore, the desalination chamber acts as an important salt bridge between the electrodes and ion transfer to electrode chambers is essential for a continued current generation [81]. If there is no anion transfer to the anode chamber, the accumulation of H^+ ions in the anolyte will attract the electrons and impede their flow towards the cathode electrode [81]. Similarly, if there is no cation transfer to the cathode chamber, the accumulation of OH^- ions in catholyte will repel electrons from reaching the cathode electrode. This will result in an immediate stop in current flow through the external circuit [81].

The anolyte solution in MDCs consists of microorganisms, substrate materials (as a food source for the microorganisms), buffer solution (for pH stability), and an optional mediator [9]. There are two kinds of microorganisms employed in MES; those that require artificially mediated electron transfer (e.g. Escherichia Coli and yeast) and those that do not (e.g. Geobacter Metallireducens and Shewanella Oneidensis) [82]. The latter are collectively termed exoelectrogens [82]. If the preference is given to desalination over wastewater treatment, then glucose or acetate can be used as substrates in the anode chamber instead of wastewater. The standard buffer solution used in MES is 1 M sodium phosphate buffer which is ideal for maintaining a solution at pH 7 [16]. Buffer solutions are essential because the control of anolyte pH is critical for optimum performance of microorganisms. The following electrochemical reaction takes place inside the anode chamber where the number of electrons released (n) depends on the substrate used.

$$\text{Substrate} + H_2O + \text{Biomass} \rightarrow CO_2 + n\,H^+ + n\,e^- \tag{1}$$

Since yeast are facultative aerobes, they perform different metabolic reactions at aerobic (Equation 2) and anaerobic conditions (Equation 3). When the substrate used is glucose, the following electrochemical reactions occur [83]:

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + 36\,\text{ATP} \tag{2}$$

$$3\,C_6H_{12}O_6 \rightarrow 6\,C_2H_5OH + 6\,CO_2 + 2\,\text{ATP} \tag{3}$$

Here, three ATPs further generate two electrons and one H^+ ion. Addition of a suitable mediator in the anode chamber significantly enhances electron transfer and reduces the size of anode chamber required for efficient desalination [84]. An oxidizing agent can function as a redox mediator in MDCs by reaching the electron transport chain of the microorganism where the mediator gets reduced after accepting the electron from electron carriers such as NADH [85]. The reduced mediator then shuttles the electrons to the electrode surface after which it turns back to its oxidized state [82]. When methylene blue (MB) is employed as the mediator, the reaction pathway includes [86]:

$$MB_{(oxidized)} + NADH_{(yeast)} \rightarrow NAD^{+}_{(yeast)} + MB_{(reduced)} \tag{4}$$

$$MB_{(reduced)} \rightarrow MB_{(oxidized)} + 2\ e^{-} + H^{+} \tag{5}$$

Electrons generated on the anode electrode travel towards the cathode via the external circuit, thus, generating electric current and potential. These electrons are picked up by the cathode electrode where they come in contact with the catholyte. The catholyte solution consists of an oxidizer and a buffer solution. The oxidizer acts as an electron acceptor and gets reduced on gaining an electron from the cathode electrode. The most commonly used oxidizers in MDC technologies are oxygen and potassium hexacyanoferrate (also called potassium ferricyanide). The electrochemical reaction at the cathode using potassium ferricyanide is [87]:

$$[Fe(CN)_{6}]^{3-} + e- \rightarrow [Fe(CN)_{6}]^{4-} \tag{6}$$

As a result of these electrochemical reactions, there is an accumulation of H^{+} ions in the anolyte and its deficiency in the catholyte. This charge imbalance drives the salt ions out of the wastewater resulting in its desalination.

2.3.3. History and background. Experiments on MDC were first performed in 2009 using a solution of mixed bacterial culture as anolyte and ferricyanide as catholyte [16]. The experiment resulted in 90% salt removal and a maximum power density of 31 W/m^{3} using artificial wastewater as substrate [16]. Further research was performed using actual wastewater as a substrate, mixed bacterial culture in anode chamber and ferricyanide in the cathode chamber. This experiment achieved 66% desalination in 16 days [88]. Since then several researchers have explored different microorganisms, chemicals and configurations to study their effect on desalination efficiency in MDCs and on power generation in MFCs. Table 2.2 provides a summary of these experiments, their main operating conditions, and their results. In this table, the parameter A/D refers to the volume ratio of anolyte solution employed to the wastewater desalinated. The experimental results of our work in this thesis will be later compared with the different MDCs appearing in this table.

Table 2.2: Comparison of performance of MDCs employed in existing literature

Microorganism	Substrate	Catholyte	A/D	MDC type	Desalination efficiency	Time (days)	Ref.
Mix microbial culture	Synthetic wastewater	Oxygen	1.43	UMDC	99% TDS	96	[89]
Mix microbial culture	Synthetic wastewater and acetate	Potassium ferricyanide	6.66	Batch MDC	97% hardness	1	[90]
Mix microbial culture	Acetate, vitamins, minerals	Oxygen	66.6	AMDC	67% conductivity	6	[80]
Mix bacterial culture	acetate	Potassium ferricyanide	2200	recirculated MDC	90% conductivity	1	[16]
Bacillus subtilis	Malachite Green dye	Potassium ferricyanide	1	Fed-batch MDC	62% conductivity	3	[91]
Bacterial strain from bioreactor	acetate	Bacterial strain from wastewater plant	1.25	Fed-batch BMDC	85% TDS	16	[92]
Mix bacterial culture	Organic content of wastewater	Bacterial strain from wastewater plant	1.4	MCDC with biocathode	27.5% conductivity	10	[93]

2.3.4. Types of MDC. A myriad of configurations of MDCs exists for achieving different purposes like chemical generation, hydrogen production and enhanced desalination. Several modifications are introduced for reducing the challenges of MDCs such as pH instability and ion accumulation in anode and cathode chambers. Many of these modifications are inspired by existing electrodialysis systems and other microbial electrochemical systems. Some of these configurations are explained below :

2.3.4.1. Air cathode microbial desalination cell (AMDC). Oxygen is the most commonly used oxidizing agent used in cathode chambers in MDCs [9]. It is usually provided by bubbling air through water inside the cathode chamber where the platinum electrode is the cathode electrode [94]. This has serious implications on MDC performance since the solubility of oxygen is low in water which results in slow mass transfer [84]. Some MDCs address this challenge by using a configuration in which the cathode electrode is exposed to air on one side and water on the other. Such MDC configurations are termed as air-cathode MDCs [84]. This reduces the cost of aeration in the cathode chamber and reduces the mass transfer limitations [84].

2.3.4.2. Biocathode microbial desalination cell (BMDC). Clauwaert et al. [95] first demonstrated the use of biocathode which employs microorganisms as the oxidizers in cathode chamber. Here, denitrifying bacteria are used to convert nitrates and nitrites into inert nitrogen gas. Yu et al [96] also modified this process by employing microorganisms for simultaneous nitrification and denitrification in the cathode compartment of an MDC.

2.3.4.3. Stack-structure microbial desalination cell (SMDC). In this configuration, which is borrowed from stacked electrodialysis cells, many desalination chambers are connected in series between the anode and cathode compartments [97]. Here, each desalination chamber is sandwiched between two chambers containing fresh water. During the operation, ions travel out of the desalination chamber and collect in the freshwater chambers, thus creating one dilute compartment and two concentrated compartments [98]. When more than one desalination chambers are connected in this way, a single electron is able to desalinate more ions. Due to the increase in internal resistance and, consequently, reduced MDC performance, it is not favorable to apply more than two desalination chambers [97].

2.3.4.4. Microbial electrodialysis cell (MEC). In this category, MDCs are modified to produce hydrogen in the cathode chamber while desalinating contaminated water [99]. However, since the electrochemical potential for hydrogen generation is higher than what typical MDCs have achieved so far, additional voltage is applied in this process [99].

2.3.4.5. Microbial electrolysis desalination and chemical-production cell (MEDCC). Certain modifications can be made into MDC configurations to produce acids and alkalis along with seawater desalination. Here, a bipolar membrane is employed by laminating AEM and CEM together and used with the anode compartment [99]. With sufficient application of large electrical potential, water is split at the bipolar membrane into OH^- ions and H^+ ions. The H^+ ions travel into the second chamber which is placed beside the anode compartment [99]. At the same time anions from the desalination chamber transport to the second chamber forming acids. Moreover, the cations from the desalination chamber travel into the cathode chamber forming alkali [99].

2.3.4.6. Microbial capacitive desalination cell (MCDC). In an MCDC, ions that accumulate in the anode and cathode chambers are deionized by getting adsorbed on activated carbon cloth membrane assemblies [100]. These ions are stored in the electrical double layer capacitors that form between the solution and activated carbon cloth membrane inside the cathode and anode chambers. Another aspect of MCDCs is that CEM is used adjacent to the anode instead of AEM. This allows cations to move freely through all the compartments which helps in maintaining electrical neutrality during desalination [100].

2.3.4.7. Up-flow microbial desalination cell (UMDC). This configuration consists of two cylindrical compartments fitted concentrically. The inner compartment contains the anode electrode and anolyte solution and it is separated from the outer compartment by an AEM [89]. The outer compartment functions as the desalination chamber and is sealed on the outside with a CEM. The CEM is coated with a platinum catalyst and carbon cloth which together act as cathode. Therefore, there is no need for an additional cathode chamber since the cathode is exposed to air and uses oxygen as its electron acceptor [89]. This configuration is operated in continuous mode where the solutions enter from the bottom and leave from the top of the cylindrical chambers. An advantage of this configuration is the increased surface area of both the IEMs exposed to the solution due to cylindrical shape [89].

2.3.4.8. Osmotic microbial desalination cell (OSMDC). Osmotic microbial desalination cells attempt to combine the concepts of dilution and desalination by using osmosis in conjunction with electric potential gradients [79]. This is achieved by replacing AEM with a forward osmosis membrane. Since the desalination chamber is filled with concentrated liquid, a relatively dilute water from the anode chamber flows into the desalination chamber through the forward osmosis membrane. This aids in reducing the salinity in the desalination chamber [79].

2.3.4.9. Submerged microbial desalination–denitrification cell (SMDDC). This type of MDC was developed for the purpose of combining direct nitrate removal from contaminated groundwater with groundwater desalination [99]. This configuration consists of two chambers – the anode and the cathode chambers which are placed inside groundwater which acts as the desalination chamber. Due to the established electric potential, nitrate ions travel from the groundwater into the anode chamber through the AEM. The effluent from this anode compartment is transferred to the cathode chamber where the nitrate is reduced by denitrifying bacteria [99].

2.3.5. Applications of MDC. Because MDCs currently generate low current densities, the conductivity of the desalination chamber is essential for high MDC performance [9]. Therefore, the desalination efficiency is higher for higher contamination concentration of seawater due to higher conductivity. On the contrary, existing electrodialysis and reverse osmosis desalination technologies face a disadvantage when highly contaminated wastewaters are treated [1]. This is because treatment high salt concentration requires much higher external energy sources which adds to the burden of operating costs [1]. For this reason, researchers envision that MDCs can be successfully applied in wastewater treatment plants in the form of pre-treatment to existing reverse osmosis and electrodialysis systems [99]. This will help to drastically reduce the typical costs for desalination [99]. Zhang et al [101] examined this hypothesis by using an upstream MDC to pretreat wastewater before an electrodialysis (ED) system. Moreover, the bioenergy generated from the MDC was used to power the ED system.

Other potential applications for MDCs include replacement of lime softening as pre-treatment unit for desalination of hard water, groundwater remediation, brackish water desalination with simultaneous production of hydrogen, or of acids and alkalis [99]. Production of acids and alkalis allows for recovery of ions that were desalinated. This helps to significantly reduce waste generation and membrane scaling [99]. Many MFCs also have a wide range of applications including their use as toxicity sensors, biosensors and for measuring water quality through biological oxygen demand (BOD) [102].

2.3.6. Merits of MDCs. MDCs have several unique advantages compared to existing desalination technologies. The microorganisms in MDCs can consume a wide range of organic matter like carbohydrates, volatile acids, alcohols, proteins, cellulose and wastewater [103]. This allows for simultaneous consumption of waste along with desalination and electricity generation. Moreover, certain microbial strains can reduce heavy metals present in wastewater in order to generate electricity [104]. Most substrates used in MDCs are low-cost chemicals which do not require additional expensive metal catalysts and electrodes for the electrochemical reactions at anode and cathode. This gives them an edge over conventional electrodialysis systems. Electricity recovery from wastewater creates a potential for unprecedented reduction in desalination costs. In some configurations, recovery of ions in the form of acids and alkalis eliminates brine generation which is typically associated with conventional desalination technologies like distillation, reverse osmosis and electrodialysis [105].

Because MDCs employ microorganisms, they perform well under mild operating conditions of temperature and pressure [106]. Moreover, a wide range of microbial strains has been employed in MDCs many of which are easily available in natural environments [89]. The best performing organisms are mix-microbial cultures that are found directly in the associated wastewater treatment plants [90]. Another advantage of using microorganisms is that they can be pre-conditioned to perform optimally at different operating conditions such as higher flow rates [107]. Use of acidogenic bacteria in mixed culture communities allows for operation of MDC in highly acidic conditions and, thus, eliminates the requirement of controlling the pH in the anode chamber [108].

2.3.7. Limitations of MDCs. The major limitation of MDCs is scaling and bio-fouling which is due to the use of ion exchange membranes [9]. The AEM is in continuous contact with the anolyte solution which contains microorganisms and other organic matter. Therefore, after a long operating time, a biofilm inevitably grows on AEM surface [92]. This has several possible implications such as physical blockage to anion transfer through the AEM and possible alteration of the polymeric structure and functional groups of the membrane [109]. These effects can intensify the hydrogen ion gradient across the AEM, increase membrane resistance, and subsequently reduce the efficiency of the current generation in MDCs [109]. Since conventional electrodialysis systems do not employ microorganisms, significant research is required to study the nature of bio-fouling on IEMs and their long-term performance [9]. Some compounds present in seawater and produced water such as calcium, magnesium and barium salts precipitate on the IEMs and form scales [110]. This results in an increase in the internal electrical resistance of the cell and causes reduction in MDC performance [110].

In MDCs, the microorganisms take several hours to get acclimatized, develop biofilm on anode electrode and release natural mediators needed to transfer electrons. For this reason, it is difficult to get a constant power supply [103]. Moreover, in mixed cultures, several different bacteria compete with each other and grow at different rates, thus, setting different potentials [103]. Thus, it is difficult to predict the potential for pure and mixed cultures. Sometimes, new bacterial species grow inside the anode chamber even when pure cultures are used [99].

