

University of Nevada, Reno

**Capturing Atmospheric Carbon Dioxide by Depleting Inorganic  
Carbon in Municipal Wastewater**

A thesis submitted in partial fulfillment of the requirements for the degree of Master of  
Science in Chemical Engineering

by

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THE GRADUATE SCHOOL

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prepared under our supervision by

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entitled

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Inorganic Carbon in Municipal Wastewater**

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requirements for the degree of

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**Abstract**

CO<sub>2</sub> removal from the atmosphere is likely necessary to limit global warming to the 2 °C goal of the Paris Agreement. This work aims to leverage the embedded conveyance energy within the existing wastewater infrastructure in the U.S. to remove inorganic carbon and develop a carbon negative CO<sub>2</sub> removal technology. Although wastewater treatment plants are designed to remove organic carbon, a total of 588 Mt of inorganic carbon also enters the plants but is not removed. To demonstrate this, a bench-scale, membrane-based wastewater carbon-capture system was optimized. Commercially available, gas-permeable membranes (PFA) and hydrophobic, porous membranes (PVDF) fabricated in-house were evaluated in the system. The effects of multiple physiochemical parameters on inorganic carbon removal were investigated, with the best-case scenario removing 15% of the inorganic carbon from the feed stream. Deploying similar full-scale systems across US wastewater infrastructure without addition of acid for pH adjustment would remove up to 12.9 Mt-C/yr. The addition of hydrochloric acid (HCl) to bring the wastewater to 5.0 (one pH unit below the bicarbonate pK<sub>a</sub>) would increase removal to 30.5 Mt-C/yr, but this is partially offset by CO<sub>2</sub> emissions from HCl production, resulting in a net removal of 22.6 Mt-C/yr. When compared to direct air capture, a more mature technology, the new system was more sustainable at reduced feed stream pH (2.5) based on net CO<sub>2</sub> removal.

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## **Chapter1: Introduction**

### 1.1 Climate Change

The Intergovernmental Panel on Climate Change (IPCC) has estimated that human activities have caused approximately 1.0 °C of global warming above pre-industrial levels, with a likely range of 0.8 to 1.2 °C [5]. It is estimated that global warming is likely to reach 1.5 °C between 2030 and 2052 if carbon emissions continue to increase at the current rate. Moreover, the Paris Agreement aims to limit global temperature increase to less than 2 °C, which will likely require removal of greenhouse gases (GHG) from the atmosphere (i.e., negative emissions) along with dramatic reductions in emissions [6]. The major effects of the change in climate are warming of the ocean and atmosphere, diminishing amounts of snow and ice, and rising sea levels. It is evident that the change in climate is causing an impact on both natural and human systems and a solution is required [7].

Anthropogenic activities, such as burning fossil fuel for energy generation, play an important role in the global environmental change since the Industrial Revolution, and they have shifted the Earth system to an unstable state (anthropogenic carbon dioxide (CO<sub>2</sub>) emissions disrupt the natural equilibrium between surface water and atmosphere) [8]. In addition to CO<sub>2</sub>, the concentration of many other GHGs in the atmosphere have also been increasing rapidly. These GHG's influence the Earth's energy balance, which is known as greenhouse effect. Four principal greenhouse gases that are emitted into the atmosphere have been identified: CO<sub>2</sub>, methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), and halocarbons (a group of gases containing bromine,

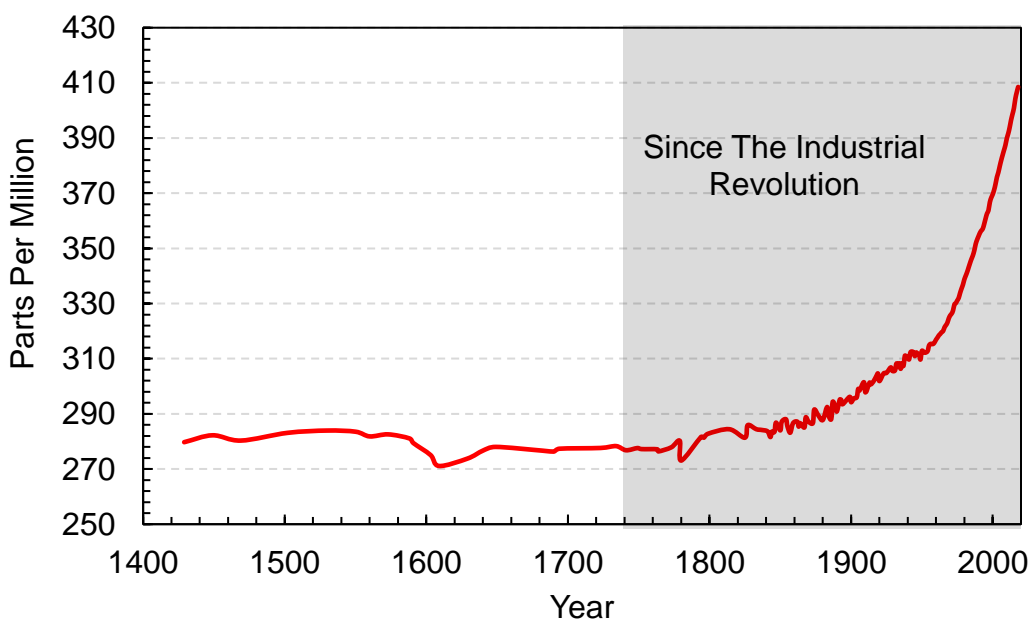
chlorine, and fluorine), with the largest contributor to global warming attributed to the increase in atmospheric concentration of CO<sub>2</sub> [5].

## 1.2 Increasing Atmospheric CO<sub>2</sub> Concentrations

CO<sub>2</sub> is the most impactful of Earth's greenhouse gases. Although it absorbs less heat than other greenhouse gases (CH<sub>4</sub> and N<sub>2</sub>O), it is more abundant and has a longer atmospheric half-life [7]. Moreover, CO<sub>2</sub> molecules can easily dissolve into the ocean and react with water molecules, generating carbonic acid and decreasing the ocean's pH and causing ocean acidification. Rising CO<sub>2</sub> levels are the result of human activities such as burning of fossil fuels for energy generation and transportation. As shown in Figure 1.1, the concentration of CO<sub>2</sub> in the atmosphere has dramatically increased over the past few decades, with an increase of 50% since the industrial revolution (270-275 ppm in 1750; 310 ppm in 1950; 412 ppm in 2019) [1]. Almost 30% of the anthropogenic CO<sub>2</sub> emissions have been absorbed by the world's oceans, causing acidification and the associated consequences (e.g. adverse effects on biodiversity) [9], [10].

Global CO<sub>2</sub> emissions are about 36 Gtonne CO<sub>2</sub>/yr, which is higher than the uptake value by natural sinks. Fossil fuel emissions represent 91% of the anthropogenic CO<sub>2</sub> emitted [9]. Natural CO<sub>2</sub> sinks, including forests and oceans, play a significant role in adjusting the concentration of CO<sub>2</sub> in the atmosphere. Many countries have decided to reduce their CO<sub>2</sub> emissions that come from their industries in an effort to decrease the atmospheric CO<sub>2</sub> concentrations [11]. Moreover, maintaining and increasing forest density would reduce the atmospheric CO<sub>2</sub> concentration, stated

as one of the main commitments of Paris agreement. One of the short-term solutions to reduce CO<sub>2</sub> emissions is the implementation of carbon capture and storage (CCS). This procedure is mainly applied to capture CO<sub>2</sub> from flue gases and the achieved CO<sub>2</sub> enriched stream is then transported to geological reservoirs to be stored. While this approach is effective for point sources, about 50% of the CO<sub>2</sub> emissions are from diffuse sources, e.g. aircraft, shipping, or automobiles [12].



**Figure 1.1:** Global average of annually mean concentration (in ppm) of atmospheric CO<sub>2</sub>. Data was collected from national oceanic and atmospheric administration (NOAA) [1].

### 1.3 CO<sub>2</sub> Capture and Removal from the Environment

Many CO<sub>2</sub> intensive industries, such as power plants, cement manufacturing, iron and steel production, and pulp and paper production plants, are employing CCS to decrease CO<sub>2</sub> emissions in effluent streams [13]. Although these efforts would

reduce the current GHG emission rates, recapturing previously emitted GHGs is another great concern. Despite the fact that CCS can reduce the CO<sub>2</sub> emissions at point sources, they are not designed to be implemented elsewhere. The use of negative emissions technologies (NETs) are rising to reduce the cumulative total anthropogenic carbon emissions; it has been estimated that exceeding 1 trillion tonne of atmospheric carbon will result in 2 °C of average global warming [14]. These NETs are implemented within the greatest natural CO<sub>2</sub> sinks (e.g. atmosphere and oceans) to make a meaningful impact on the global carbon cycle. There are several advantages to using NETs [15], including (i) capturing CO<sub>2</sub> from any economic activity emitted at different locations and time; (ii) eliminating the cost of transportation between capture unit location and storage sites (NETs are usually applied near a CO<sub>2</sub> storage site); and (iii) the separation mechanism in NETs is not effected by other pollutants due to their lower atmospheric concentration [9,13,14]. Many NETs have been proposed and tested in recent years. Technologies such as afforestation and reforestation [18], direct air capture (DAC) of CO<sub>2</sub> [4], and bioenergy with carbon capture and storage (BECCS) [19] are focused on reducing the existing CO<sub>2</sub> in the atmosphere. Others, such as dissolved CO<sub>2</sub> capture [20] and ocean liming [21] are target dissolved inorganic carbon (IC) in oceans. However, delivering NETs often requires substantial cost and regulatory innovation. Most present NET systems or processes are few and operate at small scale., with large-scale operations not expected to be deployable within the decade [22].

### *1.3.1 Afforestation and Reforestation*

Afforestation and reforestation is capturing CO<sub>2</sub> by absorption from atmosphere through plant growth. A positive point is that these are natural processes that can be implemented at low cost. However, they are limited by the availability of land suitable for tree growth. Smith et al., [23] estimated that capturing 1.1-3.3 Gt CO<sub>2</sub> per year would require very large areas of land, approximately 20-60% of the current arable land [18]. Other concerns, such as release of captured carbon during planting disruption, N<sub>2</sub>O emissions due to use of fertilizer, and impacts on biodiversity, are must also be addressed [24].

### *1.3.2 Direct Air Capture*

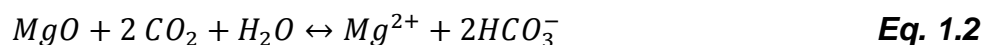
In DAC technologies, atmospheric air flows over CO<sub>2</sub>-selective absorbents and CO<sub>2</sub>-depleted air is then returned to the atmosphere. Captured CO<sub>2</sub> is released as a concentrated stream for disposal or alternative use while the sorbent is regenerated for reuse. The absorbents can be either liquid or solid. The main advantages of these systems is the ease of CO<sub>2</sub> release and absorbent regeneration mechanisms, and the low energy inputs for flowing the air into the system. However, critical studies show that significant cost challenges [25], energy requirements associated with absorbents regeneration [26], and water demand (mainly from desalination processes) to replace evaporation [27] are the main drawbacks for DAC systems.

### 1.3.3 Bioenergy with Carbon Capture and Storage

Bioenergy with carbon capture and storage (BECCS) involves growing forest biomass to replace fossil fuels for energy generation and capturing emitted CO<sub>2</sub> during combustion and storing it. More radical examples include generating biofuels by algae cultivation [28] and using municipal solid wastes as a feedstock for BECCS [29]. The most important advantage of BECCS is both biomass growth and CCS are existing and viable technologies. However, BECCS results in a net increase in CO<sub>2</sub> release to the atmosphere due to the energy used across the biomass supply and processing chain [30]. Moreover, nutrient demand for biomass growth would be another great concern [31].

### 1.3.4 Ocean Liming and Dissolved CO<sub>2</sub> Capture

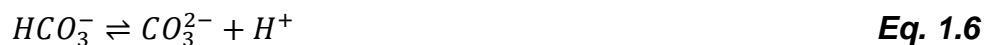
Apart from the previously mentioned technologies, ocean liming and dissolved CO<sub>2</sub> capture processes are focused toward dissolved CO<sub>2</sub> in water. It is important to note that the concentration of CO<sub>2</sub> in oceans is 125 times greater than it is in the atmosphere [32]. This fact makes oceans a more viable option than the atmosphere for employing NETs such as ocean liming and indirect ocean capture. Ocean liming involves a reaction that increases ocean pH by adding alkalinity in the form of calcium/magnesium oxide/hydroxide (Equations 1.1 and 1.2).



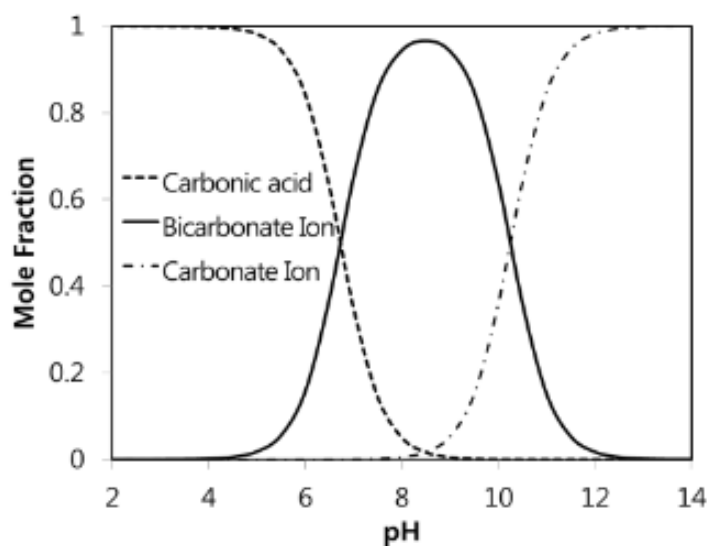
Two moles of atmospheric CO<sub>2</sub> dissolve into the ocean to re-establish the CO<sub>2</sub> equilibrium between the atmosphere and surface ocean. Although ocean liming processes have the potential to reduce CO<sub>2</sub> concentration in the aqueous phase, energy intensive calcination process that produced Lime (CaO), massive land-based mineral extraction, and transportations are some of its drawbacks. Dissolved CO<sub>2</sub> capture is another evolving NET leveraging the ocean-atmosphere equilibrium and pH control to extract the CO<sub>2</sub> from oceans.

#### 1.4 Chemistry of Aqueous Phase CO<sub>2</sub>

The greenhouse gas effect will undoubtedly impact aquatic ecosystems. Depending on pH, the dissolution of CO<sub>2</sub> in water occurs as a variety of forms including dissolved CO<sub>2</sub>, bicarbonate (HCO<sub>3</sub><sup>-</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>), and carbonic acid (H<sub>2</sub>CO<sub>3</sub>). The concentration of carbonic acid is less than 0.3% of total [CO<sub>2</sub> (aq)]. The sum of [H<sub>2</sub>CO<sub>3</sub>] and [CO<sub>2</sub> (aq)] is the total [CO<sub>2</sub>] and total dissolved inorganic carbon (DIC) in water is the sum of [H<sub>2</sub>CO<sub>3</sub>], [HCO<sub>3</sub><sup>-</sup>], and [CO<sub>3</sub><sup>2-</sup>]. The chemical basis of the water-carbonate system is the hydration of CO<sub>2</sub> with water to form carbonic acid and subsequent dissociation chemical reaction (Equations 1.3 to 1.6):



The concentration of dissolved  $\text{CO}_2$  in water is relatively small as  $\text{CO}_2$  reacts with water to form a weak acid, carbonic acid.  $\text{H}_2\text{CO}_3$  then rapidly dissociates and leads to the formation of two ionic species, bicarbonate (Eq. 1.4) and carbonate (Eq. 1.5). The speciation within this acid-base system is a function of pH. The dissociation constants for bicarbonate and carbonate formation are  $K_4=10^{-6.35}$  and  $K_5=10^{-10.33}$ , respectively. When the concentration of bicarbonate equals that of carbonic acid, the pH of the water is 6.35, considered to be in the acidic region as it is less than the neutral pH of 7. Moreover, as the concentration of carbonate and bicarbonate becomes equal, the pH of the water would be 10.33. Therefore, bicarbonate ions are the dominant species in most neutral waters with pH between 6.35 and 10.33 (Figure 1.2).



**Figure 1.2:** Bjerrum plot showing the activities of inorganic carbon species as a function of pH [2].

### 1.5 CO<sub>2</sub> Extraction by pH Adjustment

By understanding the CO<sub>2</sub> behavior in aqueous phase, it can be concluded that basic waters (pH>10.33) have more carbonate ions than other carbon species and dissolved CO<sub>2</sub> is the dominant species in acidic waters (pH<6.35). Thus, the addition of acid to the water-carbonate system can convert all the DIC to CO<sub>2</sub> gas, which is a desirable speciation for CO<sub>2</sub> extraction due to the fact that it can be extracted from aqueous phase as gas molecules. Lannoy, et al., [20] introduced a new process leveraging the ocean-atmosphere equilibrium and the pH adjustment to extract CO<sub>2</sub> in the ocean. In this process, a weak acid stream is generated by pushing ocean water into a bipolar membrane electro-dialysis system. The generated acid stream is then injected to the main feed stream to decrease the pH of ocean water. In the next step, CO<sub>2(g)</sub> is stripped from the feed stream by implementing a liquid-gas membrane contactor. The CO<sub>2</sub> deficient stream is then returned to the ocean surface to recapture CO<sub>2</sub> from the air. Although dissolved CO<sub>2</sub> capture processes have great potential in CO<sub>2</sub> extraction [33], high electrical energy demand for running the system (e.g. acid/base generation, pumping streams, and generated vacuum in gas-liquid membrane contactor) are major concerns. Lannoy, et al., [18] made a critical assumption that the electricity consumption of their system is carbon free. Membrane efficiency enhancement is another concern that has not been covered properly in scientific literature. It is estimated that a single membrane can remove up to 65% DIC in the ocean water [20], while membrane modification (e.g. facilitated transport membranes and

mixed matrix membrane) could potentially increase the removal rate and improve the separation efficiency.

## 1.6 Separation by Membranes

Membranes act as a barrier where a permeable component passes through the membrane faster than other components. This transport is driven by a partial pressure, fugacity, or concentration gradient of the component across the membrane. Membrane technology has become an attractive and competitive alternative to conventional separation technologies over the past few decades [34]. Separation by membranes has many advantages, including high energy efficiency, low capital cost, and ease of scale-up [35]. The permeability-selectivity tradeoff relationship (membranes with high permeability are generally less selective and vice versa) is one of the biggest challenges in this technology and many studies have focused on membrane efficiency enhancement by simultaneously increasing the selectivity and permeability [35, 36, 37]. Membranes with higher permeability lead to higher productivity and lower capital cost, whereas membranes with higher selectivity lead to more efficient separations, higher recovery, and lower power costs.

Transport through membranes can be on the basis of size (molecular sieving mechanism), molecular weight (Knudsen diffusion), or solubility (solution diffusion). Membranes can be categorized in many ways, with classification by their morphology or structure common as membrane structure determines the separation mechanism and hence the application.

### *1.6.1 CO<sub>2</sub> Capture using Membrane Technology*

Most studies have focused on three ways to capture CO<sub>2</sub> from the point sources at pre-combustion, oxy-combustion, and post-combustion [39]. The choice between these technologies is determined by the total pressure of an exhaust gas, partial pressure of CO<sub>2</sub>, and the type of fuel utilized (gas, liquid, or solid) [40].

Pre-combustion capture is a process that removes CO<sub>2</sub> from other fuel gases before the gas combustion. First, it initiates by converting solid, liquid, or gaseous fuel into a mixture of syngas (H<sub>2</sub> and CO) and CO<sub>2</sub> by coal gasification or steam reforming. Afterwards, a water-gas shift reaction is conducted to reduce the content of CO, thus more H<sub>2</sub> and CO<sub>2</sub> are generated. Membrane separation is then applied to separate the resulting H<sub>2</sub> and CO<sub>2</sub>. Upon compression, the CO<sub>2</sub>-rich stream is transported to a storage or utilization site and the pure H<sub>2</sub> stream enters the combustion chamber for power generation, which mainly emits water vapor in the exhaust [31]. Pre-combustion membranes are generally categorized into two types: H<sub>2</sub>-selective membranes and CO<sub>2</sub>-selective membranes. Different types of membranes, such as palladium-based membranes, carbon membrane, silica membranes, and nonporous polymeric membranes, have been used for pre-combustion capture [41]. Nonporous polymeric membranes permeate the desired component via the solution-diffusion mechanism. There is a wide range of polymeric membranes available for H<sub>2</sub>/CO<sub>2</sub> separation. High CO<sub>2</sub> selectivity has been achieved by using polybenzimidazole and poly (vinyl chloride) membranes [42, 43]. High permeabilities have also been observed for polyimides such as 6FDA-durene [44].

Membrane separation for post-combustion is a more mature technology than pre-combustion capture. To capture CO<sub>2</sub> from flue gas, a membrane should have high CO<sub>2</sub> permeability, high CO<sub>2</sub>/N<sub>2</sub> selectivity, high thermal and chemical stability, and acceptable costs. Among different types of materials, polymeric membranes are viable for CO<sub>2</sub> removal from flue gas, such as cellulose acetate, polyimides, polysulfone, and poly carbonates [45, 46]. In oxy-fuel combustion, oxygen is supplied for combustion instead of air. This avoids the presence of nitrogen in the exhaust gas, which is the major issue to be solved by post combustion CO<sub>2</sub> capture technologies [47].

### *1.6.2 Hydrophobic and Hydrophilic Membranes*

Based on the affinity to water, membranes can be classified as either hydrophobic (contact angle (CA) > 90°) or hydrophilic (CA < 90°) [3]. Common hydrophobic membranes are polyethylene, polypropylene, and poly-difluoroethene, where hydrophilic polymers include polyethersulfone and cellulose acetate. Polar solvents such as water can easily wet and pass through a hydrophilic membrane; however, hydrophobic membranes are wetted by non-polar solvents such as hexane [48]. Hydrophilic membranes are used for aqueous liquid filtration, where wetting across a hydrophilic membrane pores ensures that the entire effective surface area is available for filtration and dry spots do not develop. Hydrophobic polymer membranes are generally used for gas separation since their wettability is much lower than that hydrophilic membranes, preventing liquid passage across

the membrane. Hydrophobic membranes are easily fouled by fatty acids, surfactants, and antifoam agents.