Another issue with MDCs is the pH instability [9]. As the electrochemical reactions proceed, excess H^+ ions are released into the anode chamber which lowers the pH. Simultaneously, if oxygen is used as an oxidizer in the cathode then OH^- ions get accumulated which continuously increases the pH [9]. The microorganisms in the anode chamber are sensitive to pH and thus, this drastically lowers current output [9]. Another disadvantage of MDCs is the high cost of ion exchange membranes and other mediators that are used to enhance electron transfer in the anode chamber. Moreover, conversion of the generated direct current to alternating current requires additional investments.

Chapter 3: Results and Discussions: Parametric Study

In the present study, several operating parameters have been selected for evaluation of their individual effects on MDC performance. These parameters include aeration rates in catholyte and anolyte, initial Total Dissolved Solids (TDS) concentration of produced water, initial pH of anolyte, the quantity of packed activated carbon granules, the concentration of different mediators and their combination, and repeated batch operation.

The influence of each parameter on MDC performance was measured over a minimum of three identical MDCs which were operated simultaneously with fixed operating conditions and time. The default concentrations of yeast, glucose, and methylene blue were fixed at 20 g/l, 90 g/l, and 0.5 mM. The default anodic environment was anaerobic and cathode air flow rate was controlled at 150 ml/min. The default produced water TDS concentration was 40 g/l. Anyone of these default conditions was only varied when a parameter associated with that condition was to be studied.

At the end of the study, a final experiment was performed under the optimized conditions and its performance is measured over 72 hours. For each experimental run, MDC performance was evaluated by measuring TDS removal percentage in produced water. Additionally, the effect of parameters on the pH and conductivity of anolyte and catholyte were also studied for particular experiments.

3.1. Preparation of Anolyte, Catholyte, and Wastewater

100 ml of anolyte solution was prepared for each experimental run in two steps. The first step involved heating a 70 ml of the following solution for 10 minutes on a hot plate (Stuart Scientific). The solution comprised of 20 g/l of deactivated yeast cells, Saccharomyces cerevisiae, (manufactured by DCL ®) and 90 g/l of D-Glucose (manufactured by Safa ®) [83]. Here, D-Glucose is provided as a substrate to be consumed by yeast cells. The packaged yeast cells also contained sorbitan monostearate which acts as an emulsifier and rehydration agent for efficient activation of yeast.

In the second step, the heated yeast solution was allowed to cool naturally for 10 minutes. Then, a 30 ml solution containing 0.1743 g Na_2HPO_4, 0.1215 g $NaH_2PO_4.2H_2O$ (both obtained from VWR Prolabo ® chemicals), and 0.0319 g of methylene blue (BDH Laboratory supplies) was added to the yeast solution [93, 101]. For experiments involving the use of a lipophilic mediator, a standard 10 ml solution of 20 mM of menadione (Sigma Aldrich) was prepared. During the experiments, respective volumes of menadione solution, of the order of microliters, were added to the anode compartments of the MDCs after completing step 2 and after transferring anolyte solution to the anode chambers of the respective MDCs.

For all experiments, the concentration of catholyte was fixed. 100 ml of catholyte was prepared by adding 2 g potassium hexacyanoferrate (III) (Merck KgaA), 0.1743 g Na_2HPO_4, and 0.1215 g $NaH_2PO_4.2H_2O$ [112]. After stirring on a magnetic plate, this solution was added to the cathode compartment of the MDC. Produced water was procured from the wastewater treatment facility of an oil and natural gas company, Dana Gas. 70 ml of produced water solution was prepared by adding 33 ml of produced water to 37 ml of distilled water to get a TDS reading of 40 g/l. Conductivity measurements of produced water solution were taken at 10 times dilution because the conductivity meter was not calibrated for conductivity values greater than 50 mS/cm. During dilution, 3ml of produced water solution was extracted using a graduated cylinder having a resolution of 0.2 ml. This was added to 30 ml distilled water which was measured in a graduated cylinder having a resolution of 1 ml.

3.2. MDC Construction and Operation

As shown below in Figure 3.1, each MDC unit consists of three acrylic cube-shaped blocks of size 10 cm x 8 cm. The anode and cathode blocks had 1.5 cm width and the desalination block had 1 cm width. The three chambers are connected together using rubber gaskets, steel rods, and steel bolts to ensure that the connections are airtight [83]. The anode and cathode electrodes used were plain weave carbon cloth (Al Khowahir Chemicals Mat.Tr. LLC). The electrode and membrane surface area exposed to the chambers was 55 cm^2. The AEM and CEM were procured from Membranes International, USA. The AEM was fixed between the anode and desalination chambers. While the CEM was fixed between the cathode and desalination chambers. The electrodes were fixed inside the anode and cathode chambers on the walls opposite to

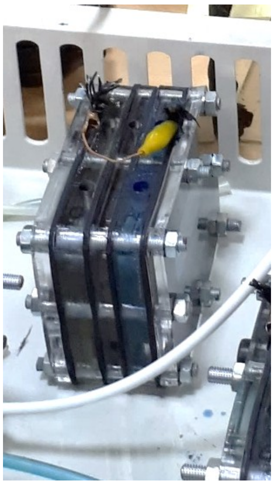


Figure 3.1: MDC setup for parametric study

the membranes. Following the instructions of Membranes International, each membrane was soaked in 5 % (w/w) NaCl solution for 24 hours before its use in MDC. The NaCl crystals, having a purity grade of 99.5%, were procured from Fisher Scientific and used to make the NaCl solution. Similar copper wires were used to connect the anode and cathode electrodes of each MDC unit. The air flow was supplied using an aquarium air pump (Boyu ®) whose supply was controlled using an air flow controller (Matheson ®). The outlet pipe of each air flow controller was immersed in the anode and cathode chambers using a 1 cm wide hole at the top of the chamber.

3.3. Measurements and Characterization Technique

The cell voltage and current were recorded using a multimeter which was supplied by UNI-T. For measuring the voltage, the multimeter was connected in parallel to the external wire and the reading was taken after 1-2 hours when it reached a stable value. Then the multimeter was connected in series and the current reading was taken in a similar manner. The same procedure was applied for each of the other two MDC units. The conductivity of the solutions was measured with a benchtop conductivity meter (Martini Instruments). The pH was measured with a benchtop pH meter (Hanna Instruments). The total dissolved solids (TDS) was measured with a TDS meter (HACH). All mass measurements were made by using a (Radwag ®) digital weighing balance with an accuracy of ± 0.0005 g. All volumes were measured using a graduated cylinder with a minimum reading of 1 ml. The resolution of the pH meter used was 0.01, that of TDS meter was 0.1 g/l and that of the thermometer was 0.1 °C. The minimum reading of conductivity meter was 0.01 μS/cm.

3.4. Results and Discussion

3.4.1. Effect of aeration in the anolyte. Aeration of the anolyte solution is an important parameter because of the facultative nature of Saccharomyces cerevisiae which allows the microorganism to metabolize substrates differently in aerobic and anaerobic conditions. As mentioned in section 2.3.2, in aerobic and anaerobic conditions, the yeast cells perform different metabolic processes and, therefore, generate electrons at different rates. While the presence of oxygen is advantageous for the generation of electrons, it may also have a negative effect on MDC performance. This is because oxygen is a good oxidizing agent and an electron acceptor. Therefore, it can consume electrons generated by the yeast cells and impede the transfer of electrons from mediator to the electrode. Previous experiments performed on yeast cells in MFCs resulted in a lower current generation with aerobic environments than with anaerobic environments [67, 92]. However, air flow rates were not specified in these studies. Therefore, present experimentation employs low air flow rates and compares their effect on MDC performance with an MDC containing anaerobic environment. Therefore, in this study, the influence of aeration of anode solution on desalination efficiency was studied for an operation time of 24 hours. Three MDC units were operated simultaneously. The first unit housed anaerobic conditions for its anode chamber. The anode chambers of the second and third MDCs had aeration flow rates of 60 ml/min and 80 ml/min.

Figure 3.2 shows the percentage reduction in TDS of the produced water in the desalination chamber. The graph suggests that as the anolyte conditions shift from anaerobic to aerobic environment at 60 ml/min of air flow rate, the desalination efficiency of MDC increases, i.e., TDS removal rate of produced water increases. Moreover, increase in aeration rate from 60 ml/min to 80 ml/min also results in higher desalination of produced water. This is because, as mentioned in section 2.3.2, under aerobic conditions, the metabolic processes of yeast generate more electrons which result in higher current and greater desalination efficiency. When aeration rate is increased, more oxygen is made available to the yeast cells. Therefore, more cells undertake the aerobic pathway and, consequently, generate more electrons. Moreover, in this study, current generation increased from 26 μA to 130 μA from anaerobic to aerobic conditions. This suggests that, contrary to previous studies [67,92], oxygen consumption for metabolic processes was dominant over the consumption of electrons by oxygen. The reason for this may be attributed to the higher concentration ratio of yeast to oxygen in the anode chamber.

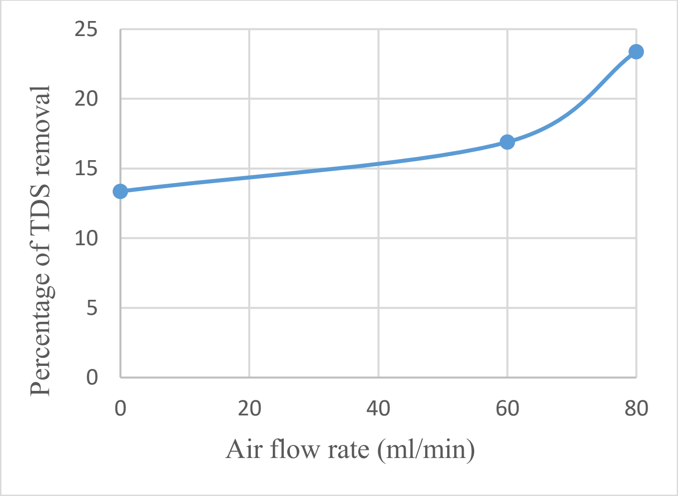


Figure 3.2: Effect of aeration in anolyte on desalination efficiency

3.4.2. Effect of aeration in the catholyte. Ferricyanide and oxygen are the most commonly used oxidizers in cathode compartments of MDCs and MFCs [9]. Although, ferricyanide has a lower theoretical redox potential than oxygen. In practice, oxygen generates a much lower reduction potential than ferricyanide due to higher overpotential [113]. Overpotential of a half-reaction is the difference between its thermodynamically calculated reduction potential and experimentally observed reduction potential [113]. Therefore, ferricyanide was employed as oxidizer at the cathode in this study due to its higher experimental reduction potential. According to two previous studies, additional aeration of ferricyanide resulted in a higher current generation in MFCs [76, 102]. Therefore, present experimentation studies the effect of aeration of ferricyanide on desalination efficiency of MDC during a 24 hour operation period.

Here, the cathode chambers of the MDCs contained air flow rates of 90 ml/min, 120 ml/min, and 150 ml/min. Figure 3.3 shows the percentage reduction in TDS of the produced water solution in the desalination chamber. The graph suggests that higher aeration rate in cathode chamber results in higher desalination of produced water. Moreover, as the air flow rate in cathode chamber increased, the voltage generated by

MDCs increased from 100 mV to 310 mV to 530 mV in agreement with the two previously cited studies [92, 94]. This is because of the role of oxygen as an electron acceptor. The electrochemical reaction (Equation 6) at cathode reduces ferricyanide anions to ferrocyanide. However, oxygen oxidizes back the ferrocyanide anions making them available for the cathode reaction again (Equation 7). These reactions are depicted below :

$$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-} \tag{6}$$

$$[Fe(CN)_6]^{4-} + O_2 + 4\,H^+ \rightarrow 2\,H_2O + [Fe(CN)_6]^{3-} \tag{7}$$

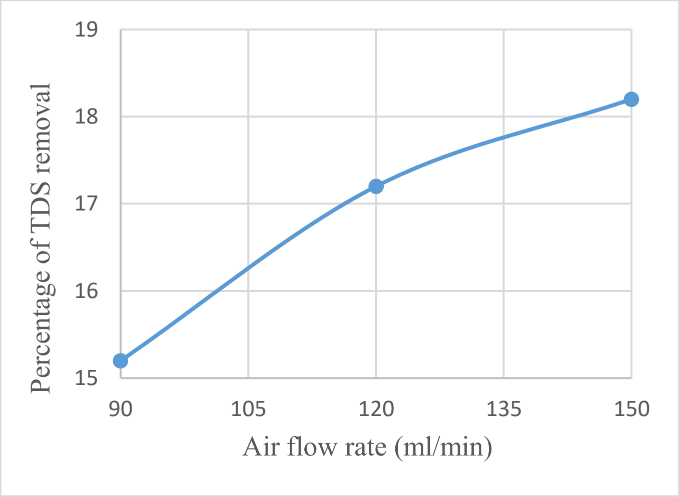


Figure 3.3: Effect of aeration in catholyte on desalination efficiency

3.4.3. Effect of initial TDS of produced water. Four MDCs were operated simultaneously for 21 hours at fixed operating conditions. The MDCs contained produced water at four different concentrations which were measured in terms of TDS. A higher concentration of contaminants in produced water results in higher TDS and electrical conductivity. TDS meters essentially measure electrical charge in a solution. Since all dissolved substances conduct a charge, TDS meters provide a good estimate of the ionic strength of the solution. Since the voltage produced by MDCs is low and of the order of millivolts, the high ionic strength of desalination chamber is critical for achieving higher desalination. This is because the desalination chamber functions as a salt bridge in an MDC. This means that current generation results in electrical potential gradient between the anode and cathode which further drives ion transfer from the desalination chamber towards the electrodes. This ion transfer is essential for the functioning of MDCs. A desalination chamber having lower ionic strength results in a lower ionic transfer which, consequently, reduces the desalination efficiency. Thus, as Fig. 3.4 suggests, as initial TDS of desalination chamber increases, desalination efficiency increases.