### *1.6.3 Separation according to the membrane structure*

Membranes can also be classified based on their structure and separation principles into porous or nonporous membranes. The characteristic of these two basic types are as follows:

#### *1.6.3.1 Porous Membranes*

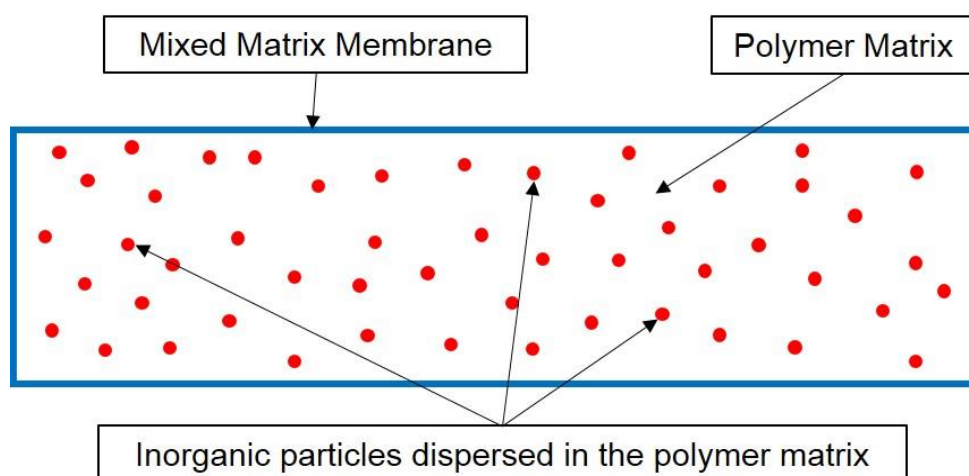
Porous membranes are a solid matrix with defined holes or pores with diameter ranging from less than 2 nm to more than 20  $\mu\text{m}$  [48]. The transport through porous membranes and the selectivity is mainly determined by molecular size and membrane pore size distribution. These types of membranes are used in microfiltration and ultrafiltration processes. The membrane material is an important factor for manufacturing the membrane, including the chemical and thermal stability of the membrane. The main problem for porous membranes is the flux rejection due to concentration polarization and fouling.

#### *1.6.3.2 Nonporous Membranes*

Membranes with pores smaller than 0.2 nm are classified as nonporous. In these types of membranes, the difference in solubility and/or diffusivity between the molecules and the membrane material play an important role. Nonporous membranes are mainly used for gas separation and pervaporation where the more condensable component have higher solubility than other components in the feed stream.

#### 1.6.3.4 *Mixed Matrix Membranes*

Most polymeric membranes currently used in industry for gas or liquid separation are based on the solution-diffusion mechanism. One way of improving their separation characteristics would be to incorporate specific fillers into the polymer matrix [49]. Mixed matrix is a blend of inorganic particles in a polymer matrix. It is suggested that mixed matrix membranes have the potential to provide membranes with higher permeability-selectivity and equivalent productivity compared with existing membrane materials. Figure 1.3 shows schematic of mixed matrix membranes.



**Figure 1.3:** Schematic of a mixed matrix membrane.

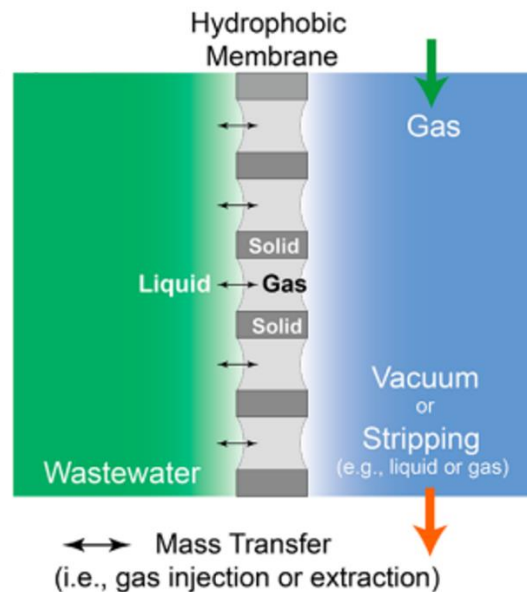
Comparing to pure polymeric membranes, mixed matrix membranes leverage good mechanical properties (to operate at higher feed pressures), processability (to form thin films, tubes, or hollow fibers), and cost of polymers combined with strength of fillers in terms of permeability and selectivity [50]. It is expected that mixed matrix membranes have better mechanical properties than regular

polymeric membranes, however, among studies on mixed matrix membranes in past few decades, only a few have reported a significant enhancement in membrane performance. The main reason is that mixed matrix membrane fabrication usually involves difficulties such as weak contact of particles in polymer [51], the rigidification of polymer chains around the filler particles [52], pore blockage by the polymer chains [53], and the aggregation of filler particles [54]. There are many inorganic nanoparticles that have been used to prepare mixed matrix membranes, including silica [55], titanium oxide [56], magnesium oxide [57], and zinc oxide (ZnO) [58]. One study found that membrane porosity increased by increasing the ZnO content from 0% to 5%, where the selectivity of mixed matrix membrane containing 3% ZnO increased by 110% compared to the membrane with 0% ZnO [58]. In another study, dispersing titanium oxide nanoparticles into polystyrene matrix increased the membrane performance in separation of CO<sub>2</sub> from CO<sub>2</sub>/N<sub>2</sub> mixtures [59].

#### *1.6.4 Hydrophobic Membranes for CO<sub>2</sub> Extraction from Wastewater Streams*

Wastewater streams contain abundant carbon, nitrogen, and CH<sub>4</sub> that can be recovered as value-added products [60]. Some gases such as CH<sub>4</sub>, H<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> are commonly produced or consumed during wastewater treatment [61]. These gases are removed or delivered by conventional energy-intensive methods such as gas sparging or liquid heating. However, an increasing number of studies have focused on using hydrophobic membranes in wastewater treatment and resource recovery. When operated below their liquid entry pressure, hydrophobic

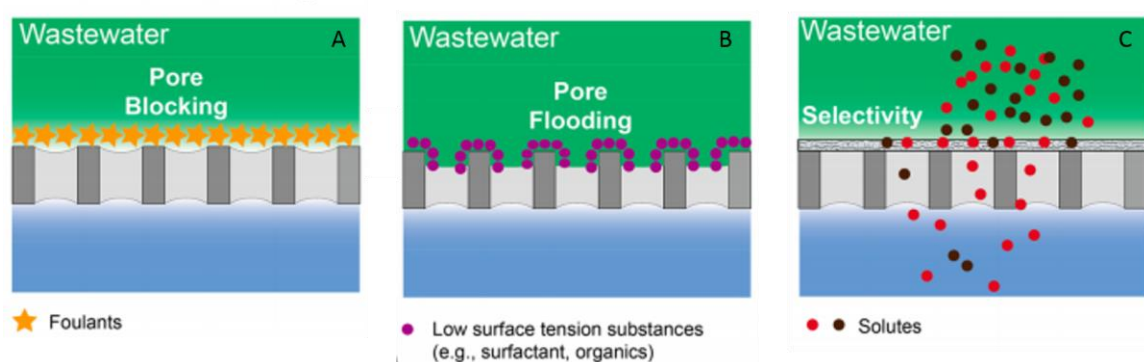
membranes repel water and generate a three-phase (solid-liquid-gas) interface that enhances mass transfer across the membrane (Figure 1.4). Based on Henry's law, the concentration of a dissolved gas is proportional to its partial pressure in the gas phase. Thus, at high CO<sub>2</sub> partial pressures, mass transfer occurs from gas to liquid. However, to change the direction of mass transfer, it is essential to reduce the CO<sub>2</sub> partial pressure in the gas phase. This could be achieved using vacuum, stripping gas, or specific solvent at the permeate side.



**Figure 1.4:** The three-phase interface created by hydrophobic membranes [3]

The role of hydrophobic membranes in harvesting gaseous products such as CH<sub>4</sub>, H<sub>2</sub>, and NH<sub>3</sub> during wastewater treatment has been proven to be highly effective and efficient [62, 63]. A hydrophobic membrane works as a liquid water barrier but allows the passage of gases. Compared with conventional gas stripping, a larger

interfacial area per volume can increase the extraction/removal efficiency in hydrophobic membranes. Despite their great potential in gas stripping from wastewater streams, the surface properties of these membranes coupled to the complex nature of wastewater streams complicate their deployment in real-world systems. Major challenges that must be overcome to allow the technology to effectively operate in industry include membrane fouling, membrane wetting, and limited selectivity and functionality (Figure 1.5).



**Figure 1.5:** Major challenges in hydrophobic membranes: (A) membrane fouling, (B) membrane wetting, and (C) membrane selectivity [3].

Most of the organic carbon is transformed into  $\text{CO}_2$  during wastewater treatment, which generates a large fraction of DIC in water. This results in low pH and high DIC concentrations in wastewater discharges. A fraction of dissolved  $\text{CO}_2$  degasses to the air through aeration, however, a large portion of that remains in water as DIC [64]. It is estimated that a total of  $105 \times 10^{12}$  gal of wastewater containing up to 1638 mg/L of DIC is treated in the U.S. every year [65]. High DIC concentrations at wastewater treatment discharge can have a negative impact on

the environment (e.g. ocean acidification). Moreover, extraction of DIC from wastewater streams allows the decarbonized discharge to potentially absorb additional  $\text{CO}_2$  from the atmosphere and reduce the atmospheric  $\text{CO}_2$  concentration in a short amount of time [32].

### 1.7 Thesis Objective

The main objective of this thesis is to provide proof-of-concept that removal of DIC from wastewater streams results in net-negative carbon emission and has the potential to provide meaningful removal of  $\text{CO}_2$  from the global carbon cycle. For this purpose, an optimized bench-scale wastewater carbon-capture system was developed and tested with commercially available membranes and also membranes fabricated in the lab. The details of the setup and results from the commercial membranes is the focus of Chapter 2 of this thesis, while the results from the membranes fabricated in house are discussed in Chapter 3.

## **Chapter 2: CO<sub>2</sub> Extraction from Wastewater Using Wastewater Carbon Capture System (WWCCS)**

This chapter is intended for submission to *International Journal of Greenhouse Control*.

### 2.1 Introduction

Global energy demand and industrialization have led to rapidly expanding use of fossil fuels that release CO<sub>2</sub> into the atmosphere, which has caused the climate to warm. The Paris Agreement aims to limit global temperature increase to less than 2 °C, which will likely require removal of CO<sub>2</sub> from the atmosphere (i.e., negative emissions) along with dramatic reductions in emissions [6]. Recent negative emissions research has focused on ocean liming [21], indirect ocean carbon capture [20], afforestation and reforestation [18], direct air capture of CO<sub>2</sub>, and bioenergy with carbon capture and storage [19]. Although each has the potential to remove carbon from the global cycle, there are also associated tradeoffs. Ocean liming takes advantage of ocean alkalinity but requires large land-based mineral extraction, conveyance, and processing [66, 20]. Afforestation and reforestation require land for tree development and have low CO<sub>2</sub> uptake during early stages of growth [67]. direct air capture faces major challenges including low CO<sub>2</sub> removal efficiency, high energy demand, and low CO<sub>2</sub> selectivity [68, 18]. Bioenergy with carbon capture and storage is the most mature of the negative emission technologies, with commercial plants and mature CO<sub>2</sub> capture technologies available for these plants. However, challenges, such as high land use intensity and higher water use compared to direct air capture systems still exist [69].

Charles et al. [20] designed and characterized an indirect ocean capture prototype that leverages the air-ocean carbon equilibrium. Two assumptions were made to offset the high rate of energy consumption: that the indirect ocean capture system was co-located with a desalination plant, offsetting pumping costs, and that energy inputs were from carbon neutral sources. Although co-location with another industry may be feasible, entirely carbon neutral energy sources are not yet readily available.

The total municipal wastewater flow for the population of the United States is estimated to be  $16 \times 10^{12}$  gal/yr; 75% is treated by publicly owned treatment facilities [65].  $93 \times 10^{12}$  gal/yr of industrial wastewater is also treated in the US, for a total of  $105 \times 10^{12}$  gal/yr, containing 50 to 250 mg/L DIC [70, 71] and 30 to 1,638 mg/L DIC [72], in municipal and industrial, respectively. Thus, removal of DIC from US wastewater discharges would result in up to 588 Mt/yr of DIC removed from the carbon cycle. After removal of  $\text{CO}_2$  from wastewater, released decarbonized effluent would equilibrate with atmospheric  $\text{CO}_2$ , representing a potential net-negative carbon removal strategy. Further, wastewater is already conveyed to treatment plants by gravity or existing pumping infrastructure, negating energy use for conveyance.

We examined the potential for WWCCS using gas permeable membrane to remove  $\text{CO}_2$  as a carbon removal strategy. We investigated typical wastewater parameters: pH, pressure, temperature, and flowrate to provide best- and worse-case scenarios for potential DIC removal from US wastewaters and to estimate

likely carbon removal versus release. The goal was to provide proof-of-concept that removal of DIC from wastewater results in net-negative carbon emission and has the potential to provide meaningful removal of CO<sub>2</sub> from the global carbon system.

## 2.2 Materials and Method

### 2.2.1 *Materials and Reagents*

A 12.5 μm thick PFA film was used as membrane in this work and is commercially available as Teflon PFA from American Durafilm (Worcester, MA). PFA was chosen for this study due to its mechanical strength and high CO<sub>2</sub> permeability ( $336 \times 10^3 \text{ cm}^3 / (\text{m}^2 \text{ hr atm})$ ; provided by manufacturer). HCl (12 M) was purchased from Fisher Chemical (Pittsburgh, PA). NaHCO<sub>3</sub> was purchased as commercially available baking soda (Clabber Girl Co., Indianapolis, IN). A conductivity transmitter and probe (Eutech instruments COND500, Vernon Hills, Illinois) were used to monitor the conductivity of the permeate stream. Feed stream pressure was monitored with a liquid-filled pressure gauge (PFP series, Winters Instruments, Houston, TX). A pH electrode and meter (Oakton PC700 meter, Cole Parmer, Vernon Hills, IL) was used to monitor the feed stream pH. Samples from feed and permeate streams were analyzed for DIC concentration using a TOC-L Laboratory Total Organic Carbon Analyzer (Shimadzu Corporation, Pleasanton, CA).

### 2.2.2 *Sample Preparation*

DI water containing alkalinity typical of domestic wastewater was prepared with 250 mg/L sodium bicarbonate ( $\text{NaHCO}_3$ ) and the pH was adjusted to 2.5, 5, 6.3, and 8.3 ( $\pm 0.2$ ) with HCl prior to circulation. Additional samples were collected from a regional wastewater reclamation facility from the secondary clarifier effluent; before filtration (52 mg/L IC) and after filtration effluents (35 mg/L IC). Wastewater samples were stored at 3 °C for < 7 days before use.

### 2.2.3 *Experimental*

Two streams of water were circulated on opposing sides of a PFA membrane with countercurrent flow in a closed system. The feed stream volume was 0.4 L and acted as the source of the IC. The permeate stream was 0.6 L of DI water. The two streams were circulated at varying flow rates, pressure, and temperature for 60 min, with samples collected immediately before and after the circulation period. A conductivity probe was inserted into the stopper of a vacuum flask in the permeate stream and conductivity of the permeate stream was monitored throughout the circulation period to ensure membrane integrity.

The effect of flow rate, temperature, pressure, and pH of the feed stream were evaluated by varying one parameter while holding others constant. Flow rate was controlled using variable-speed gear pumps (Cole Parmer, Vernon Hills, IL). Temperature was controlled using a hot plate (Henan Aibote Science and Technology Development C., Henan, China) with an inline digital thermometer inserted through the stopper of the feed-side vacuum flask. Pressure on the feed

side of the membrane was created and controlled with a globe valve downstream of the membrane. Permeate samples (15 mL) were taken immediately before and after 1 hr of operation. A sample from the feed stream was also taken as a reference for total DIC removal.

Based on experimental results and calculations, the best and worst operational conditions with respect to DIC removal are defined and summarized in Table 2.1. Alkalinity spiked DI water sample at the lowest pH and the highest temperature, pressure, and flowrate tested was used as the feed streams for the best-case scenario, while after filtration wastewater at the highest pH and the lowest temperature, pressure, and flowrate tested was used for the worst-case scenario.

**Table 2.1:** Specification of feed stream parameters, along with the best- and worst-case scenarios with respect to DIC removal. DI water feed samples had 35 mg/L IC.

	<b>Feed Stream Type</b>	<b>Temp. (°C)</b>	<b>Pressure (psig)</b>	<b>Flowrate (mL/min)</b>	<b>pH</b>
	Alkalinity spiked Water	23	0	200	2.5
	Wastewater	30	3	500	5.0
		35	5	750	6.3
		40	10	1000	8.3
Best case scenario	Alkalinity spiked water	40	10	1000	2.5
Worst case scenario	Wastewater	23	0	200	8.3

#### 2.2.4 Analytical

IC was quantified with a Shimadzu TOC-L, calibrated using  $\text{NaHCO}_3$ , by injection of the non-sparged sample into the combustion tube and measurement of gaseous  $\text{CO}_2$  by nondispersive infrared spectroscopy. The instrument was calibrated at 0.5, 1, 3, 5, 10, and 20 mg/L IC. Blank samples were run periodically between individual samples to flush the TOC analyzer and reduce potential cross over of DIC from sample to sample. Once analyzed, the DIC contents of both samples were used to calculate the total mass of DIC in each sample and subsequently the total transfer of DIC from the feed stream to the permeate stream.

#### 2.3 Results

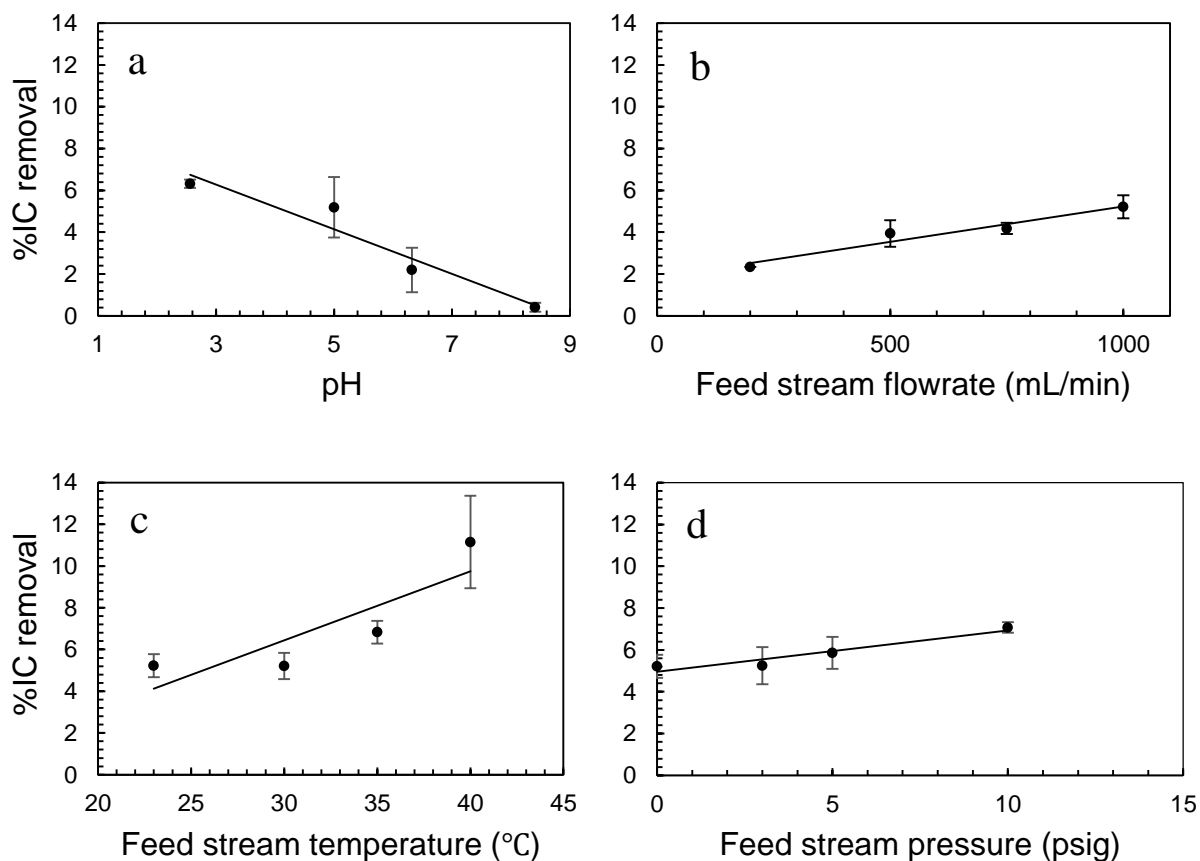
The effect of pH on DIC removal from alkalinity-spiked DI water at room temperature (23 °C) was evaluated first. The feed and permeate pressure was <1 psig and the flow rate was 1,000 mL/min. Decreasing the pH from 8.3 to 2.5 increased DIC removal from 0.4% to 6.3% (Figure 2.1a). The effect of feed flowrate on DIC removal (Figure 2.1b) was also evaluated at 23 °C with <1 psig feed stream pressure. Increasing the flowrate from 200 to 1,000 mL/min increased the DIC removal linearly from 2.3% to 5.2%.

The effect of temperature was evaluated using temperatures typical of wastewater. Flow rate (1,000 mL/min), pH 2.5 ( $\pm 0.3$ ), and feed pressure (<1 psig) were held constant for four different feed stream temperatures: 23, 30, 35, and 40 °C. Increasing the temperature from 23 to 30 °C did not appear to result in a significant change in DIC removal. However, from 35 to 40 °C there was a considerable increase in DIC removal, from 6.7% to 11.2% (Figure 2.1c). It is important to note

that the feed side temperature is hard to control due to the rapid heat transfer between feed and permeate side (the only heat resistance is the membrane with 12.5  $\mu\text{m}$  thickness) and causes variability in the data.

IC removal from the feed stream was also measured at varying feed stream pressures: 0 (hydrostatic pressure only), 3, 5, and 10 psig. Other parameters were held constant at 23 °C, 1,000 mL/min, and pH 2.7-2.8. Increasing the feed pressure from 0 to 10 psig resulted in increased DIC removal from 5.2% to 7.1% (Figure 2.1d).

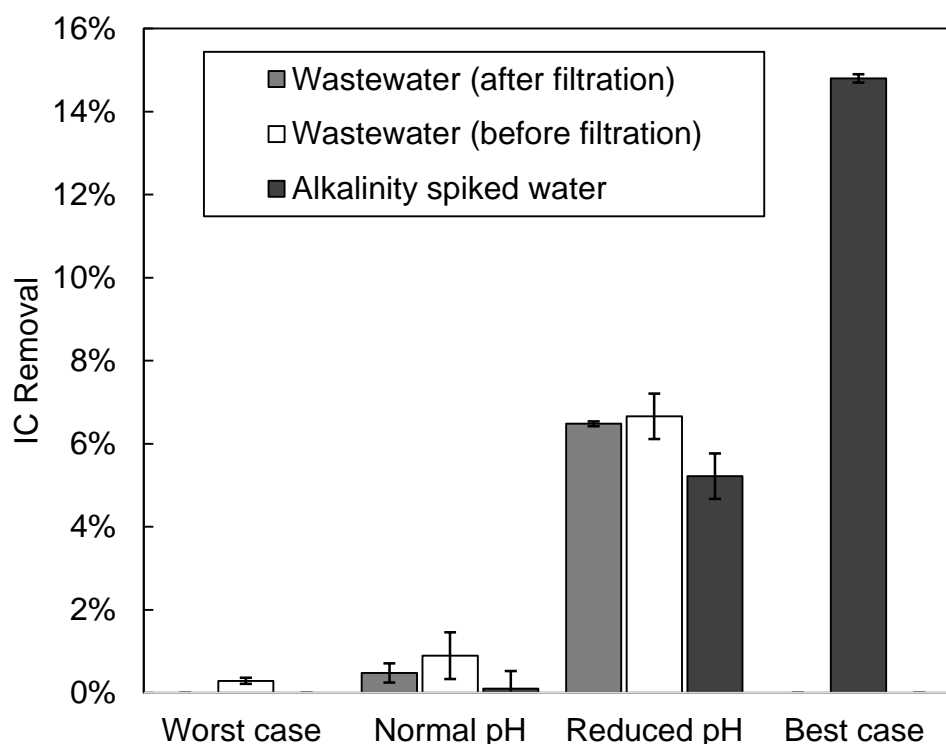
Overall, an increase in DIC removal occurred with increasing feed temperature and pressure from 23 °C to 40 °C and 0 psig to 10 psig, respectively. Acid addition to decrease the feed stream pH from 8.3 to 2.5 resulted in an increase in DIC removal.