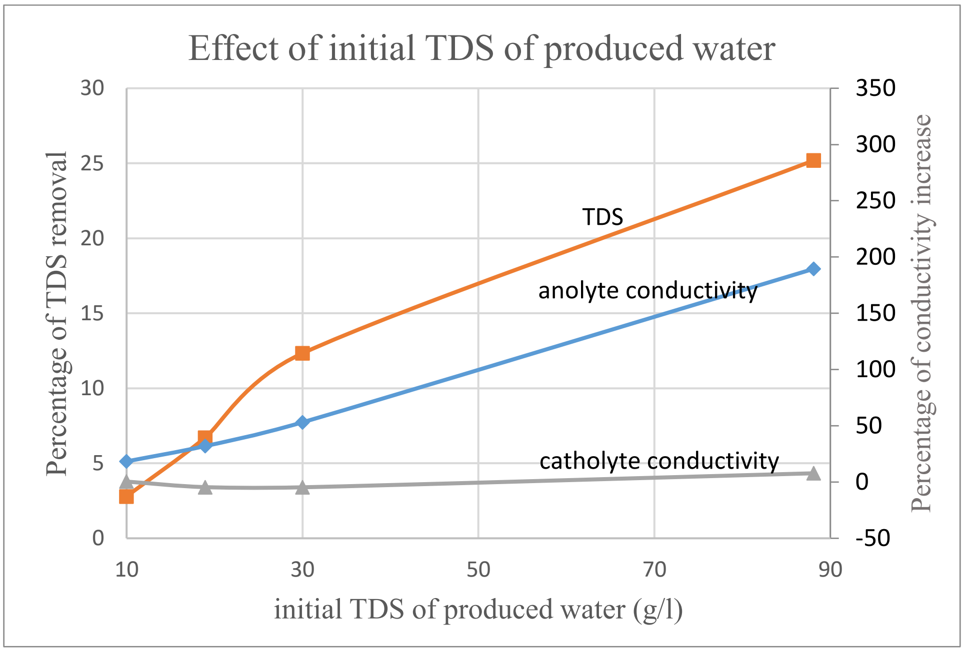


Figure 3.4: Effect of initial TDS of produced water on desalination efficiency and conductivity of anolyte and catholyte

Figure 3.4 also depicts the effect of TDS of produced water on anolyte and catholyte conductivity. The percentage of increase in anolyte conductivity is positive for all TDS values of produced water. This implies that the ionic strength of anolyte increases during MDC operation. This result also corroborates the results of previous experiments where anolyte conductivity was shown to increase during the desalination process in MDCs [80]. This is because of the transfer of anions from the desalination chamber to the anode chamber. After 24 hours of operation when the MDC apparatus was opened, deposits of crystals were found on the AEM towards the side of desalination chamber, thus, corroborating the transfer of anions from desalination chamber to the anode chamber. Therefore, as the initial TDS increases, and desalination efficiency increases, more anions transfer from the middle chamber to the anode chamber, and therefore, the electrical conductivity of anolyte increases.

Figure 3.4 also suggests that changes in catholyte conductivity are small compared to changes in anolyte conductivity. While anolyte conductivity changes from 18% to 189%, catholyte conductivity changes from -4.6% to 7.8%. This result is unexpected since catholyte conductivity is also expected to increase due to the transfer of cations from desalination chamber to the cathode chamber. In a previous publication, the conductivity of catholyte increased during MDC operation [80]. However, they had used oxygen as the oxidizer instead of ferricyanide. In the present study, as will be discussed in the proceeding section 3.4.9, during a 3-day operation of one MDC unit, it was observed that catholyte conductivity reduces during the first day of operation and increases continuously in the following days. Moreover, throughout the parametric study, it was observed that when the operation time was approximately one day, catholyte conductivity either reduced significantly or changed by a small amount. This reduction in catholyte conductivity during the first 24-hour operation may be attributed to osmosis between the catholyte and produced water solution due to the difference in concentration.

Moreover, during the present experiment, white crystal deposits were observed on the CEM towards the side of cathode chamber. There was no visible deposition towards the side of desalination chamber. This suggests that the anions from cathode chamber probably migrated towards the membrane, towards the direction of the anode electrode, in the electric field and formed scales on the membrane. Therefore, scale formation of the ions from the catholyte solution may also have contributed to a reduction in catholyte conductivity during the first 24-hour operation.

Figure 3.5 shows the effect of initial TDS on pH in the anode and cathode chambers. The pH decreases for both the anolyte and catholyte during all experimental runs. The pH in the anolyte decreases because of the release of H^+ ions, despite the addition of buffer solution. One experiment was carried out without the addition of buffer which showed a much higher pH drop in both anolyte and catholyte solutions. Because the pH is a critical factor for the metabolic processes of microorganisms [89], this suggests that there is a need to optimize the quantity of phosphate buffer in the anolyte in order to achieve lower pH reduction in the anolyte.

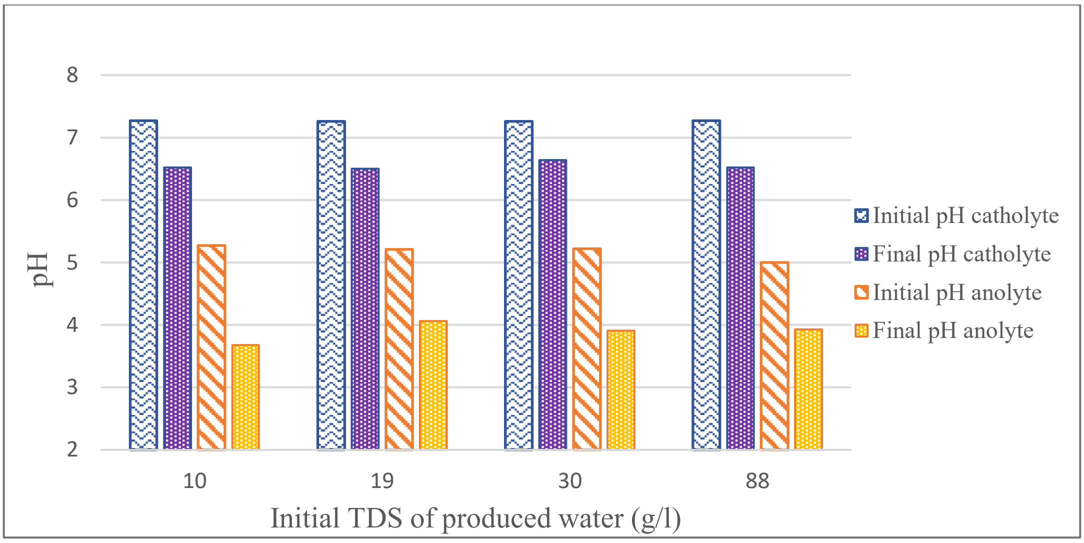


Figure 3.5: Effect of initial TDS of produced water on pH of anolyte and catholyte

Figure 3.5 also suggests a consistent pH drop in cathode solution as the initial TDS of produced water is increased. Two experiments were carried out to check the drop in catholyte pH when water or seawater (of 43 g/l TDS) is used instead of produced water. In both experiments, the catholyte pH decreased. This suggests that this drop is probably due to the electrochemical reaction at the cathode. Only two studies have been reported to employ a combination of ferricyanide and oxygen in the cathode chamber [92, 94]. However, they did not investigate the change in pH of catholyte. Moreover, no explanation could be found in existing literature for pH reduction in catholyte solution. As the TDS of produced water increases, the pH drop for the catholyte is consistent suggesting that this pH drop is not significantly affected by the change in produced water contamination concentration. The pH drop for the anolyte is approximately 1.3-1.5 for all TDS values of produced water with no observable correlation between the two.

3.4.4. Effect of activated carbon quantity. Three MDCs were operated simultaneously for 45 hours at fixed operating conditions. The operation time was longer than 24 hours in order to allow time for biofilm development on activated carbon granules [114]. All the anode chambers were provided anaerobic conditions. Activated carbon granules of particle size between 1 mm and 4 mm were employed based on existing literature [114]. Activated carbon granules were used because they provide a higher surface area for biofilm growth and enhance electrical conductivity in the anode solution [64, 85]. The first MDC contained no activated carbon. The second and third MDCs were packed with 4 g and 12.5 g of activated carbon particulates which covered one-fourth and one-half the anolyte volumes respectively. Figure 3.6 shows a rise in TDS removal from 27% to 31 %. The overall desalination efficiencies in this study were high due to a longer operation time of 45 hours. Moreover, another reason for high efficiencies is that the three MDC units had been operated for a day at equal operating conditions which had led to biofilm growth prior to starting the operation of this experimental set.

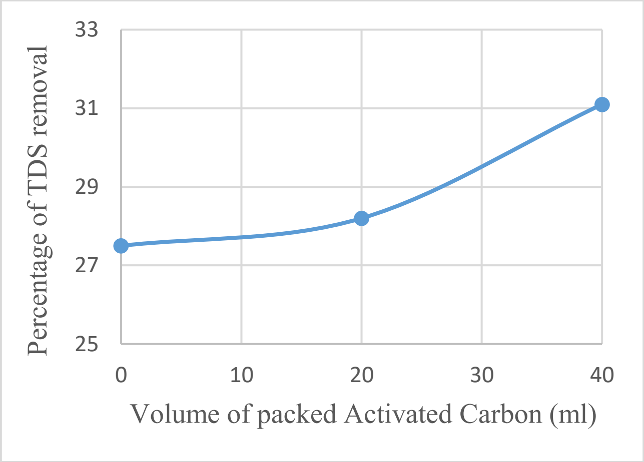


Figure 3.6: Effect of activated carbon quantity on desalination efficiency

3.4.5. Effect of initial pH of anolyte.

As mentioned in section 3.4.3, pH of the anolyte solution is a pertinent factor for the optimum performance of microorganisms. However, the optimum pH value varies for different organisms. For example, pH values between 7 and 8 were found to be optimum for highest desalination efficiency in an MDC where the bacterial strain, Bacillus subtilis was employed in the anode chamber [91]. However, no information exists on the effect of pH on the performance of microbial electrochemical systems employing Saccharomyces cerevisiae. Moreover, because of the high acidification capacity of S. cerevisiae, it is difficult to maintain a constant pH value in the anode chamber [115].

A recent study employed a pH-stat to ensure a constant pH value in a yeast solution by using either 1 N NaOH or 1N KOH as the base [115]. The study, however, revealed that there was growth inhibition in S. cerevisiae at pH values between 8 and 9. At pH 9, the cell cycle stopped due to growth arrest and also because the cells required time to adjust to the highly alkaline conditions.However, pH 9 did not inhibit other activities of S. cerevisiae including potassium transport, respiration, and amino acid transport [115]. It was also suspected that the cause for that growth inhibition was the high concentration of Na^+ or K^+ ions at high pH and not because of the pH itself. Furthermore, the study revealed that the rate of the fermentation process in S. cerevisiae decreased and respiration rate increased as the pH was increased from 4 to 9 [115]. Therefore, aerobic respiration process was more dominant at high pH values [115]. Since section 3.4.1 of the present study revealed that aerobic respiration results in higher desalination efficiency than anaerobic respiration as per Equations 2 and 3. Higher desalination efficiencies may be obtained when S. cerevisiae in MDCs have higher pH values. As a result, three initial pH values were chosen above7 and below pH 9 so as to investigate their effect on desalination efficiency during an operation time of 6 hours. In order to avoid accumulation of Na^+ ions, phosphate buffer was used instead of NaOH to increase pH of anolyte.

Most of the experiments performed on MDCs and MFCs use 1 M phosphate buffer solution in the anode chamber in an attempt to control its pH [80]. A buffer solution consists of a weakly acidic chemical and its conjugate base. Both components of buffer solutions are required to control the pH of a solution if the solution is likely to shift in both directions of pH. However, anolyte solutions employed in MDCs only shift towards a lower pH and this change is significant and fast in the case of S. cerevisiae. For this reason, in this experiment, the acidic component of the buffer solution was eliminated. Addition of greater quantities of the basic component of phosphate buffer was employed to raise the pH more efficiently. Therefore, three MDC units were operated simultaneously containing three different quantities of disodium hydrogen phosphate (Na_2HPO_4), i.e., 0.2 g, 1 g, and 5 g. Sodium dihydrogen phosphate (NaH_2PO_4) was not added to the solution.

Figures 3.7 and 3.8 delineate the effect of anolyte pH on various parameters such as desalination efficiency, conductivity change in catholyte and pH change in anolyte and catholyte. For initial pH values of 7, 7.7 and 8.3, the final pH values were 5.2, 6.3 and 7.3. Figure 3.7 suggests that among the final pH anolyte values, highest desalination efficiency is achieved for pH 6.3. The slightly lower desalination efficiency at final pH of 7.3 may be attributed to a reduction in growth rate of S.

cerevisiae. This is because a lower growth rate could have affected the metabolic processes resulting in lesser electrons being supplied to the anode electrode. This might have led to lower current generation as well as lower desalination efficiency.

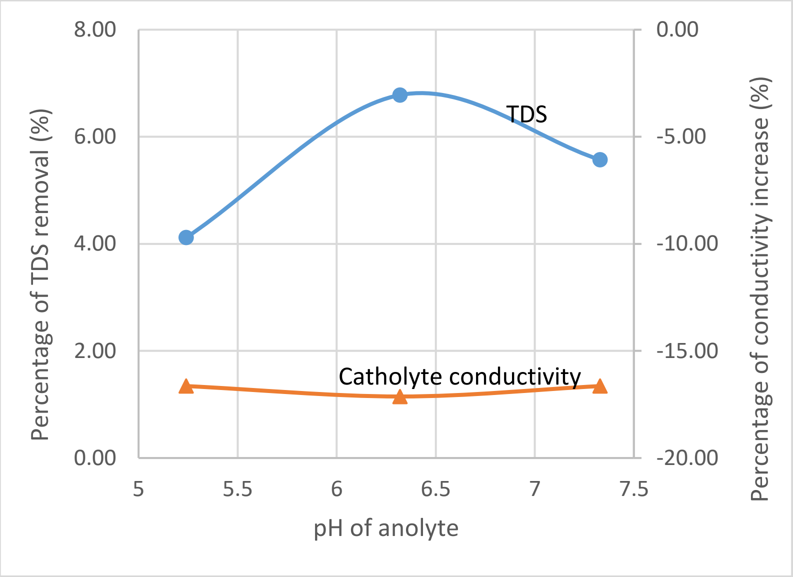


Figure 3.7: Effect of pH of anolyte on desalination efficiency and catholyte conductivity

The overall desalination efficiencies in this experiment are low compared to previous experiments because the operating time was only 6 hours. From the Figure 3.7, the conductivity of the catholyte decreases consistently with a slightly greater decrease at pH 6.3. Therefore, there seems to be a correlation between removal of ions from the desalination chamber and reduction of conductivity in the cathode chamber. As is shown later in section 3.4.10, catholyte conductivity decreases during the first 24 hours of operation and increases thereon. Theoretically, the catholyte conductivity should increase because of transfer of cations from desalination chamber to the cathode chamber. This initial trend of reduction in catholyte conductivity could likely be due to osmosis of catholyte into the desalination chamber. Although, there was no visible change in the color of the produced water in the desalination chamber.

The results of Figure 3.8 are in corroboration with previous experiments in the present study. The pH of anolyte and catholyte solutions decreases during the three experimental runs. From Figure 3.8, it can be concluded that higher initial pH of anolyte mitigates the problem of pH reduction during operation. Therefore, for initial anolyte pH values of 7, 7.7 and 8.3, the change in anolyte pH lowered from 1.8 to 1.4, and finally to 0.9. Therefore, this study reveals that while an initial anolyte pH of 7.7 is optimum for desalination efficiency, initial pH of 8.3 is better for reducing pH change in anolyte. The change in catholyte pH follows a trend similar to desalination efficiency and change in catholyte conductivity. Therefore, at an initial anolyte pH of 7.7, desalination efficiency is maximum, reduction in catholyte conductivity is greatest and reduction in catholyte pH is greatest.

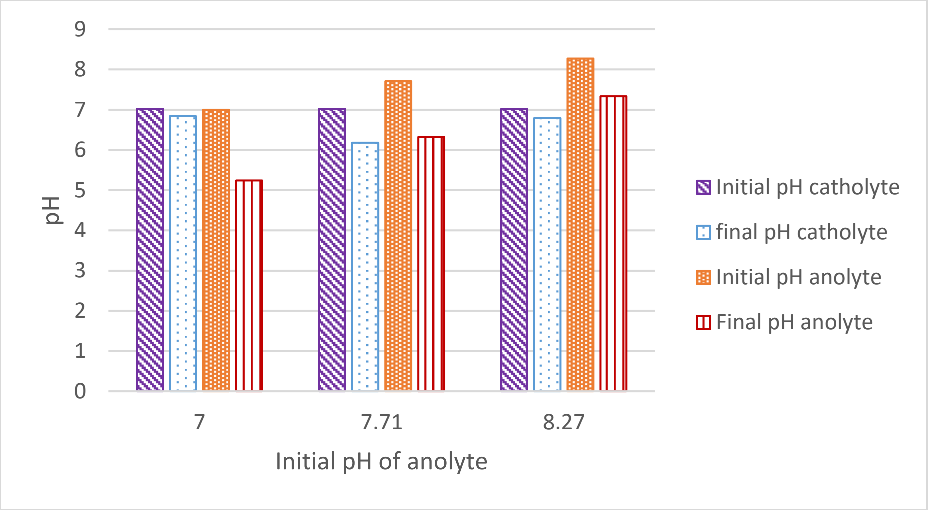


Figure 3.8: Effect of initial pH of anolyte on the pH change in anolyte and catholyte

3.4.6. Effect of concentration of methylene blue mediator. There are several chemicals that can act as hydrophilic mediators for microorganisms employed in microbial electrochemical systems (MES). In one study, methylene blue was reported to generate the highest efficiency in a microbial fuel cell (MFC) employing the yeast strain, Candida melibiosica. Other mediators used in this study were methyl orange, methyl red, neutral red and bromocresol green. Few studies also reported using methylene blue and Saccharomyces cerevisiae in MFCs [94, 96]. In the present study, methylene blue is employed as a mediator in MDC units containing Saccharomyces cerevisiae. Here, methylene blue concentration in anode chamber was varied from 0.05 mM to 5 mM [111]. Since yeast is a eukaryote, its electron transport chain exists inside its cytoplasm and the mitochondria which cannot be accessed by hydrophilic mediators. This is in contrast to prokaryote cells, whose most of the redox centers are accessible extracellularly. Fortunately, like prokaryotes, eukaryotes have trans-Plasma Membrane

Electron Transport (tPMET) systems which are present near the periplasm of the cell and can be available to hydrophilic mediators [116].

The purpose of mediators in MES systems is to interact with substances used in the catabolic pathways of the microorganism (e.g. NADH) in order to capture their electrons and shuttle them to the electrodes present in the anode chamber [85]. The reaction pathways that enable methylene blue (MB) to speed up electron transfer include [86]:

$$\mathrm{MB}_{(\mathrm{oxidized})} + \mathrm{NADH}_{(\mathrm{yeast})} \rightarrow \mathrm{NAD}^{+}{}_{(\mathrm{yeast})} + \mathrm{MB}_{(\mathrm{reduced})} \tag{4}$$

$$\mathrm{MB}_{(\mathrm{reduced})} \rightarrow \mathrm{MB}_{(\mathrm{oxidized})} + 2\,\mathrm{e}^{-} + \mathrm{H}^{+} \tag{5}$$

In this research, three MDCs were operated simultaneously for 22 hours at fixed operating conditions where methylene blue concentrations of 0.2, 1, and 5 mM were employed. The effect of MB concentration was studied on desalination efficiency, catholyte conductivity, and pH of anolyte and catholyte solutions. Figure 3.9 suggests that as the concentration of MB increases, desalination efficiency increases substantially. This is because more mediator is available to shuttle more electrons from the yeast cells to the anode electrode.

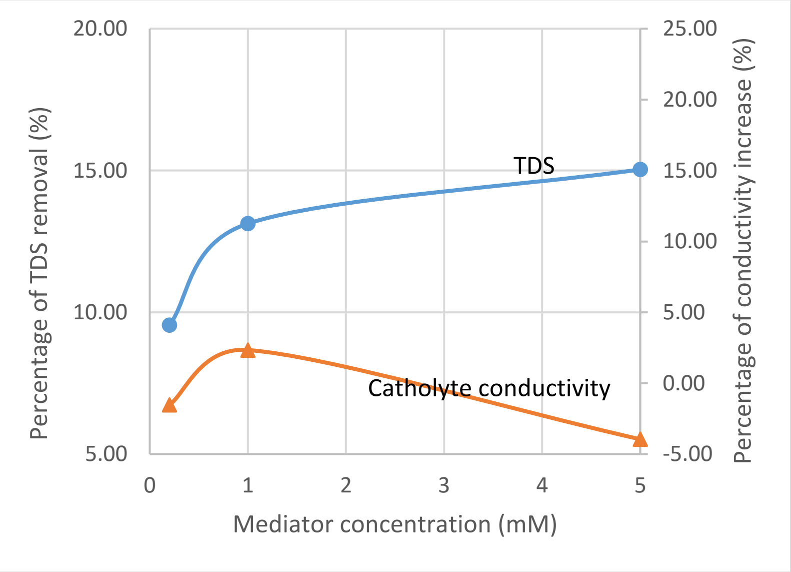


Figure 3.9: Effect of methylene blue concentration on desalination efficiency and catholyte conductivity

From the Figure 3.9, it can also be seen that as mediator concentration increases, the percentage of catholyte conductivity changes by -1.5 %, +2.3% and -3.9% respectively. These changes may seem larger in terms of percentage, they are however small in terms of absolute values. For an initial catholyte conductivity of 12.39 mS, the final catholyte conductivities are 12.20 mS, 12.68 mS, and 11.90 mS. Therefore, it can be seen that these changes are less than 1 mS/cm and may be assumed small compared to conductivity changes in the previous sections of this study. However, keeping aside the direction of conductivity change, it can be noted that the magnitude of conductivity change increases slightly as the mediator concentration increases and as desalination efficiency increases.

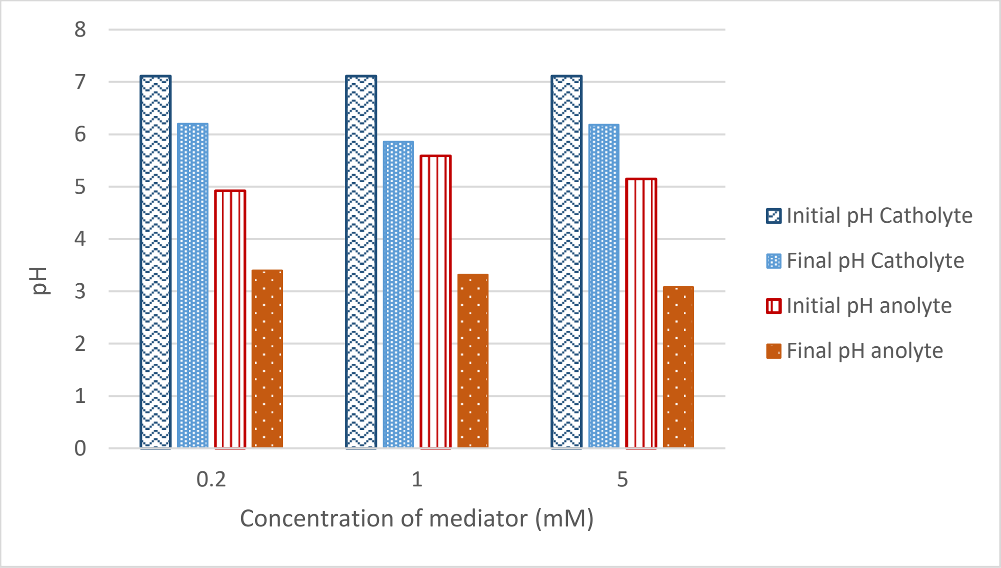


Figure 3.10: Effect of methylene blue concentration on pH of anolyte and catholyte

Figure 3.10 depicts the change in pH reduction in anolyte and catholyte solutions as the mediator concentration is varied. Here, it is noted that the reduction in anolyte and catholyte pH follow a similar trend where methylene blue concentration of 1 mM gives slightly higher pH reduction than 0.2 mM and 5 mM. However, unlike previous experiments in this study, the pH reduction trend is not similar to the trend followed by desalination efficiency. While the desalination efficiency is maximum at highest methylene blue concentration, the reduction of anolyte and catholyte pH is maximum at 1 mM concentration.

3.4.7. Effect of different mediators and their combination. While hydrophilic mediators are able to capture electrons present at the periplasm of eukaryotic cells, they do not have access to those present beyond the cell membrane [116]. In such cases, lipophilic mediators can be used since they can cross the cell membrane due to their high solubility in lipids, fats, and organic solvents. Lipophilic mediators interact with redox centers inside the cytoplasm, get reduced and diffuse out of the cell. However, because they have low solubility in aqueous solutions such as anolytes of MES systems, they cannot transfer electrons from outside the cell to the anode electrodes [116]. To overcome these challenges, some studies have employed double mediator systems that comprise one hydrophilic and one lipophilic mediator to enhance current generation. In this case, the lipophilic mediator transfers the electrons to the hydrophilic mediator after it diffuses out of the cell into the aqueous solution [117]. Menadione has been proven to be among the most effective lipophilic mediators for Saccharomyces cerevisiae when used in conjunction with a hydrophilic mediator [97, 99].

In this section, several experiments were carried out simultaneously at fixed operating conditions for 22 hours. The first experimental run comprised an anode chamber containing yeast cells and glucose in the absence of any mediator. Its desalination efficiency was 4.1% (not shown in Figure 3.11). Three sets of experiments were performed using menadione as the only mediator with each experiment having a concentration of 20, 50 and 100 μM. Another set of experiments comprised a combination of methylene blue and menadione. For these experiments, 0.2 mM of methylene blue was used while concentrations of menadione were varied between 20, 50 and 100 μM. The results of these experiments together with those in section 3.4.6 are shown in Figure 3.11.

The desalination efficiency for all concentrations of menadione was below 8% but above the efficiency for the MDC without any mediator. It should be noted that very small concentrations of menadione were added to these experiments. While 200 μM of methylene blue was required to increase desalination efficiency to 9.5 %, only 20 μM of menadione was added to raise the efficiency to 7.5%. Moreover, the combination of menadione and methylene blue was the most effective for desalination efficiency. This is because, as can be seen in Figure 3.11, a much higher concentration of mediator was required by methylene blue to achieve desalination efficiency comparable with that achieved by the combination of menadione and methylene blue. While 300 µM of both mediators achieved 12.7% TDS removal, 1000 µM of methylene blue was required to achieve similar TDS removal of 13.13%.

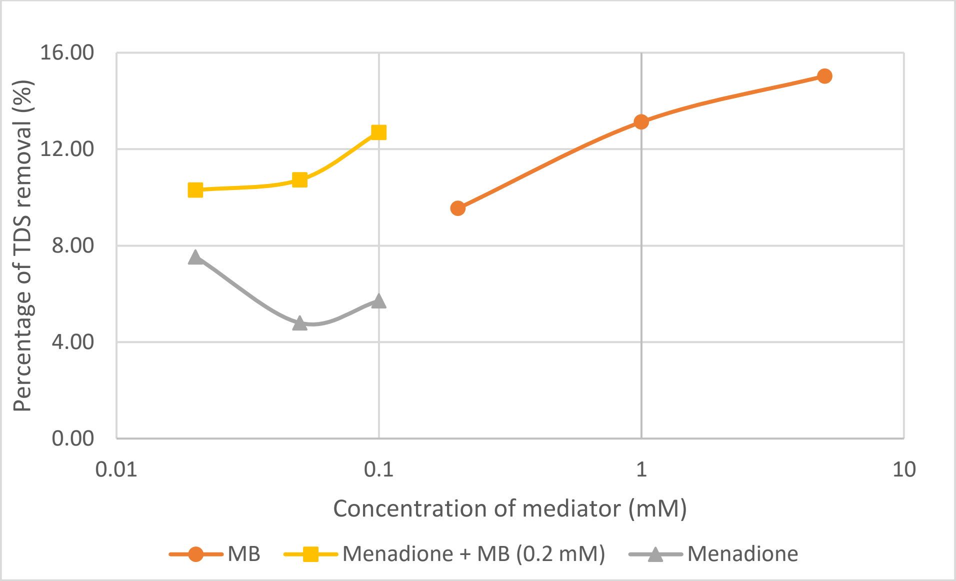


Figure 3.11: Effect of different mediators on desalination efficiency

In the experiments where only methylene blue was used, as the concentration of methylene blue was raised from 200 µM to 5000 µM, desalination efficiency increased substantially from 9.5% to 15%. For the experiments where 200 µM of methylene blue was combined with different concentrations of menadione, there was a substantial rise in desalination efficiency. This efficiency was higher than the desalination efficiencies using only 200 µM methylene blue and only menadione. These experiments suggest that the combination of hydrophilic and lipophilic mediators achieves higher desalination efficiency than the individual mediators when the total concentration of mediators is the same. This result corroborates the results of previous studies that compared the performance of microbial electrochemical systems using a combination of mediators with those using individual mediators [117]. Figure 3.11 also suggests that the double mediator system used in the present study has higher oxidizing strength than the individual mediators, menadione, and methylene blue.

3.4.8. Effect of repeated batch process. For this experiment, one MDC unit was operated multiple times for a duration of 24 hours and using same operating conditions. The anode and cathode chambers were aerated at 80 ml/min and 150 ml/min respectively and the produced water TDS was 40 g/l During the period of 12 days, the membranes and electrodes were not replaced. This allowed the biofilm on the anode electrode to grow with each addition of anolyte solution. Before and after each 24-hour operation (or cycle) the MDC unit was rinsed twice with water to remove excess salts or chemicals deposited on the base of the chambers. Each operation of the MDC was used as a reference while performing a few sections of the optimization study where the other MDC units were also at a similar stage with respect to their membranes and electrodes.