**Figure 2.1:** Effect of pH (a), feed stream flowrate (b), temperature (c), and pressure (d) on DIC removal. Experimental conditions where a) 23°C, 0 psig, and 1,000 mL/min, b) 23 °C and 0 psig and pH 2.5 ( $\pm 0.3$ ), c) 1,000 mL/min and 0 psig and pH value 2.5 ( $\pm 0.3$ ), d) 1,000 mL/min and 23°C and pH 2.5 ( $\pm 0.3$ ). The errors bars represent the standard deviation of triplicate experiments.

Wastewater samples collected from secondary and filtered effluent of a regional wastewater treatment plant (WWTP) were also evaluated as feed streams. It is important to note that the waste streams in secondary and filtered effluents contain suspended solids and dissolved and colloidal compounds that may impact DIC removal by blocking the membrane pores. Using wastewater samples would help to investigate any significant drop in DIC removal due to membrane fouling (e.g.

pore blockage). The pH was adjusted to 2.5 and 8.3 (operating conditions maintained at: 1000 mL/min; <1 psig, and 23 °C) and compared to results achieved from alkalinity spiked water samples (Figure 2.2). Both filtered and unfiltered wastewater at pH = 2.5 had slightly higher DIC removal than the alkalinity spiked water under the same conditions.



**Figure 2.2:** Percent DIC removal with the best-case (reduced pH (2.5), with highest pressure (10 psig), temperature (40 °C), and flowrate (1000 ml/min); and the worst-case (natural pH (8.3), with lowest pressure (0 psig), temperature (23 °C), and flowrate (200 ml/min) scenarios. Moreover, three different feed stream types were used to measure the DIC removal at pH value 2.5 (reduced pH) and 8.3 (typical wastewater pH).

## 2.4 Discussion

### 2.4.1 pH Adjustment

Based on US industrial and municipal wastewater flow rates, DIC concentrations, and wastewater normal pH range (6.5 to 9.0) [73] we estimate that wastewater DIC capture could remove up to 12.94 Mt-C/yr without acid addition. Increasing DIC removal with decreasing pH was expected; at pH less than the pKa of  $\text{HCO}_3^-$ ,  $\text{CO}_2$  dominates, and leads to a corresponding increase in the  $\text{CO}_2$  gradient across the membrane and greater flux. In select industrial or municipal wastewaters, influent pH values may be as low as 5.0 [74, 75], reducing the required addition of HCl in select scenarios. Reducing pH at full-scale would result in greater captured IC, but requires acid addition, which has embedded energy and carbon emissions.

Typical municipal wastewater pH is in the range of 6.5 to 9 [73]. To reduce the pH of the alkalinity spiked water from 6.5 to 2.5, 0.14 gr of HCl was added per liter of the feed stream solution. According to the life cycle assessment of HCl production [76], 0.14 gr HCl releases 47 mg of DIC to the environment, reducing the overall removal of DIC by 54% (i.e., half of the DIC removed is released in production of the required acid).

In this study, a commercially available acid (HCl) has been added to reduce the feed stream pH. However, many studies have focused on production of dilute acids and bases from inputs of electricity and water that may result in less  $\text{CO}_2$  emissions to the environment than using commercially available acids [77, 78, 79]. The energy requirements for operating these systems generally releases more  $\text{CO}_2$

than is capture. In one recent study focused on capturing CO<sub>2</sub> from the ocean, the critical assumption was made that all energy inputs, including the acid-base production system, are carbon free [20]. Thus, from a CO<sub>2</sub> generation prospective, using electricity to produce acid for pH adjustments is an appealing alternative.

Most existing CO<sub>2</sub> in wastewater is produced by organic carbon degradation during the wastewater treatment processes. Some of the generated CO<sub>2</sub> degasses to the air during aeration while the remaining part dissolves in the treated wastewater, which decreases the wastewater pH values and changes the total alkalinity. Furthermore, to maintain a high nitrogen removal efficiency, the pH of wastewater should be between 7 and 8 [80] during the nitrification and denitrification processes. Thus, it is necessary to increase the pH values and the wastewater alkalinity by using chemicals such as CaO or caustic soda (NaOH) before further wastewater biological treatments [81]. The decarbonized feed stream can be neutralized by this process and safely redirected to the treatment process. It is important to note that the main goal of lime addition is to increase the higher nitrogen removal efficiency rather than water acidification and/or enhance CO<sub>2</sub> release [64]. Moreover, pH adjustment would be also necessary during reverse osmosis process since the pH of wastewater drops as low as 5.0 after the wastewater exit the reverse osmosis process [73].

#### *2.4.2 Flowrate Effect on DIC Removal*

The effect of feed-side flowrate on DIC removal was evaluated at 23 °C with 0 psig feed stream pressure. Increasing the flowrate from 200 to 1,000 mL/min linearly

increased the DIC removal from 2.3 % to 5.2 % (Figure 2.1b). Increased removal was linear because the flow regime was laminar ( $17 \leq Re \leq 87$ ) at all flow rates. Increasing flow further would likely increase removal but comes at a cost of pumping energy. The linear relationship between flow and removal would likely begin to fail at  $Re > 500$  due to turbulent flow. Again, this may not be practical at many wastewater treatment facilities without significantly more pumping energy.

#### *2.4.3 Temperature Effect on DIC Removal*

The temperature effect on DIC removal was evaluated using temperatures typical of wastewater. The results showed a significant improvement in DIC removal by increasing the temperature from 23 to 40°C. Lower CO<sub>2</sub> solubility at higher temperatures could be the main reason of this improvement. At the elevated temperatures, dissolved CO<sub>2</sub> tends to release in gaseous phase, which leads to CO<sub>2</sub> gas diffusion into the hydrophobic membrane pores. Diffused CO<sub>2</sub> then enters the permeate side and dissolves into liquid phase [82]. Although using heat to increase the water temperature will remove more dissolved IC, increasing temperature is energy intensive; Increasing the temperature from 40 to 50 °C would result in 3.2 Mt-C released to the environment as CO<sub>2</sub>, based on the average US grid emission factor of  $5.59 \times 10^2 \text{ t}(\text{CO}_2)/\text{GWatt}$  [20].

#### *2.4.4 Pressure Effect on DIC Removal*

IC removal from the feed stream was measured while using different applied feed stream pressures: 0, 3, 5 and 10 psig at 1000 mL/min, 23 °C, and pH=2.5. Although

increasing the feed pressure from 0 to 10 psig resulted in DIC removal increasing from 5.2 to 7.1% (Figure 2.1d), feed stream pressure above 10 psig were unsustainable and caused membrane failure. As with increasing temperature, increasing feed pressure will increase the required energy input, and subsequently raise CO<sub>2</sub> emissions, thus feed stream pressures above 10 psig were not investigated due to the fact that the pressure of wastewater discharge streams would not exceed the atmospheric pressure since all streams would be dumped into the environment. Thus, higher pressures would not be applicable in this study.

#### *2.4.5 WWCCS Global Impact*

Based on DIC removal in the best case scenario, the maximum amount of captured DIC from the US waste streams was calculated and the numbers were compared with the total annual US CO<sub>2</sub> emissions. As shown in Figure 2.2, the WWCCS removed almost 15% of DIC in the best-case scenario, but less than 1% of DIC in the worst-case scenario. Results from wastewater feed streams did not show a significant difference compared to alkalinity spiked DI water samples under comparable operating conditions (Figure 2.2). The wastewater was selected over alkalinity spiked DI water for the worst case scenario because the presence of other constituents in wastewater was expected to decrease DIC removal and potentially degrade membrane integrity or permeability (Figure 2.2).

More than 10<sup>14</sup> gallons of treated municipal and industrial wastewater are discharged from WWTPs in the US annually. Many factors, including treatment process type, influent type, and location, effect the wastewater alkalinity and DIC

content, resulting in DIC content ranging from 30 to 1,638 mg/L [72]. Based on this concentration range, US wastewater streams contain between 12.8 and 588 Mt-C/yr. Capture of inorganic carbon contained in US wastewater flows would result in removal of up to 12.9 Mt-C/yr without acid addition (Table 2.2). Reducing the pH to 2.5 would increase DIC removal up to 37.16 Mt-C/yr, although the acid production processes will also increase the amount of CO<sub>2</sub> emitted to the environment (~10 Mt-C/yr). Further, the acid would likely need to be neutralized before release, further diminishing CO<sub>2</sub> captured by acid addition. The US Environmental Protection Agency reports total DIC emissions in the US were about 5,270 Mt in 2017 [83]. Moreover, 588 Mt-C in wastewater streams accounting for 11.2% of the total US CO<sub>2</sub> emissions. Thus, employing the WWCCS in WWTPs has the potential (>90% DIC removal from feed stream) to remove up to 11.2% of total DIC emissions in US. It is important to note that CO<sub>2</sub>-deficient streams exiting the WWCCS will be released to the environment, and these streams have the potential to adsorb additional CO<sub>2</sub> from atmosphere. As the best-case scenario, the WWCCS is able to remove 15% of total DIC from wastewater streams (Figure 2.2), corresponding to 88.2 Mt-C removal from the global C cycle.

**Table 2.2:** Total carbon removal from the US wastewater streams at different pH values (total carbon removed at pH values 2.5 and 5 has a range due to the range of CO<sub>2</sub> emissions from HCl production)

<b>pH (±0.3)</b>	<b>IC removal (%)</b>	<b>Total carbon removed (Mt- C/yr)</b>
2.5	6.3	17.7 - 37.2
5.0	5.2	22.6 - 30.5
6.3	2.2	12.9
8.3	0.4	2.4

The potential to remove carbon from the global carbon system using full-scale US deployment of wastewater carbon capture is shown in Table 2.3. The total carbon removal from the global carbon system in different feed stream pressure shows that pressurizing the feed stream to 10 psig has almost the same total carbon removal as heating the feed stream to 35 °C.

**Table 2.3:** Total carbon removal from the US wastewater streams, using WWCCS at pH 2.5. Carbon emissions caused by use of HCl to control the pH is considered at four temperatures and applied pressures.

	<b>Percent DIC removal (%)</b>	<b>Total C removal from the US wastewater streams (Mt-C/yr)</b>
<b>Temperature (°C)</b>		
23	5.2	0.7 – 30.7
30	5.1	0.7 – 30.2
35	6.7	0.9 – 39.3
40	11.2	1.4 – 65.6
<b>Pressure (psig)</b>		
0	5.2	0.7 – 30.7
3	5.3	0.7 – 30.7
5	5.9	0.8 – 34.5
10	7.1	0.9 – 41.6

## 2.5 Conclusion and Future Work

The overall goal of the described WWCCS is to provide proof of concept that removal of DIC from wastewater streams can result in net negative carbon emissions. Wastewater streams contain up to 1,638 mg/L DIC as they enter the plants and experience different ranges of temperatures and flowrates during the treatment process [75], eliminating energy and emissions from use of electricity for running the pumps and heating the feed. However, one area of concern with this process is the use of acid to reduce the pH of the feed stream to allow for the dissolution of CO<sub>2</sub> and to generate the driving force between two sides of the

membrane. We optimized the feed stream parameters (pH, pressure, temperature, and flowrate) to investigate their effects on the amount of DIC removal. As the best-case scenario, the WWCCS can remove up to 88.2 Mt-C/yr from US wastewater stream. Future improvements, such as membrane modifications, setup optimization, and cost analysis are critical to increase the CO<sub>2</sub> permeability and selectivity, reduce the consumed energy during the WWCCS operation, and make the system economically feasible.