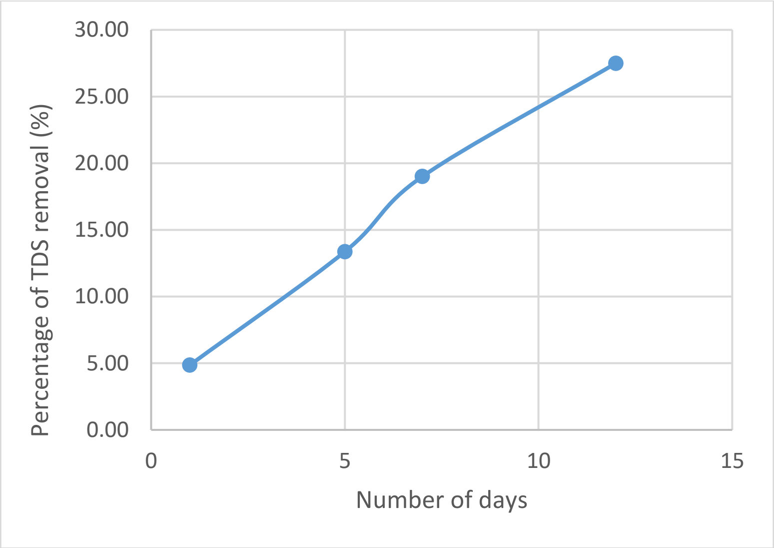


Figure 3.12: Effect of multiple batch cycles on desalination efficiency

The MDC unit was operated for 24 hours on the first, fourth, sixth and eleventh consecutive day. During the days when there was no operation, the MDC unit was emptied of all its solutions and the external wire was removed. Removing the external wire allows the yeast cells to use their electrons for their growth [118]. Figure 3.12 shows the effect of multiple batch cycles on desalination efficiency. The rise in desalination efficiency is much higher than it was for any of the parameters discussed previously in this study. This shows that development of biofilm is a much more important contributor to current generation and desalination at the employed operating conditions and mediator concentrations.

It should be noted this experimental study of repeated batch cycles differs from the long-term operation of one batch cycle. In the present study, each 24-hour batch cycle resulted in higher desalination efficiency due to the growth of biofilm on anode electrode prior to beginning the batch cycle. In contrast, long-term operation of one MDC batch cycle, which is performed in the following section 3.4.9., did not have any biofilm development prior to beginning the batch cycle. This was further ensured by using new electrodes and membranes for the construction of MDC unit employed in section 3.4.9. It should be noted that the repeated batch experimental study was not performed under optimized conditions whereas the study in section 3.4.9. was performed at most of the optimized conditions. Yet, the repeated batch study resulted in 27.5 % desalination efficiency in 24 hours. This was higher than the desalination efficiency obtained in 24 hours by an MDC unit performed at optimized conditions, which was 17.3%. This study has been discussed in the following section.

3.4.9. Effect of operation time. For this experiment, an MDC unit was operated in batch mode for 72 hours at the following optimized conditions: the anolyte consisted of 20 g/l yeast, 90 g/l D-Glucose, 5 mM methylene blue, 100 μM menadione and initial anolyte pH of 7.63. The initial TDS of produced water was 88 g/l. The air flow rate in anode and cathode chambers was 80 ml/min and 150 ml/min respectively. Activated carbon was not added to the anolyte so that anolyte conductivity and pH could be measured. Moreover, a fresh batch of membranes and electrodes were employed in order to study the effect of other parameters without the effect of biofilm development.

Figures 3.13 and 3.14 depict the changes in produced water TDS and conductivity changes in produced water, anolyte, and catholyte solutions during the 72-hour operation. Figure 3.13 reveals that the percentage of TDS removal from produced water increases significantly from 17.3% after 24 hours to 35.9% after 72 hours. This means that there was a significant drop in produced water TDS during the 72-hour operation. This suggests that operation time is an important factor for increasing MDC performance. Following the trend of produced water TDS, Figure 3.14 shows that the conductivity of produced water decreased significantly during the 3-day operation. Both of these results suggest that produced water contaminant concentration decreased continuously during the 72-hour operation.

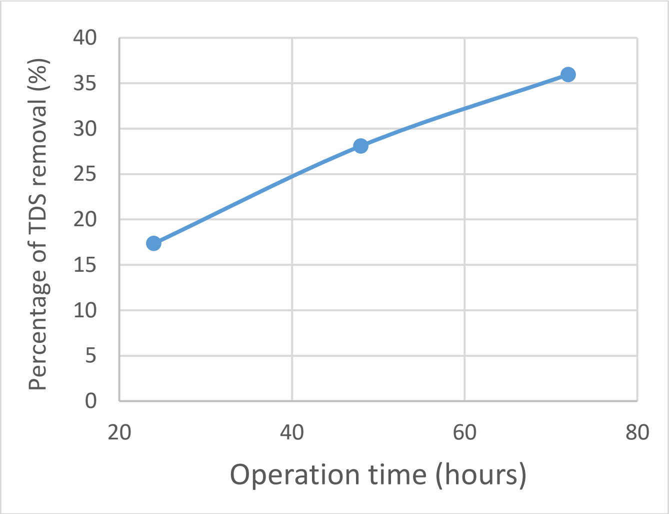


Figure 3.13: Effect of operation time on desalination efficiency

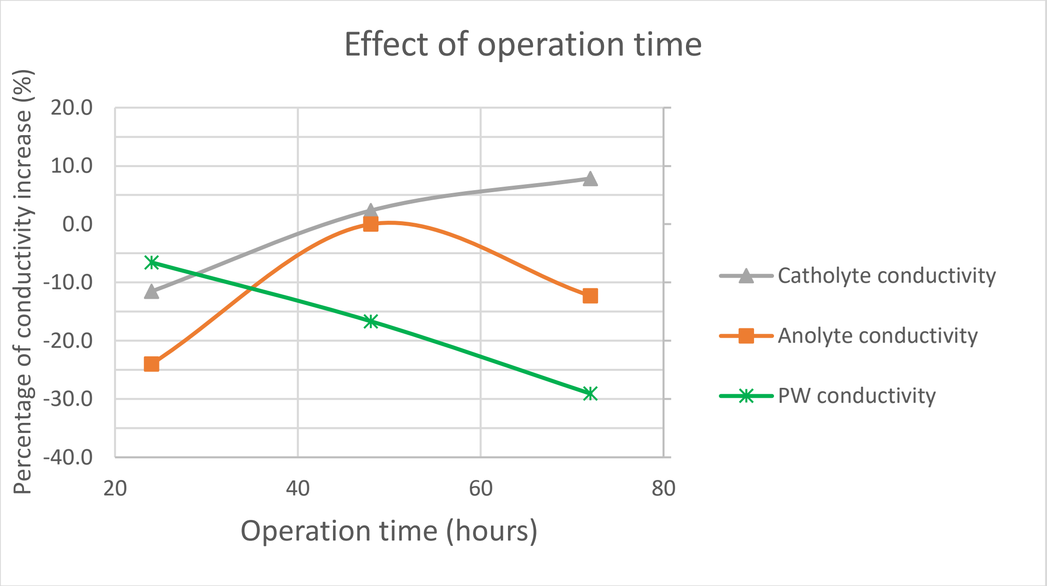


Figure 3.14: Effect of operation time on solution conductivity

According to Figure 3.14, the change in percentage conductivity for a catholyte solution is negative after the first day, close to zero after the second day, and positive on the last day. This implies that the catholyte conductivity decreased during the first 24 hours of operation and increased in the following days. This result is in agreement with the results of previous experiments in the parametric study which were all operated for 24 hours or less and where the catholyte conductivity decreased after the operation. In this experiment, during the first 24 hours, while the catholyte and anolyte conductivity decreased, the produced water TDS and conductivity also decreased (Figures 3.13 and 3.14). This might suggest that osmotic transport may have caused some of the anolyte and catholyte to transfer to the desalination chamber, thus diluting the concentration of produced water. The large difference in initial TDS between the produced water and the electrolytes had created high osmotic pressure difference. This was confirmed by a change in color and increase in the volume of produced water observed after the first day of operation. The color of produced water had changed from transparent to slightly greenish because of the transfer of anolyte solution which is blue in color and catholyte solution which is yellow in color. During the first 24 hours, the pH of produced water also decreased. This may have also been caused by the addition of some components of catholyte solution which was at a lower initial pH than produced water.

Although catholyte conductivity decreased during the first day, it increased during the next two days. But the produced water TDS and conductivity continued to decrease for all three days of operation. This may suggest that ion transport out of the produced water to the electrode chamber was the main cause for desalination of produced water in the next two days. This is because previous studies in the literature have confirmed that during desalination by ion transfer in MDCs, the conductivity of saline water should decrease and electrolyte conductivity should increase [80]. The conductivity of anode solution showed an unexpected trend. It decreased during the first day, increased during the second day and decreased during the third day. This is in contrast to experimental results available in the literature on the long-term performance of MDCs where the anolyte conductivity continuously increases during operation [80]. A possible reason for the decrease in anolyte conductivity on the first and third day might be attributed to the reduction in anolyte volume observed in the MDC apparatus during those days. In general, it can be concluded from Figures 3.13 and 3.14, that when there is large concentration difference between the electrolytes and saline water, osmosis aids in reducing contaminant concentration of saline water and, therefore, aids in desalination. However, further research and experimentation is required to measure the concentration of different salts present in the solutions and how their concentrations vary with long operation time. This will aid in truly understanding the different mechanisms and transports that may occur in MDCs employing ferricyanide and oxygen in their cathode chambers and yeast cells in their anolyte.

Figure 3.15 depicts the changes in pH of all the solutions during the 3-day operation. The anolyte pH decreases and seems to approach a stable value of 7 after the third day. The reason for a slightly stable anolyte pH can be attributed to the addition of optimized concentration of disodium hydrogen phosphate (10 g/l) as per section 3.4.5. The pH of produced water decreased initially and then increased slightly. Its initial decrease was likely due to dilution by anolyte and catholyte solutions. The increase in produced water pH on the second day might be due to different transfer rates of anions and cations traveling out of the produced water to the electrolytes. On the second day, the anolyte and catholyte conductivity also increased, confirming that there was ion transfer into the electrolytes.

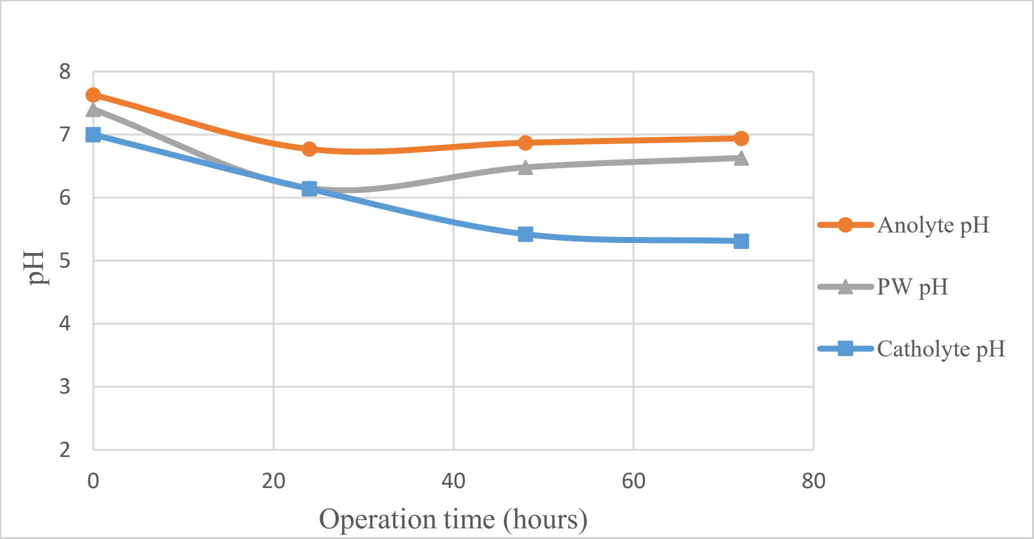


Figure 3.15: Effect of operation time on the pH of produced water, anolyte and catholyte

From Figure 3.15, it can be noted that the catholyte pH decreased substantially even in the presence of phosphate buffer solution. This is due to the electrochemical reaction that takes place in the cathode chamber in the presence of oxygen and potassium ferricyanide, as confirmed previously in section 3.4.3. However, as discussed previously, only two studies have been reported to employ a combination of ferricyanide and oxygen in the cathode chamber [92, 94]. However, they did not investigate the change in pH of catholyte. Moreover, no explanation could be found in existing literature for pH reduction in catholyte solution.

After the third day, the MDC was disassembled and similar trends were observed for deposition of crystals on the membrane surface. The AEM had scale formation on its side facing the desalination chamber only, suggesting that there was significant anion transfer from the desalination chamber to the anolyte. And the CEM had scale formation on its side facing the cathode chamber only, suggesting that the anions in the catholyte chamber were probably attracted towards the desalination chamber. In general, Figure 3.15 helps conclude that while the combination of ferricyanide and oxygen considerably increases current generation and desalination efficiency in 24-hour operations, it may not increase desalination performance by the same magnitude in the long run. This is because, it creates a decrease in catholyte pH, as a result of which, the catholyte may not attract cations from the desalination chamber by a significant magnitude. This can negatively affect the desalination efficiency of MDCs.

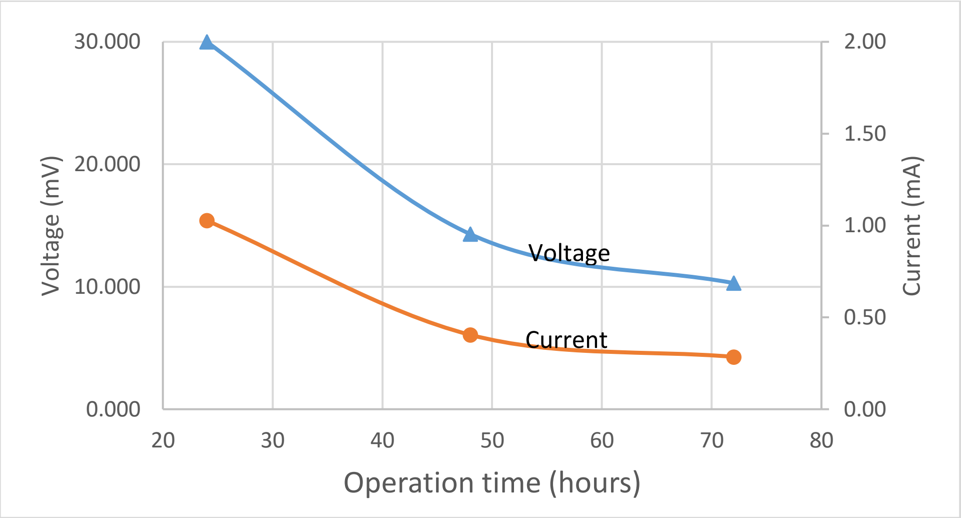


Figure 3.16: Effect of operation time on the voltage and current produced by MDC

Figure 3.16 depicts the change in voltage and current in the MDC during the 3 day period. The current generated by the MDC was very high on the first day. The voltage generated was low because of the low resistance of external wire (8 ohms). During the next two days, the voltage dropped significantly. This is due to the reduction in the volume of catholyte in the cathode chamber. After the second day, the catholyte volume reduced to half its initial volume and by the third day, it reduced to one-third of its initial volume. This reduction in catholyte volume was due to the osmotic pressure difference between the catholyte and produced water which resulted in catholyte solution transferring from the cathode chamber to the desalination chamber. This reduction in catholyte volume significantly reduced the contact surface area between the cathode electrode and catholyte, thus, lowering the reduction reaction rate at the cathode. A lower reduction reaction rate will generate a lower electrical potential between the electrodes in the MDC, thus reducing the current generation as well as desalination efficiency. Therefore, if ferricyanide is to be employed as an oxidizer in cathode chambers in MDCs, then ferricyanide needs to be replaced continuously. Lower voltage drives lower current through the circuit and for this reason, there was a significant drop in current from 1.04 mA to 410 μA, and finally to 290 μA on the last day. Moreover, significant scale deposition was observed on the external electrical wire where the wire was in contact with the anode electrode and cathode electrode. This scale deposition caused an increase in external resistance of the wire from 8 ohms on the first day to 107 ohms on the last day of operation. This increase in external resistance also contributed to the reduction in current generation across the external wire.