## **Chapter 3: Life Cycle Assessment of WWCCS and Fabrication of PVDF Membranes to Enhance CO<sub>2</sub> Removal Efficiency**

### **3.1 Introduction**

In the first part of this chapter, a comparative cradle-to-gate life cycle assessment (LCA) conducted for the WWCCS is described. Various environmental impact categories such as global warming potential (GWP), abiotic depletion (AD), and acidification potential (AP) were investigated. The main objective of the LCA was to investigate the impacts of all WWCCS-involved processes and materials on environmental and human health categories.

In the second part of this chapter, the performance of pure PVDF membranes prepared by phase inversion technique to enhance the CO<sub>2</sub> removal efficiency was evaluated. Inorganic ZnO nanoparticles were used as a dispersed phase in polymer solution to fabricate PVDF mixed matrix membranes for maximizing the DIC removal. The overall goal of this section is to enhance the WWCCS potential in DIC removal from wastewater streams.

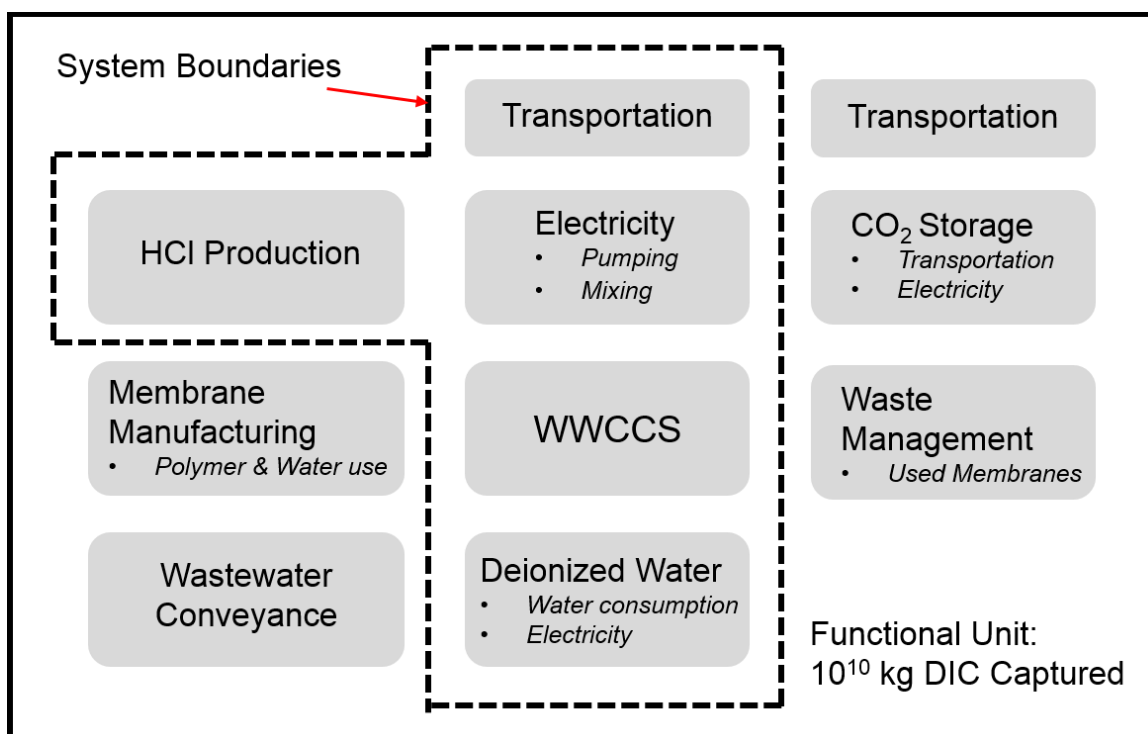
### **3.2 LCA of WWCCS**

Based on the WWCCS product, which is decarbonized wastewater, a comparative LCA provides results that can be used to calculate net CO<sub>2</sub> emissions by the system and track the processes and/or materials that contribute the most to GHG emissions.

#### *3.2.2 Functional Unit and System Boundaries*

Comparative cradle-to-gate LCAs were conducted at different feed stream pH values (2.5, 5.0, and 6.3) and all gate-to-grave processes including carbon

storage, transportation, and its corresponding electricity usage were eliminated all have the same impact. It was estimated that the WWCCS can remove up to 37.16 Mt-C per year (section 2.4.5), however, the WWCCS must be able to capture over  $10^{10}$  kg of DIC to make a meaningful impact on global carbon cycle. For this purpose,  $10^{10}$  kg captured DIC was used as functional unit. The system boundaries and functional unit for the LCA are shown in Figure 3.1.



**Figure 3.1:** System boundaries and functional unit for LCA of WWCCS

### 3.2.3 Databases and Life Cycle Inventory

The LCA model was assembled using the Gabi ts LCA modeling software, and required data and processes were extracted from Gabi database, experimental observations, and literature review. The breakdown of data sources is summarized in Table 3.1.

**Table 3.1:** Data collection for LCA of the WWCCS

<b>GaBi Database</b>	<b>Experimental</b>	<b>Literature</b>
Electricity usage	Pumps' electricity usage	HCl production
Transportations	%DIC removal	
Fresh water usage		

Energy requirements for each section are detailed in Table 3.2, where the numbers presented are based on the 1000 kg of CO<sub>2</sub> extraction capacity. Energy consumption by the pumps is considered due to different flowrates. Fresh water consumption is affected by the CO<sub>2</sub> removal. Heating the feed stream from 25 to 40 °C (best case scenario, Section 2.4.5) has been included as an input energy. It is estimated that capturing 10<sup>10</sup> kg of DIC from wastewater would require 1,340 m<sup>2</sup> of membrane. Energy requirements for membrane manufacturing were excluded from system boundaries as all scenarios have the same functional unit, and thus the same required membrane area. Moreover, many LCA studies related to membrane separations (e.g. desalination process [84] and carbon capture and storage process [85]) have reported that the membrane manufacturing has a relatively minor effect on global impacts.

**Table 3.2:** Energy requirements for the WWCCS operated at best-case scenario of 15% DIC removal.

Source/Material	Energy (kJ/hr)	Energy (10 <sup>6</sup> kJ/tonne CO <sub>2</sub> removal)	Ref.
Electricity (pumping)	432	192	Provided by company
Fresh Water (using desalination process)	130	57.7	[72]
Electricity (heating)	37.6	16.7	[82]
Acid Addition (HCl)	238	105.8	[86]

Fresh water and chlorine are feed streams to the hydrochloric acid production unit and are included in the life cycle impact assessment (LCIA). Energy requirements (electricity) for these processes are provided from uranium (5%), crude oil (23%), and coal (72%). It is important to note that each of these processes have different impacts on environmental and health indices and that each can affect the final results based on their contribution. The energy required to run the pump is significantly higher than the other sources or materials and the required electricity to heat the feed stream is relatively low (Table 3.2).

Based on the selected impact assessment method, the following environmental impact categories were evaluated: GWP, AD, AP, ozone depletion potential (ODP), eutrophication potential (EP), human toxicity potential, ecotoxicity potential, water depletion, ground level ozone creation potential (POCP), and photochemical oxidant formation potential (POFP). Of these, GWP is the most

directly relevant to WWCCS CO<sub>2</sub> emissions. The impact assessment was carried out using the Traci version 2.1 method.

#### *3.2.4 Process Diagram and Assumptions*

Based on the experimental data and accessible databases, the following assumptions were used:

- Energy requirements for wastewater conveyance has been excluded from the LCA because the wastewater stream is already conveyed to and within treatment plants by gravity or existing pumping infrastructure.
- Electricity use to mix the feed stream is neglected because
  - It is much lower than electricity usage of pumps, and
  - Wastewater streams are assumed to be well-mixed before entering the WWCCS.
- System tubing was not considered as the WWCCS is expected to be integrated into existing wastewater treatment facilities, thus the majority of the piping infrastructure will already exist.
- Transportation distances for chemicals, such as HCl, to the WWCCS site is assumed to be 100 km.

#### *3.2.5 Results and Discussion*

Based on the system boundaries (Figure 3.1) and assumptions, production of HCl has the greatest impact on the environmental and health indices when operating under the best-case scenario. This is due to HCl production being an energy

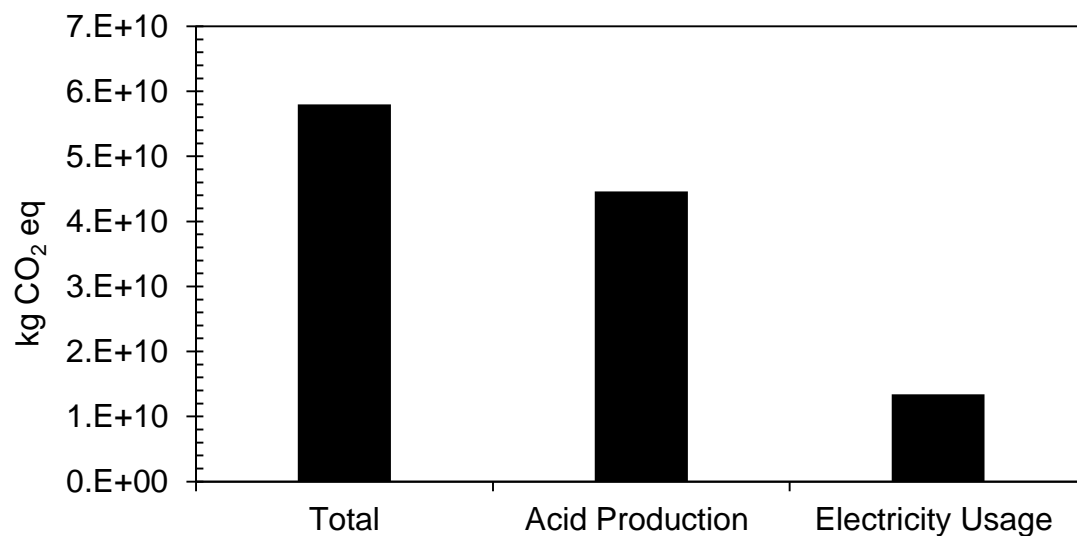
intensive process. The WWCCS is designed to have a positive global impact on the carbon cycle, which means the system should capture more CO<sub>2</sub> than it releases. The results for the different impact categories are summarized in Table 3.3.