These experimental results suggest that the optimized parameters were successful in generating an enhanced current and desalination efficiency during the first day of operation. However, it is not recommended to employ produced water at its high TDS value of 88 g/l. Even though the hypersaline water increases current generation and desalination efficiency, it also causes osmotic transport of anolyte and catholyte into the desalination chamber. Although this transport aids in TDS reduction of produced water, it contaminates the water with microorganisms and ferricyanide which would later require further treatment for their removal. Therefore, desalination efficiency of MDC is highest without bacterial contamination at a TDS of 40 g/l based on these experimental results. However, hypersaline wastewaters having high TDS can still be employed in MDCs without bacterial contamination, if microorganisms and mediators are immobilized on the anode electrode and oxidizing agents are immobilized on the cathode electrode.

Chapter 4: Results and Discussions: Two-level factorial design

This chapter investigates the effects of four operational parameters on the performance of MDCs employing Saccharomyces cerevisiae as microorganisms and methylene blue as mediator. This study has been designed using a resolution IV fractional factorial design. The four operational parameters that are studied include the presence of oxygen, initial TDS of produced water, the concentration of methylene blue, and the MDC unit as a block variable. The response variables that are studied include TDS reduction in produced water and conductivity change in anolyte. Furthermore, the resulting factorial design mathematical model has been used to discuss the single and interaction effects of the selected operational parameters. Finally, the adequacy of the model has been verified using the normal probability plot of residuals.

4.1. Introduction

Design of experiments (DOE) is a statistical approach to designing and planning of experiments in order to draw the most valid and accurate conclusions regarding the effect of treatment factors on a response variable. DOE helps optimize the process of experimentation and allows the generation of substantial information using the minimum number of experiments and resources [10]. A full factorial design addresses the effect of each individual factor on the desired response variable. A special case of a general factorial design is that of k factors, where each factor consists of only two levels. This means that each factor is varied from a certain low value to another high value. A complete set of (non-repeated) experiments of such a design requires a 2^k experimental runs and is, therefore, called the 2^k factorial design.

Among the most widely used types of designs in industrial, research and business experimentation, are the fractional factorial designs. These designs can be used if certain high-order interactions can be assumed negligible. In such a scenario, a fraction of the total set of experiments can be run in order to obtain the main effects and low-order interactions of treatment factors. In this study, a resolution IV fractional factorial design is carried out which involves four factors. This design is a one-half fraction of the 2^4 factorial design and is designated by 2^{4-1}. A 2^{4-1} design becomes a resolution IV design (2^{4-1}_{IV}) when $I = ABCD$ and as a result of which two-factor interactions are aliased with each other and individual interactions are aliased with three-factor interactions [10]. Here, *A*, *B*, and *C* represent the three treatment factors, *D* represents the block variable, and I is an identity element which represents the total or overage of all experiments.

One objective of this study is to investigate the influence of oxygen, methylene blue (MB) and initial TDS of produced water on the desalination efficiency of MDC. The second objective is to study the individual and interactive effects of oxygen and mediator on the properties of the anolyte solution. This analysis is important because the combination of oxygen and mediator in anolyte has generated conflicting results in existing literature [67, 94, 96]. While the metabolic processes of Saccharomyces cerevisiae generate more electrons in the presence of oxygen, which leads to higher current generation and higher desalination efficiency, oxygen oxidizes the mediator present in anolyte solution by accepting electrons and thus, impedes their transfer towards the anode electrode. This reduces current generation and desalination efficiency. The third objective of this study is to analyze the effect of initial produced water TDS on the properties of the anolyte solution and its contamination by ion transfer from the desalination chamber. The final objective is to investigate the effect of an important blocking factor which is the MDC unit that is presumably consisting of the exact same dimensions and operating under the same conditions.

4.2. Factorial design methodology and calculations

In resolution IV fractional factorial design that is employed in this study, each factor is varied between two levels: the high level represented by +1 and the low level represented by -1. A statistical model is developed based on the experimentally generated values of the response variables.

Table 4.1: Symbols, high, and low levels of factors studied in the factorial design.

Factor	Symbol	Low Level	High Level
Presence of oxygen	*A*	anaerobic	Aerobic at 150 ml/min air flow rate
Produced Water TDS	*B*	20 g/l	40 g/l
Methylene blue concentration	*C*	0.5 mM	2 mM
MDC Unit	*D*	Unit 1	Unit 2

However, this model (also known as the linear effects model) assumes a linear relationship between the response and each factor. Therefore, the high and low levels of each factor have been carefully chosen based on existing literature and the optimization study discussed in chapter 3. The high and low levels chosen for each factor are demonstrated in Table 4.1.

Table 4.2: The $2_{\mathrm{IV}}^{4\text{-}1}$ design matrix with the defining relation *I = ABCD*

Run	*A=BCD*	*B=ACD*	*C=ABD*	*D=ABC*	*AB =CD*	*AC =BD*	*BC =AD*	**Treatment combination**
1	-	-	-	-	+	+	+	(1)
2	+	-	-	+	-	-	+	*ad*
3	-	+	-	+	-	+	-	*bd*
4	+	+	-	-	+	-	-	*ab*
5	-	-	+	+	+	-	-	*cd*
6	+	-	+	-	-	+	-	*ac*
7	-	+	+	-	-	-	+	*bc*
8	+	+	+	+	+	+	+	*abcd*

Furthermore, the experimental runs involved in the $2_{\mathrm{IV}}^{4\text{-}1}$ factorial design are delineated in Table 4.2. Each experimental run depicted in Table 4.2 was performed in duplicates (two trials) in to order to increase the number of degrees of freedom and thus reduce the standard error. Moreover, all the experimental runs were performed in a random order which is an important criterion for the application of factorial designs. The value of each response variable was obtained after averaging the values obtained during trial 1 and trial 2 for each experimental run. These response values are combined with the contrast of each treatment combination in order to find the effect of each treatment combination using mathematical formulae prescribed for the $2_{\mathrm{IV}}^{4\text{-}1}$ design [10]. Finally, a regression model is obtained for each response variable using Equation 8.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (8)$$

In Equation 8, y represents any of the three variable responses: percentage of TDS removal in produced water, the percentage of conductivity increase in anolyte or percentage of pH decrease in anolyte. $\beta_1, \beta_2, \beta_3, \beta_4$ represent the single effects *A*, *B*, *C* and, *D* factors. $\beta_{12}, \beta_{23}, \beta_{13}$ represent the interaction effects *AB*, *BC* and *AC*. The parameters x_1, x_2, x_3, and x_4 are the coded factors *A*, *B*, *C* and *D* whose values are normalized between -1 and 1. Parameters x_2 and x_3 are calculated based on Equations 9 and 10. Parameter x_1 is assigned a value of -1 when factor *A* is at the low level and a value of +1 when *A* is at the high level. Similarly, parameter x_4 is assigned a value of -1 when factor *D* is at a low level and a value of +1 when *D* is at high level. The values of $\beta_1, \beta_2, \beta_3, \beta_4, \beta_{12}, \beta_{23}, \beta_{13}$ have been calculated based on the mathetical formulae prescribed for the 2^{4-1}_{IV} design [10]. β_0 represents the grand average of the respective response variable in all experimental runs along with their trials.

$$x_2 = \frac{TDS - \left[\frac{TDS_{high} + TDS_{low}}{2}\right]}{\left[\frac{TDS_{high} - TDS_{low}}{2}\right]} \tag{9}$$

$$x_3 = \frac{Molarity - \left[\frac{Molarity_{high} + Molarity_{low}}{2}\right]}{\left[\frac{Molarity_{high} - Molarity_{low}}{2}\right]} \tag{10}$$

Using the regression model for each response variable, single effects plots and interaction plots are generated by substituting the appropriate values for the betas and the parameters. Finally, the normal probability plot of residuals has been generated by calculating residuals for each experimental run along with its trials. The residuals are calculated as the difference between the experimental response of a treatment combination and the response predicted by the regression model. The residuals are then arranged in ascending order of their values and plotted against their probability P which is evaluated as per Equation 11.

$$P\% = \frac{(j - 0.5) \times 100}{n} \tag{11}$$

Where *P* is the probability in terms of percentage, *j* is the order of residual after arrangement in ascending order, and *n* is the number of residuals.

4.3. Experimental

4.3.1. Experimental set-up. Both MDC units 1 and 2 consisted of three acrylic cube-shaped blocks. Each block had 8.2 cm length and 6.2 cm height. The anode and cathode blocks had 2.5 cm width and the desalination block had 1 cm width. The volume of desalination chamber is 72 ml and that of anode and cathode chambers is 140 ml. The three chambers are connected together using gaskets, rods, membranes and electrodes as previously described in section 3.2 in chapter 3. Following the instructions of Membranes International, each membrane was soaked in 5 % (w/w) NaCl solution for 24 hours before its use in MDC. The NaCl crystals that were used to make the NaCl solution were procured from Fisher Scientific. Two copper wires of the exact same length, material, and similar clutches were used to connect the electrodes in Unit 1 and in Unit 2. The air flow rates were set up as previously described in section 3.2 in chapter 3. The cathode chamber was aerated in all experiments at a constant air flow rate of 150 ml/min. For experiments in which the anode chamber was aerated, the air flow rate was fixed at 150 ml/min. The resistance of the external wire used in Unit 1 and Unit 2 is 8 ohms.

4.3.2. Preparation of anolyte solution. The volumes of the anode chamber in Unit 1 and Unit 2 are 139 ml and 145 ml. For all experiments, anolyte and catholyte volumes of 100 ml were used. 100 ml of anolyte solution was prepared for each experimental run in two steps. The first step of heating a solution of the yeast cells and glucose is performed as per section 3.1 in chapter 3. In 10 minutes the solution reached a temperature of 35 ^{0}C and a froth was observed at the surface due to the release of CO_2 by the yeast cells. The digital thermometer was used to measure the temperature of the solution. In the second step, the heated yeast solution was allowed to cool naturally for 10 minutes. Then, a 30 ml solution containing phosphate buffer and methylene blue is added to the yeast solution as per section 3.1 in chapter 3. The anode solutions are then immediately transferred to the anode chambers of MDC unit 1 and unit 2 and they are transferred at the same time.

4.3.3. Preparation of catholyte solution. The volumes of the cathode chamber in unit 1 and unit 2 are 143 ml and 140 ml. For all experiments, the concentration of catholyte was fixed. 100 ml of catholyte was prepared by adding 2 g potassium hexacyanoferrate (III) (Merck KgaA), 0.1743 g Na_2HPO_4, and 0.1215 g $NaH_2PO_4.2H_2O$. After stirring on a magnetic plate, this solution was added to the cathode compartment of MDC.

4.3.4. Preparation of produced water solution. Produced water was procured from the wastewater treatment facility of an oil and gas industry. 70 ml of produced water solution was prepared by adding 33 ml of produced water to 37 ml of distilled water to get a TDS reading of 40 g/l.

4.3.5. Experimental procedure. A single protocol was followed for each experiment. New carbon cloth electrodes were cut out with the dimensions of 9.5 cm x 11 cm. The electrodes were soaked in acetone for 24 hours before use. The acrylic blocks, which constitute the anode, cathode and desalination chambers of the MDC, were sterilized by soaking in 1 M NaOH. The container was covered with aluminum foil and placed in a sterilizer (Memmert GmbH, model number SNB200) for 1 hour at 60 ^{o}C. After one hour the acrylic blocks were removed from the sterilizer, allowed to cool while cleaning with distilled water. They were then cleaned with 70% ethanol and kept in an oven overnight for drying [18]. The same acrylic blocks were used as components of unit 1 and unit 2 for all experiments. The gaskets, rods, and bolts along with glassware used in the preparation of solutions were heated in a sterilizer at 120 ^{o}C for a 15-minute duration. After all the components were removed from the sterilizer, they were allowed to cool naturally and assembled for setting up units 1 and 2 of MDC.

Distilled water was poured into each chamber after set up in order to ensure there was no leakage in the MDCs. Distilled water was then poured out of the MDC units completely. The cathode solution was prepared, its pH and conductivity were measured after which it was poured into the cathode chamber of Units 1 and 2. The produced water solution was prepared in slightly excess quantity and its TDS was measured using TDS meter (HACH). The produced water solution was poured into the desalination chambers of units 1 and 2 so as to fill the chambers completely. The external wires of the MDC units were connected. The anode solutions were prepared as described in section 4.3.2, their pH and conductivity were measured after which they were poured into the anode chambers of the units at the same time. As soon as anolyte was added, the aeration tubes were inserted into the respective chambers at a fixed air flow rate. At this point, the process had begun.

The cell voltage and current were recorded using a multimeter which was supplied by UNI-T. The pH and conductivity of anolyte and TDS of desalination chamber were measured after 72 hours for each experimental run. All of the experiments were run in a temperature-controlled laboratory for three days at the American University of Sharjah. The instruments, that were used to take readings and measure volumes, and their resolutions were described previously in section 3.3 in chapter 3. All the weights were measured using a weighing balance (Radwag ®) with an accuracy of +/- 0.0001 g.

4.4. Results and Discussion

4.4.1. Effect of factors on the TDS removal in produced water. A summary of the response values of TDS percent removal for all experimental runs has been delineated in Table 4.3.