**Table 3.3:** WWCCS environmental and health indices results (Traci version 2.1 impact assessment method)

<b>Index</b>	<b>Total Quantity</b>
Global Warming Air, incl. biogenic carbon [kg CO <sub>2</sub> eq.]	5.8×10 <sup>10</sup>
Acidification [kg SO <sub>2</sub> eq.]	2.2×10 <sup>8</sup>
Eutrophication [kg N eq.]	2.38×10 <sup>7</sup>
Ozone Depletion Air [kg CFC 11 eq.]	1.86
Human toxicity, cancer (recommended) [CTUh]	20.3
Human toxicity, non-canc. (recommended) [CTUh]	3.13×10 <sup>3</sup>
Resources, Fossil fuels [MJ surplus energy]	5.3×10 <sup>10</sup>
Smog Air [kg O <sub>3</sub> eq.]	3.9×10 <sup>9</sup>

#### 3.2.5.1 *Global Warming Potential*

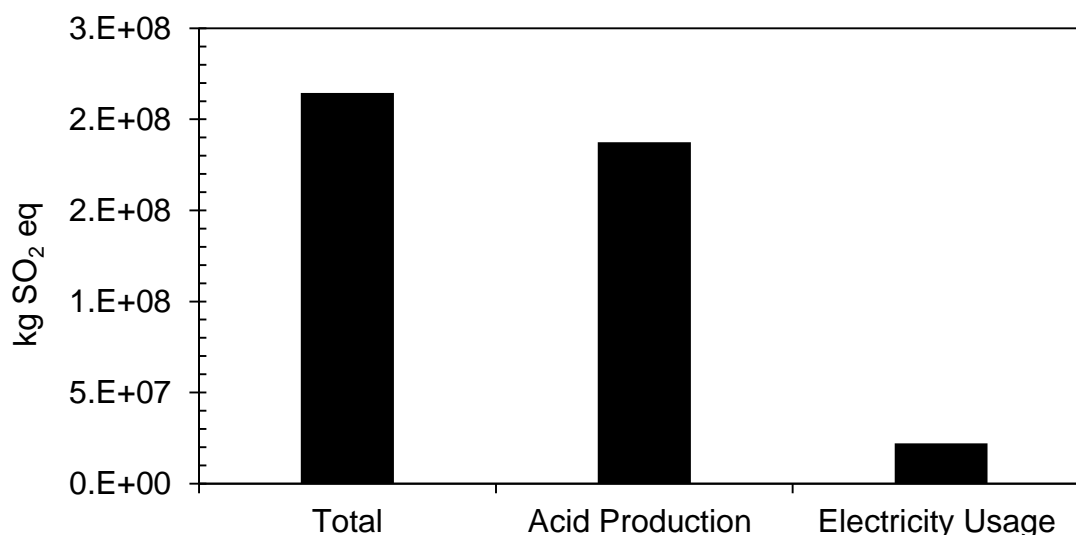
Figure 3.2 presents the distribution of GWP on the WWCCS model. HCl production was identified as the primary contributor, with 4.46×10<sup>10</sup> kg CO<sub>2</sub> eq emissions (76.9% of the total) generated primarily due to the energy required to deionize the process water. Electricity usage accounted for the remaining 23.1% of the CO<sub>2</sub> emissions, and is primarily attributed to the deionized water production and pumping the permeate side.



**Figure 3.2:** Distribution of GWP from the WWCCS model.

#### 3.2.5.2 *Acidification Potential*

Emissions contributing to AP were a result of SO<sub>x</sub> remaining after acid processing and the production of electricity. The major contributor to AP (Figure 3.3) is direct emission from the HCl production, with a relative contribution of 88.9%, as the processes takes place onsite and involves an acidic product that releases pollutants into the atmosphere. The other contribution is from electricity usage, with a relative contribution of 11.1%.



**Figure 3.3:** Distribution of AP from the WWCCS model

### 3.2.5.3 *Other Environmental and Health Indices*

The HCl production also has the largest contribution to the EP (86.2%); which indicates the enrichment of the aquatic ecosystem with nutritional element due to the emission of nitrogen or phosphor containing compounds; AD (92.03%), and ODP (62.7%), with the remaining percentage attributed to electricity usage in all cases. Dissolution of hydrogen chloride in water is the traditional process for HCl production, however, the large-scale production of HCl is almost always integrated with the industrial scale production of other chemicals such as chlorination reaction [87]. Therefore, high contribution of HCl production in OD can be explained by CFC emissions to air that cause the destruction of the stratospheric ozone layer. The on-site HCl production infrastructure is the primary contributor to total HTP (99.6%)

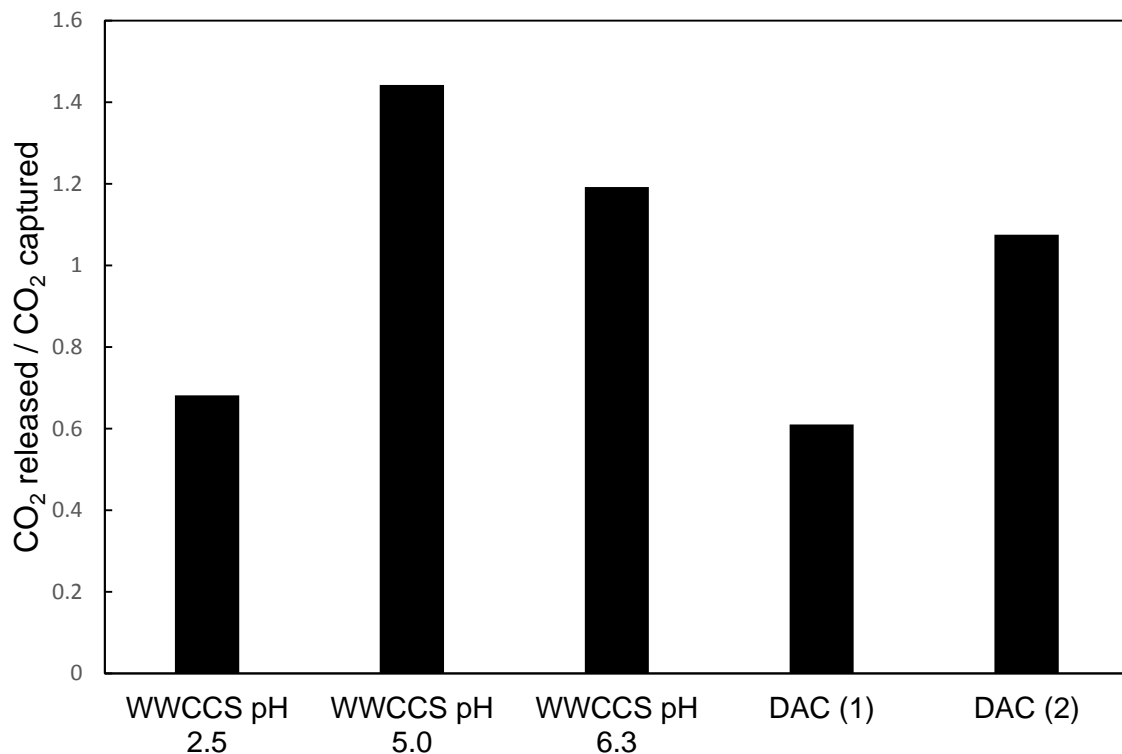
due to the corrosive nature and concentration of the HCl produced. The distilled water infrastructure contributed the remaining total HTP.

#### 3.2.5.4 *CO<sub>2</sub> Released versus CO<sub>2</sub> Captured by the WWCCS*

Based on the environmental impacts of LCAs conducted at three different feed stream pH values, the hydrochloric acid production process is the largest contributor to GWP. However, the GWP index can change significantly by changing the feed stream pH value, as this dictates the amount of acid addition to the system required. Under the best-case scenario with respect to CO<sub>2</sub> removed from the wastewater, the most hydrochloric acid was required to reduce the feed stream pH to 2.5. Although the WWCCS can remove more DIC at lower pH values, it also releases more CO<sub>2</sub> to the environment due to acid addition.

Considering the experimental results (DIC removal) at different pH values and by calculating the amount of DIC removed from feed stream, it can be concluded that at feed stream pH values lower than 4.8, the WWCCS is able to capture more CO<sub>2</sub> than it releases. A comparison between the WWCCS at three pH values and two different DAC systems is shown in Figure 3.4. In one study, a DAC system (DAC(1)) with strong hydroxide sorbents would release up to 0.85 ton of CO<sub>2</sub> while capturing 1 ton of CO<sub>2</sub> [26]. Another study shows that DAC (DAC(2)) can remove only 0.93 ton of CO<sub>2</sub> per ton of CO<sub>2</sub> released [4]. As shown in Figure 3.4, the ratios of CO<sub>2</sub> released to CO<sub>2</sub> captured for WWCCS at pH values 5.0 and 6.3 are 1.44 and 1.19, respectively. It is clear that the WWCCS is not capturing sufficient CO<sub>2</sub> at pH 5 and 6.3. However, at a pH of 2.5 the system is comparable with other DAC

systems in terms of captured versus released CO<sub>2</sub>. It is important to note that the two DAC systems compared are more mature than the WWCCS and are currently deployable at an industrial scale.



**Figure 3.4:** Life cycle greenhouse gas emissions emitted per amount of carbon captured (a comparison between WWCCS and DAC system [4]).

### 3.3 Fabrication of pure and Mixed Matrix Hydrophobic PVDF Membranes Containing ZnO Nanoparticles

#### 3.3.1 Introduction

In this section, a pure hydrophobic PVDF membrane was fabricated using the phase inversion technique to investigate the effects of different membranes on feed stream DIC removal. ZnO nanoparticles were also dispersed in the PVDF

polymer solution at varied concentrations to create mixed matrix membranes for DIC removal from a wastewater stream. Prepared pure and mixed matrix membranes were used in the WWCCS to enhance the removal efficiency.

The hydrophobic, porous PVDF membranes provide gas-filled pores that prevent water and dissolved ions from passing through the membrane. At different operational conditions, the CO<sub>2</sub> molecules can easily be absorbed by the membrane surface and pass through the membrane via the solution-diffusion mechanism.

To capture CO<sub>2</sub> gas molecules from wastewater, it is necessary to use a hydrophobic polymer that repels water but allows gas molecules to pass through the membrane pores. In PVDF membrane interactions with water, existing C-F bonds in polymer structure cannot compete with a variety of internal interactions of liquid phase water (e.g. van der Waals forces, dipole interactions, and hydrogen bonding), thus, water would make a contact angle higher than 90° with membrane surface which prevents the water molecules to penetrate into the membrane pores.

Hydrophobic membranes are particularly susceptible to organic fouling (Dissolved organic and inorganic matters and colloids). This could be explained by Hydrophobic – hydrophobic interactions between the membrane surface and hydrophobic domains that are nearly always present on natural organic matter. To overcome this challenge, wastewater streams after secondary treatment would be the best choice as feed stream for WWCCS due to the fact that all organics would change to inorganics through oxidation process during secondary treatment.

*Hydrophobic PVDF membranes are widely used in pressure-driven water and wastewater treatment (e.g. ultrafiltration, membrane bioreactor), and membrane contactors operations (e.g. membrane distillation, gas absorption, and stripping) [88]. The performances of PVDF membranes could be considerably limited by fouling in pressure-driven operations [89] and wetting in membrane contactors applications [90]. One way to overcome membrane fouling problems is to blend the polymer with chemical modifiers or other hydrophilic modifications during membrane fabrication. Using hydrophilic polymers, such as polyvinylpyrrolidone, or employing inorganic nanoparticles, such as TiO<sub>2</sub> and ZrO<sub>2</sub>, in the polymer matrix can also decrease the chance of membrane fouling [91]. However, using more hydrophobic polymers (e.g. perfluoropolymers) or co-polymers with higher fluorine content in PVDF polymer matrix can be used to increase membrane hydrophobicity [92]. PVDF membranes can also be treated after the fabrication process by physical surface modification (e.g. hydrophilic polymer layer coating) or chemical treatment (e.g. plasma grafting of polymer groups) [93].*

### **3.3.2 Materials and Methods**

#### **3.3.2.1 Materials**

Commercial PVDF polymer powders were supplied by (Fisher Scientific, Auburn, AL, USA) and dried at 60 °C in an oven for 24 hr to remove moisture content. ZnO nanoparticles with spherical morphology at two different sizes (10-30 nm; 80-200 nm) were purchased from US Research Nanomaterials (Houston, TX). Based on the manufacturer's specification sheet, the purity of nanoparticles was 99% with a density of 5.606 g/cm<sup>3</sup>. N-Methyl-2-pyrrolidone (NMP; 99.9% purity) solvent was

purchased from (Fisher Scientific, Auburn, AL, USA) and used as a polymer solvent to prepare the dope solutions. A commercially available micrometer adjustable film applicator (MTI Corporation, Richmond, CA) was used to cast the polymer solutions.