Table 4.3: Response values of TDS percent and the respective residuals

Runs	Experimental TDS percent	Average Experimental TDS percent	Predicted TDS percent (Equation 12)	Residuals
1	16.95	16.49	16.49	0.4601
	16.03			-0.46
2	17.55	17.905	17.906	-0.356
	18.26			0.3542
3	22.5	21.85	21.85	0.6502
	21.2			-0.65
4	23.75	23.965	23.966	-0.216
	24.18			0.2142
5	14.85	14.245	14.244	0.6056
	13.64			-0.604
6	8.6	8.845	8.844	-0.245
	9.09			0.2452
7	23.25	22.94	22.93	0.3108
	22.63			-0.309
8	21	21.455	21.455	-0.455
	21.91			0.4552

$$y_{TDS\%} = 18.46 - 0.41x_1 + 4.09x_2 - 1.59x_3 + 0.402x_4 + 0.5769x_1x_2 - 1.302x_1x_3 + 1.2356x_2x_3 \quad (12)$$

Equation 12 represents the regression model that has been developed for calculating TDS percent. Using this model the TDS percent can be obtained by plugging one coded value between -1 and +1 for the quantitative parameters x_2 and x_3.

For the qualitative x_1 and x_4 parameters, either one value of -1 or +1 should be chosen. Figure 4.1 depicts the single effects of each of the four input factors on the TDS removal percentage. Aeration of anode solution and change in MDC unit have minimal effects on TDS removal. As explained previously in chapter 3, oxygen in the anode solution has two opposing effects on the current generation, and therefore, on desalination efficiency. However, it was shown in Chapter 3 that changing anode environment from anaerobic to aerobic significantly increased TDS removal percentage. It is to be noted that experiments in that study (Chapter 3) were performed for 24 hours and maximum anode air flow rate was 80 ml/min, whereas, in this scenario, each experimental run was performed for three days where the aerobic environment had an air flow rate of 150 ml/min. Figure 4.1 reveals that at high air flow rates, aeration has an overall negative effect on desalination efficiency. This is because the reduction of mediator by oxygen is more dominant over the consumption of oxygen by yeast cells. However, the magnitude of this negative effect is 0.41 which is very low. This means that TDS removal is lesser by 0.41% when anode environment is changed from anaerobic to aerobic at air flow rate of 150 ml/min.

Initial TDS of produced water has the maximum effect on desalination efficiency. Increasing initial TDS from 20 g/l to 40 g/l increases desalination efficiency by 8%. This result is qualitatively in agreement with what was found previously in Chapter 3. The desalination chamber acts as a salt bridge for the MDC, hence higher conductivity in the desalination chamber results in lower resistance to ionic transport during the application of the electric potential. This results in the higher transfer of ions from the desalination chamber to the electrode chambers.

Increasing MB concentration has a negative effect on desalination efficiency according to Figure 4.1. This result is in contrast with the results found in the parametric study where increasing MB concentration substantially increased desalination efficiency. The reason for this contradiction is as follows. In this study, Tables 4.2 and 4.3 show that the effect of the increase of MB concentration was highly dependent on the level of aeration and the TDS of the produced water. In anaerobic conditions, increasing MB concentration increased desalination efficiency by a small magnitude. Whereas, in aerobic conditions and at low TDS, increasing MB concentration decreased desalination efficiency by a comparatively large magnitude. Therefore, the combination of the change in desalination efficiency at each treatment combination, which is used to calculate the single effect of MB concentration, results in an overall decrease in desalination efficiency when MB concentration is increased.

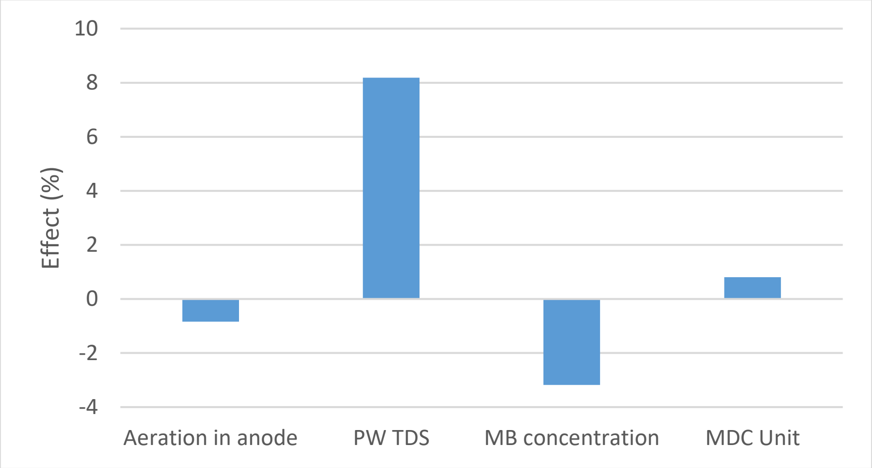
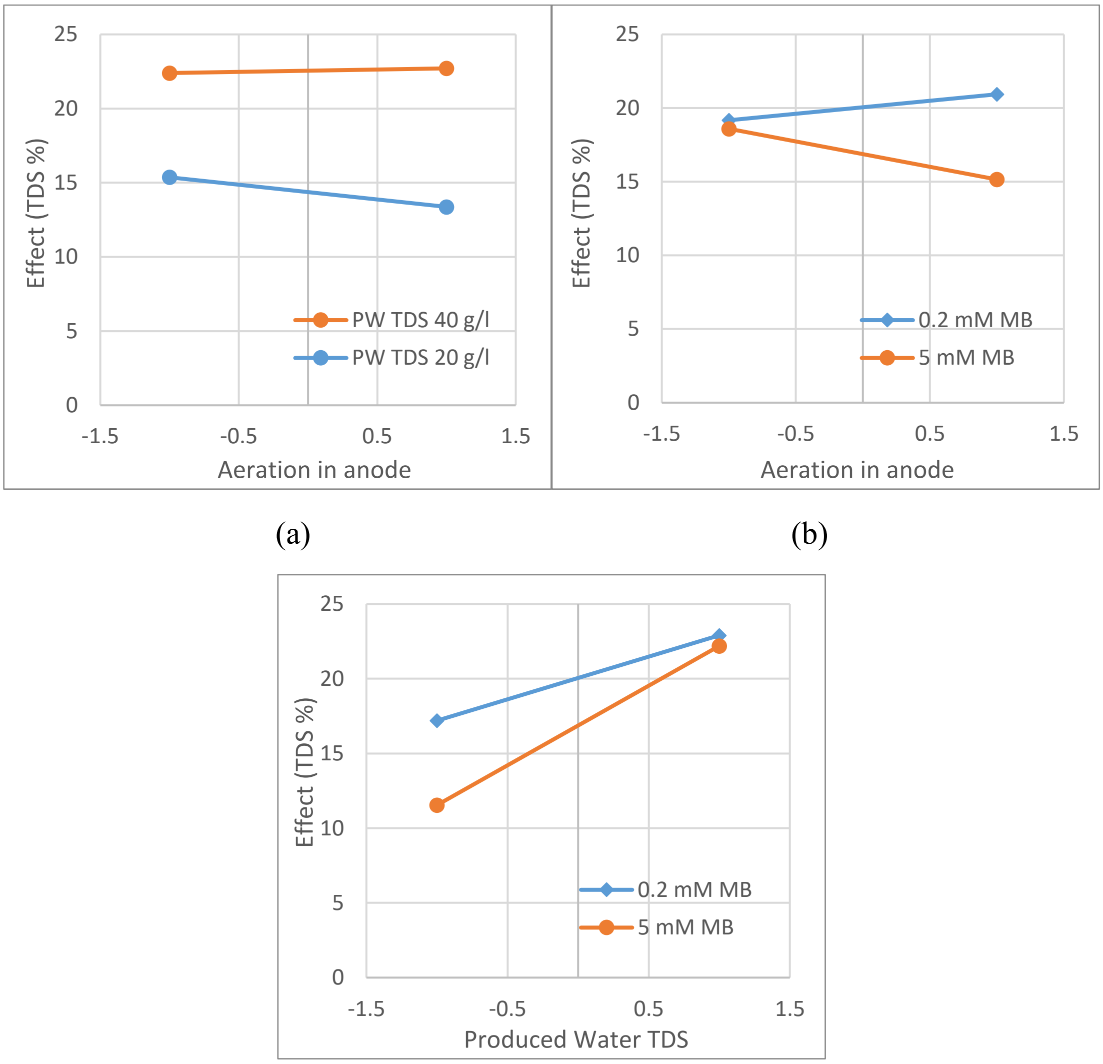


Figure 4.1: Single effects of factors on TDS percent removal in produced water

Figure 4.2 depicts the interaction effects of the main factors on the percentage of TDS removal in produced water. The Figures 4.2: (a), (b), and (c) are based on the response values generated by the regression model when the appropriate levels are plugged into the parameters of Equation 12. The Figures 4.2: (a), (b) and (c) suggest that there is a significant interaction between aeration and MB concentration. There is also a significant interaction between initial produced water TDS and MB concentration and comparatively very low interaction between aeration and produced water TDS.

Figure 4.2 (b) shows that the desalination efficiency is highest at low MB concentration along with high aeration rate. The efficiency is slightly lower and is between 18% and 19% during anaerobic conditions for both MB concentrations. The lowest desalination efficiency is observed for the combination of high aeration rate and high MB concentration. Moreover, during anaerobic conditions, the change in MB concentration has a very little effect on desalination efficiency. This is probably because a concentration of 0.2 mM is adequate for transfer of the smaller number of electrons which are released as a result of the anaerobic environment. Therefore, increasing the MB concentration to 5 mM might not aid further in electron transfer from the yeast cells to the anode electrode. Moreover, during the three-day operation of MDC, the resistance of the external wire increased substantially from 8 ohms to 160 ohms for all experimental runs. This increase in resistance reduced the desalination efficiency during the three days. This increase in resistance was due to uncontrollable factors like scale formation on the external wire where it was in contact with the cathode electrode and biofilm formation on the external wire where it was in contact with anode electrode.



(a) (b)

(c)

Figure 4.2: Interactions effects of (a) Anode aeration and produced water TDS (b) anode aeration and MB concentration (c) produced water TDS and MB concentration

Figure 4.2 (c) shows that highest desalination efficiency is obtained when produced water TDS is high for both MB concentrations. At high TDS, a change in MB concentration has a very low effect on desalination efficiency. However, at low TDS, lower MB concentration gives higher desalination efficiency. This result is likely due to the fact that in an anaerobic environment, lower MB concentration gives slightly lower desalination efficiency at low TDS (Table 4.3). However, at high aeration rate, lower MB concentration gives significantly higher desalination efficiency at low TDS. Therefore, the overall effect of lowering MB concentration at low TDS increases desalination efficiency. Figure 4.2 (a) suggests that there is a low interaction between anode aeration and produced water TDS. Under conditions of the aerated anode, increasing produced water TDS generates slightly higher change in desalination efficiency than at anaerobic conditions. This could likely be due to the small interaction between the oxygen in anode and ions that transfer to the anode during desalination.

4.4.2. Effect of factors on the conductivity increase in anolyte. A summary of the response values of percentage increase in anolyte conductivity for all experimental runs has been delineated in Table 4.4. Equation 13 represents the regression model that has been developed for calculating conductivity percent change. Using this model conductivity percent change values can be obtained by plugging one coded value between -1 and +1 in the parameters x_2 and x_3. For x_1 and x_4 parameters, either one value of -1 or +1 should be chosen.

Table 4.4: Response values of conductivity percent and the respective residuals

Runs	Anolyte conductivity percent	Average anolyte conductivity percent	Predicted TDS percent (Equation 13)	Residuals
1	84.4	82.04	82.032	2.378
	79.68			-2.352
2	116.8	118.555	119.56	-2.755
	122.31			2.755
3	244.82	243.12	243.13	1.95
	241.42			-1.705
4	130.9	134.565	134.56	-3.662
	138.23			3.6678
5	37.32	33.115	33.115	4.205
	28.91			-4.205
6	110.738	112.583	112.59	-1.854
	114.428			1.8358
7	134.128	131.281	131.28	2.8038
	128.476			-2.806
8	105.91	109.17	109.17	-3.255
	112.43			3.265

$$y_{C\%} = 120.678 - 1.71x_1 + 33.855x_2 - 24.14x_3 + 5.5614x_4 - 30.96x_1x_2 + 16.05x_1x_3 - 10.17x_2x_3 \qquad (13)$$

Figure 4.3 depicts the single effects of each factor on the percentage increase in anolyte conductivity. Figure 4.1 and Figure 4.3 show that the effect of single factors on TDS percent and conductivity percent follow a similar trend. This is corroborated by the parametric study performed in chapter 3 where percentage increase in anolyte conductivity was higher when desalination efficiency was higher for all experimental runs. This is because higher desalination in the middle chamber results in higher ion transfer to the electrode chambers. Consequently, the conductivity of anolyte and catholyte solutions increases.

Another comparison between Figures 4.1 and 4.3 shows that the magnitude of single effects on change in anolyte conductivity is much higher than their effect on desalination efficiency. This is because the concentration of ions in the (middle) desalination chamber is much higher than ion concentration in anolyte solution. While the initial TDS levels of produced water employed in this study were 20 g/l and 40 g/l, the initial TDS of anolyte solutions was in the order of 1 g/l. This means that transfer of around 5 g/l of ions from the desalination chamber results in much higher percentage increase in anolyte conductivity than the percentage decrease in produced water conductivity.

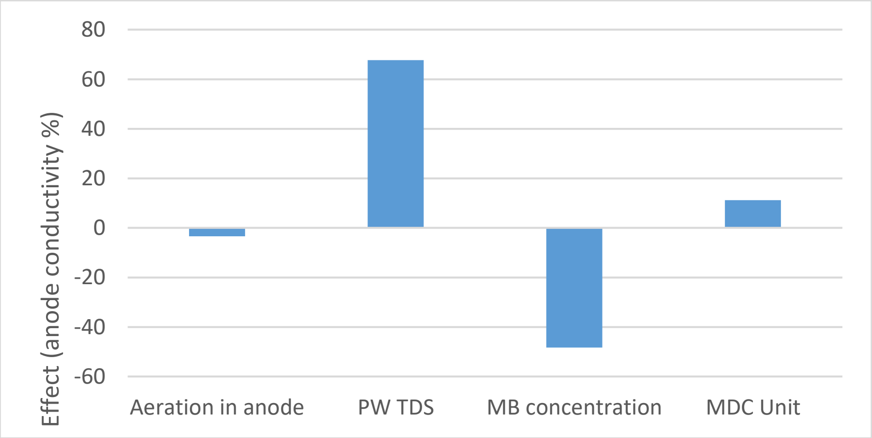
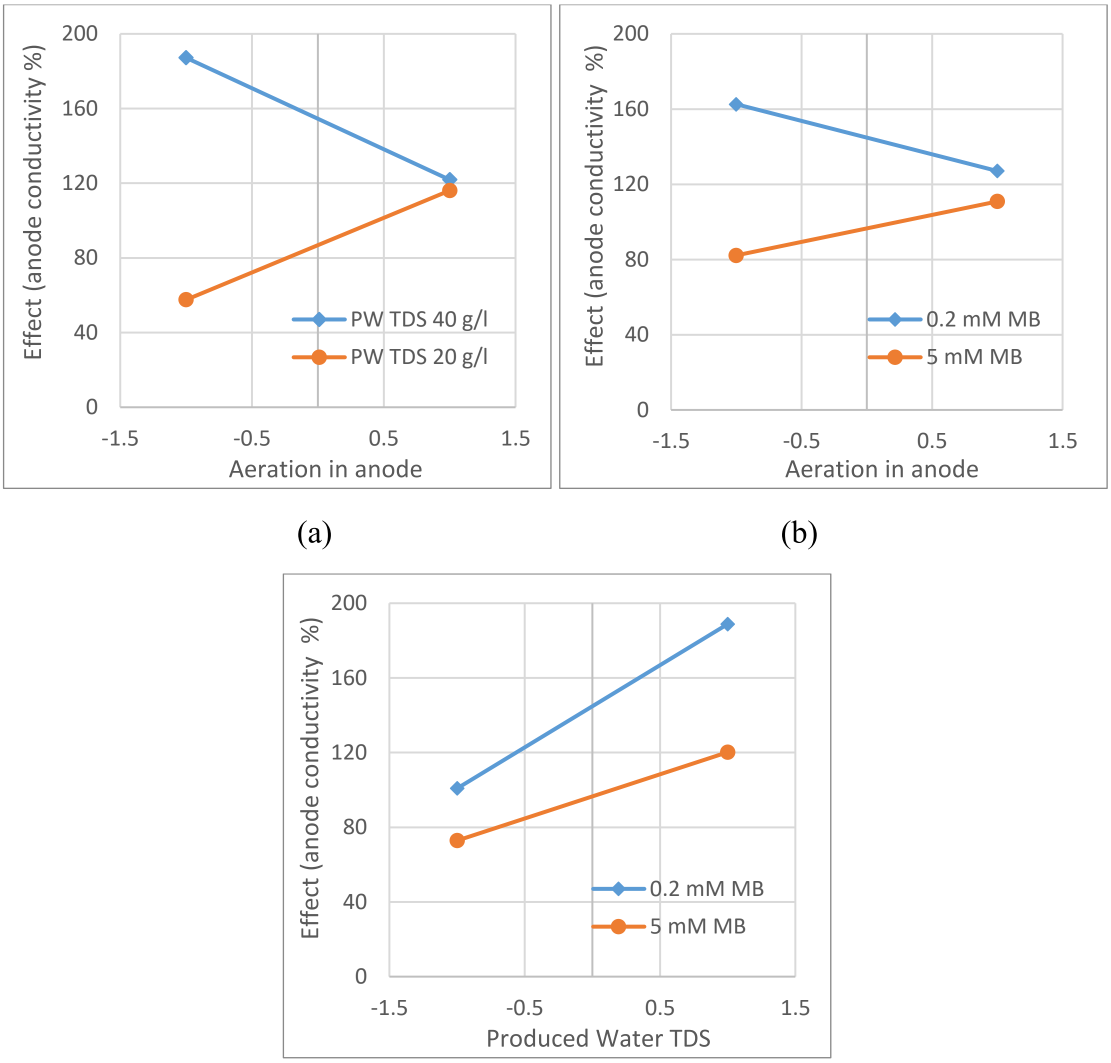


Figure 4.3: Single effects of factors on percent increase in anolyte conductivity



(a) (b)

(c)

Figure 4.4: Interactions effects of (a) Anode aeration and produced water TDS (b) anode aeration and MB concentration (c) produced water TDS and MB concentration

As revealed by Figure 4.3, aeration of anode and change in MDC unit have minimal effects on the percentage increase in anolyte conductivity. While initial produced water TDS has the highest proportional effect on anolyte conductivity increase, MB concentration has a comparatively lower and inversely proportional effect on anolyte conductivity increase. Moreover, the single effect of a change in MDC unit is higher on anolyte conductivity than on desalination efficiency. Figure 4.4 depicts the interaction effects of the main factors on the percentage increase in anolyte conductivity. The Figures 4.4: (a), (b) and (c) are based on the response values generated by the regression model in Equation 13. The Figures 4.4: (a), (b) and (c) suggest that there is a significant interaction between all three factors. Figure 4.4 (a) shows that at high TDS, changing from the anaerobic environment to aerobic environment reduces the change in anolyte conductivity. However, at low TDS, change in aeration increases the change in anolyte conductivity. Figure 4.4 (b) suggests that in anaerobic conditions, MB concentration has a high influence on the change in anolyte conductivity. This is probably because oxygen is not available in the anode chamber to interact with the ions transferred to the anode chamber due to desalination. At high aeration, MB concentration has a much lower influence on anolyte conductivity percentage. This is likely due to the fact that oxygen in the anode chamber consumes electrons and H^+ ions and gets reduced to water. This addition of water may have a diluting effect on anolyte conductivity. Moreover, the effect of MB concentration on desalination efficiency, and therefore, on anolyte conductivity is reduced by aeration because of continuous re-oxidation of methylene blue in the anode chamber.

Figure 4.4 (c) shows that there is some interaction effect between initial TDS and MB concentration for the response to the change in anolyte conductivity. However, this interaction effect is less than the interaction effects in Figure 4.4 (a) and Figure 4.4 (b). Comparison between Figure 4.2 (c) and 4.4 (c) suggests that lower MB concentration results in higher desalination efficiency and therefore, a higher change in anolyte conductivity for both TDS concentrations in produced water. While in Figure 4.2 (c), at low TDS, change in MB concentration resulted in a higher change in desalination efficiency than at high TDS. The opposite is true for anolyte conductivity. At higher TDS, change in MB concentration has a higher effect on anolyte conductivity than at low TDS.

4.4.3. Model adequacy checking. Figure 4.5 and Figure 4.6 show the normal probability plot of residuals for two response variables, the desalination efficiency and percentage increase in anolyte conductivity. The residuals plots in each figure are compared with a best-fitting straight line. The Figures 4.5 and 4.6 suggest that the residuals are distributed close to the straight line which represents the ideal normal distribution plot. Therefore, the residual plots are approximately distributed normally. Moreover, the residual plots in both figures are symmetric around the median. The residuals for the TDS percentage removal are generally lower than those for percentage increase in anolyte conductivity. Therefore, the errors occurring from uncontrollable factors are higher in anolyte conductivity measurements than in TDS measurements.

This can also be corroborated by evaluating the error sum of squares for the two response variables. While the error sum of squares is 1.74 for TDS removal, it is -364.6 for percentage increase in anolyte conductivity.

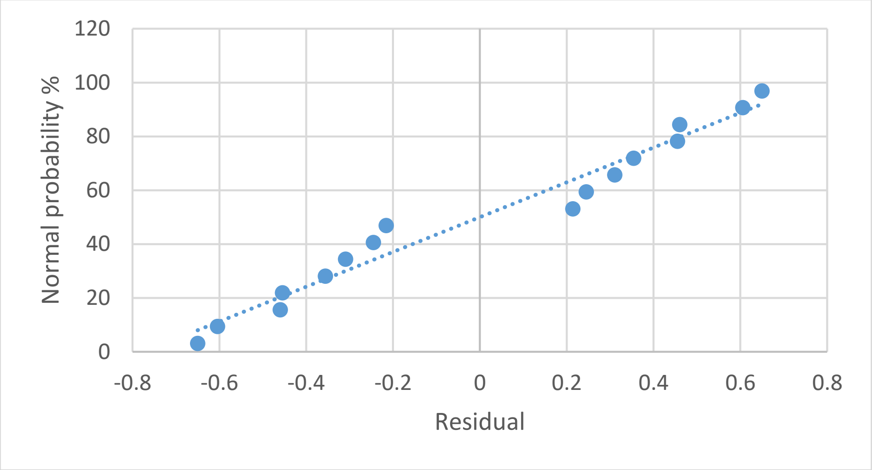


Figure 4.5: Normal probability plot of residuals for TDS percent removal in produced water

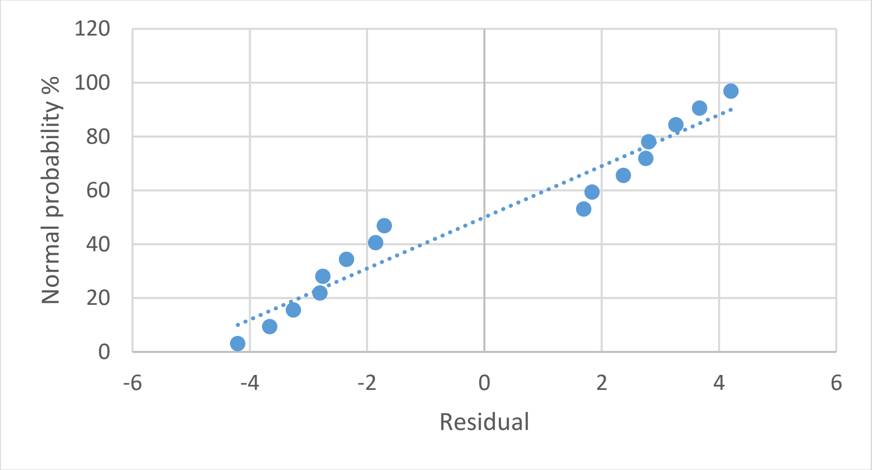


Figure 4.6: Normal probability plot of residuals for percent increase in anolyte conductivity

Chapter 5: Conclusion

In this thesis, Saccharomyces Cerevisiae was used for desalination of produced water and silmultaneous electricity generation using a Microbial Desalination Cell assembly. In the parametric study, eight different operating parameters were investigated in order to achieve the optimum conditions for best performance. Moreover, an MDC unit intensively studied while being operated at the optimized conditions over a long period of time. In the two-level factorial design study, MDC desalination efficiency was investigated for three input factors and one block variable. The experimental data was statistically evaluated using single effect plots, interaction plots and regression models. Moreover, the accuracy of the regression model was verified using the normal probability plot of residuals.

5.1. Findings and Conclusions

5.1.1. Parametric Study. A parametric study was performed by investigating the effects of several operating parameters on MDC performance. The effects of initial TDS of produced water and multiple batch cycles on desalination efficiency were the highest causing a rise in desalination up to 27%. Aeration in anode and cathode chambers also resulted in significant increase in desalination efficiency. However, while varying the aeration rates in the anode chamber, the maximum air flow rate was low (80 ml/min). At this flow rate, aeration had a positive effect on desalination efficiency. Moreover, increase in methylene blue concentration at this air flow rate also had a positive effect on desalination efficiency.

Addition of activated carbon granules increased desalination efficiency by only 4%. However, it should be noted that the size of MDC units was small where the volume of electrode chambers was 120 ml. During scale-up of MDC units, the effect of activated carbon on desalination efficiency may become more significant. Adjusting the initial pH of anolyte to 7.7 gave higher desalination efficiency. Moreover, increasing anolyte pH mitigated the pH fluctuation in the anolyte. This shows that anolyte pH is an important factor to be considered while optimizing MDC operations. The parametric study also revealed that employing a double mediator system of hydrophilic and lipophilic mediators results in higher desalination efficiency than using individual mediators. Finally, an MDC unit was operated for an extended operation time of 3 days at several optimized conditions. The experiment revealed that from the first day to the third, desalination efficiency doubled from 17% to 36%.

In the parametric study, the properties of anolyte and catholyte solutions were also investigated for a set of experiments. It was shown that the anolyte conductivity increases continuously during MDC operation due to the transfer of anions from desalination chamber to the anode chamber. Catholyte conductivity decreases on the first day and then increases during subsequent days. The reason for this was attributed to possible dilution of desalination chamber by catholyte during the first day of operation. Moreover, the pH of anolyte and catholyte solutions decreases continuously during MDC operation. This decrease is attributed to the electrochemical reactions that occur in the anode and cathode chambers. Finally, it was observed that the catholyte solution gets depleted during 3-day operation of the MDC unit. This reduces the voltage and current generated by the MDC and affects its desalination efficiency.

5.1.2. Factorial Design. Applying a factorial design analysis helped in identifying the complex interactions between mediator concentration, aeration in the anode chamber and produced water TDS. The most significant factor that affected desalination efficiency is initial TDS of produced water. The second most significant single effect on desalination was that of mediator concentration. The other two factors: anode aeration and change in MDC unit had minimal single effects on desalination efficiency. The combination of parameters that gave the highest desalination efficiency of 23.9% was aerobic anode, 40 g/l TDS of produced water, 0.2 mM methylene blue and MDC unit 1. The second highest desalination efficiency of 22.9% was achieved by the anaerobic anode, 40 g/l TDS of produced water, 5 mM methylene blue and MDC unit 1.

The most significant factor that affected the increase in anolyte conductivity is initial TDS of produced water. The second most significant single effect was that of mediator concentration. The other two factors: anode aeration and change in MDC unit had minimal single effects on this response. The combination of parameters that gave the highest conductivity increase of 244% was the anaerobic anode, 40 g/l TDS of produced water, 0.2 mM methylene blue and MDC unit 2.

The interaction effects between mediator concentration, produced water TDS and anode aeration were significantly high for both response variables. This implies that none of the factors have a simple direct relationship with desalination efficiency and with anolyte conductivity. Therefore, the effect of each factor significantly depends on the state of the other two factors. A major conclusion drawn from the factorial design is that at high air flow rates of 150 ml/min in the anode chamber, higher MB concentration reduced desalination efficiency and reduced change in anolyte conductivity. Moreover, at high air flow rates, aeration in anode has a negative effect on desalination efficiency and a negative effect on change in anolyte conductivity.

5.2. Recommendations

Based on the results obtained from the parametric study, it is recommended to maximize the biofilm development on the anode electrode of MDCs by using repeated batch processes to significantly improve desalination efficiency. Desalination efficiency can also be enhanced by using produced water that has the highest TDS concentration. However, in this case, the microorganism, mediator, and potassium ferricyanide should be immobilized on the respective electrodes in order to prevent their transfer to the produced water. During long operations, it is recommended to investigate the use of other oxidizing agents in place of potassium ferricyanide in the cathode chambers due to fast depletion of ferricyanide which makes it unsustainable.

Based on the results obtained in the parametric and factorial design studies, if facultative microbes are employed and aerated in the anode chamber, high air flow rates should not be used. The aeration rates should be optimized through experimentation before being employed for other studies. It is also recommended to perform further research and experimentation to measure the concentration of different salts present in the anolyte, catholyte and saline water solutions in MDCs and to investigate how their concentrations vary with long operation time. This will aid in truly understanding the different mechanisms and transports that may occur in MDCs employing ferricyanide and oxygen in their cathode chambers and yeast cells along with mediators in their anolyte.

It is also recommended to compare the effect of prokaryote and eukaryote microorganisms on MDC desalination efficiency and current generation. This is because although several publications have compared few prokaryotic microorganisms, none of them have directly compared yeast cells with bacterial strains and mixed bacterial cultures at the same operating conditions. It is highly important to investigate the combination of microorganisms and mediators that can result in the highest desalination efficiency for MDCs.

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Vita

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