### 3.3.2.2 *Methods*

The first step of membrane fabrication is to make a homogeneous solution by choosing the solvent to dissolve or easily disperse the polymer powder. For a homogenous solution to occur, the driving force in the solution process, which is free energy  $G$ , should decrease (shown in Equation 3.1) [94].

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (\text{Eq. 3.1})$$

where  $\Delta H_{\text{mix}}$  and  $\Delta S_{\text{mix}}$  are equal to the change in enthalpy and entropy at constant temperature during the mixing process. The rate of mixing (if  $\Delta G_{\text{mix}} < 0$ ) increases with temperature because of increased diffusivities. To predict when mixing is possible,  $\Delta S_{\text{mix}}$  and  $\Delta H_{\text{mix}}$  should be calculated. For ideal solutions is equal to zero, however, polymer solutions cannot be classified as ideal solutions due to the size differences between solvent and polymer molecules, which leads to an increase in entropy and enthalpy of mixing. The entropy of mixing can be calculated using Boltzmann's equation in the lattice model presented by Flory and Huggins [95]. The enthalpy of mixing is considered as the energy arising from the formation of polymer-solvent contact on mixing, by replacing some of polymer-polymer and solvent-solvent contacts. Flory and Huggins represented the enthalpy of mixing

using the Van Laar equation and introduced the Flory-Huggins interaction parameter,  $\chi_{12}$  (Equation 3.2).

$$\Delta H_{\text{mix}} = RT \chi_{12} X_1 \phi_2 \quad (\text{Eq. 3.2})$$

where R is the gas constant, T is temperature,  $X_1$  is the mole fraction, and  $\phi_2$  represents the volume fraction. Equation 3.1 can be rearranged and Equation 3.2 incorporated to give:

$$\Delta G_{\text{mix}} = RT [X_1 \ln \phi_1 + X_2 \ln \phi_2 + X_2 \phi_2 \chi_{12}] \quad (\text{Eq. 3.3})$$

where the first two terms represent the combinatorial contribution and the last term represents the enthalpic contribution. Flory and Huggins introduced this expression for the Gibbs free energy of mixing based on the lattice model, which presented the dimensionless Flory-Huggins interaction parameter. In other words,  $\chi_{12}$  is composed of enthalpic and entropic contributions. The Flory-Huggins theory is widely used to predict the equilibrium behavior between liquid phases containing a polymer. It can also be used as a measure of solvent power. For high-molecular weight polymer-solution systems, the critical polymer concentration is close to zero and the interaction parameter has a value equal to 0.5. The value of  $\chi_{12}$  decreases for good solvents for a specific polymer [96]. The Flory-Huggins interaction parameter is estimated for PVDF and different solvents experimentally using inverse gas chromatography measurements [94]. Solvents such as hexane and m-xylene have  $\chi_{12}$  higher than 0.5, however, 3-heptanone and 3-hexanone showed a better interaction with PVDF polymers, having  $\chi_{12}$  equal to 0.5. Polar solvents such as NMP and DMA have  $\chi_{12} \ll 0.5$ .

The fabrication of pure and mixed matrix PVDF membranes was as follows. Pure 20 wt% PVDF membranes were fabricated by mixing 12 g of PVDF and 60 g of NMP solvent using the phase inversion technique [59]. Briefly, the NMP solvent was stirred and 2 g of PVDF powder was added to the mixture and stirred for 2 hr. The remaining 10 g of PVDF powder was added to the solution and stirred until a homogenous solution was obtained. The polymer solution was continuously stirred for more than 24 hr to ensure a completely homogenous solution. The prepared solution was then left idle for 6 hr until all the generated air bubbles were released from the solution.

Preparation of the mixed matrix membranes followed the same procedure, except with an additional step for nanoparticle addition. ZnO nanoparticles (0.12, 0.25, and 0.5 wt%) were added to 5 g of NMP solvent and stirred continuously for 2 hr. The well-dispersed mixture was then added to the homogenous polymer solution and stirred for 24 hr, then left idle for 6 more hr. The prepared doped solutions were sonicated at room temperature to achieve uniform nanoparticle dispersion.

Pure and mixed matrix membranes were fabricated in a flat sheet by the phase inversion method. The prepared doped solutions were poured over a glass plate and cast with a stainless steel micrometer adjustable film applicator at a thickness of 50  $\mu\text{m}$  (fabricated membrane characteristics are shown in Table 3.4). The cast membranes were exposed to the atmosphere for 40 sec, then put in a coagulation bath of deionized water until the membranes peeled off the glass plate. The obtained membranes were soaked in the coagulation bath for 24 hr and then

immersed in an ethanol bath for 2 hr for post treatment. The final prepared membranes were dried for 48 hr at room temperature and atmospheric conditions.

**Table 3.4:** Characteristics of fabricated membranes.

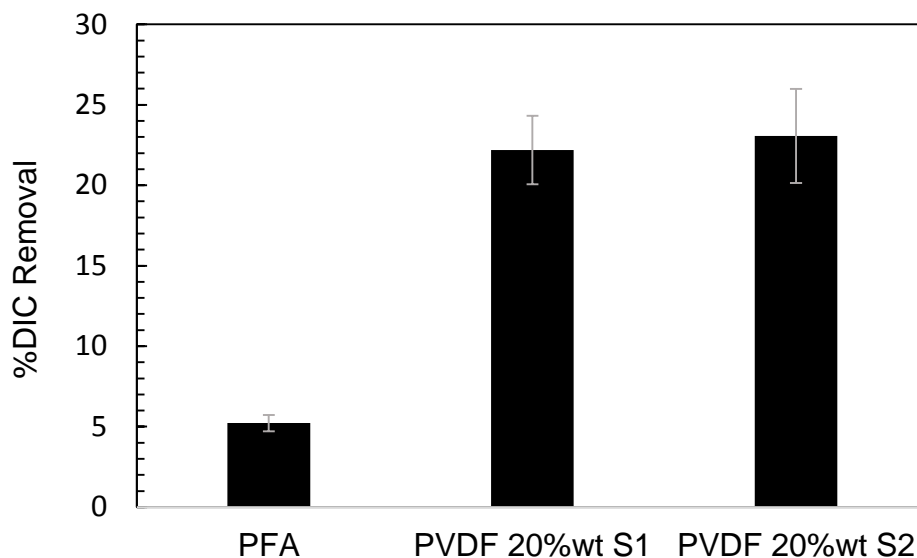
<b>Membrane</b>	<b>wt% ZnO</b>	<b>wt% PVDF</b>
Pure PVDF	0	20
PVDF 0.12	0.12	20
PVDF 0.25	0.25	20
PVDF 0.50	0.50	20

### 3.3.3 Results and Discussion

After preparing pure and mixed matrix PVDF membranes, they were used in the WWCCS to evaluate their DIC removal from feed stream. To compare DIC removal for each fabricated membrane, the feed stream operating conditions were kept constant (flowrate: 1000 ml/min, temperature: 23 °C, pressure: 0 psig, and pH: 2.5). The amount of DIC captured by the WWCCS was monitored by permeate-side conductivity measurements during each trial. Tested membranes were stored for further morphological investigation.

A comparison between two samples of pure PVDF and PFA membranes for DIC removal is shown in Figure 3.5. The pure PVDF membranes enhanced the DIC removal from the feed stream by 425%. According to the DIC concentration in the US wastewater (section 2.4.5), WWCCS using pure hydrophobic PVDF

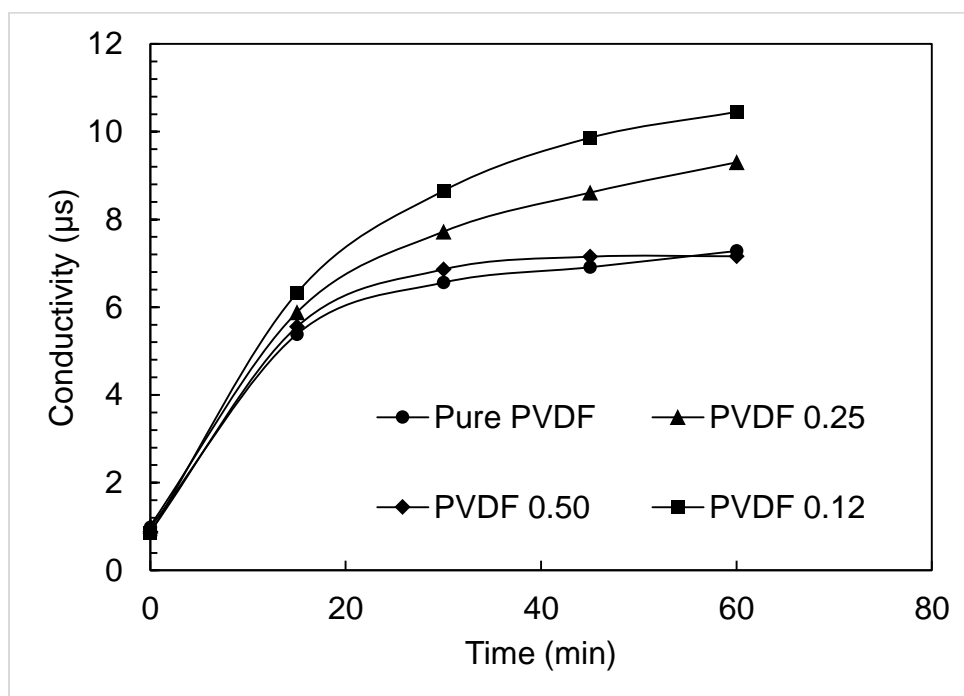
membranes would remove up to 135.24 Mt-C/yr from the US wastewater which is equivalent to 2.6% of the total US CO<sub>2</sub> emissions.



**Figure 3.5:** Percent DIC removal using commercial PFA membranes versus fabricated pure PVDF membranes. S1 and S2 indicate membrane samples from individual fabrication processes.

Mixed matrix membranes with three different ZnO (10-30 nm) concentrations were fabricated and used in WWCCS. The conductivity measurements for these three samples is shown in figure 3.6. According to the results, adding ZnO nanoparticles to polymer matrix increased the permeate side conductivity which is used as an indication of increase in DIC removal from feed stream. The highest measured conductivity was recorded using PVDF 0.12 in WWCCS. ZnO nano particles disrupt the polymer chains in the membrane and increase the free volume in the polymer for diffusion of CO<sub>2</sub> molecules. However, the permeate side conductivity decreased by increasing the ZnO content from 0.12 wt% to 0.50 wt%. this could

be explained by the rigidification of polymer chains around the filler particles [52], pore blockage by the polymer chains [53], and/or the aggregation of filler particles [54]. More specific conclusions would require membrane morphology analyses such as SEM and TEM.



**Figure 3.6:** Permeate side conductivity measurements using mixed matrix membranes.

## Chapter 4: Conclusions and Future Work

### 4.1 Conclusions

The main goal of this study was to provide proof-of-concept that removal of DIC from wastewater results in net-negative carbon emission and has the potential to provide meaningful removal of CO<sub>2</sub> from the global carbon system. The WWCCS was able to successfully remove up to 15% of DIC from the feed stream in the best-case scenario. One of the main positive points in this system was the elimination of energy and emissions from use of electricity for running the pumps and heating the feed. As a result, the WWCCS could potentially remove 88.2 Mt of inorganic carbon from the US wastewater streams.

A comparative cradle-to-gate LCA of WWCCS showed that the HCl production unit has the largest contribution to GWP and AP indices. Therefore, the CO<sub>2</sub> emissions caused by WWCCS was significantly affected by changing the feed stream pH from 6.3 to 2.5. Based on captured versus released CO<sub>2</sub>, the WWCCS can operate as negative CO<sub>2</sub> emission system at pH values lower than 4.2. A comparison between WWCCS and DAC systems showed a sufficient amount of DIC could be captured at feed stream pH of 2.5, which is comparable with more mature NETs such as DAC.

A porous hydrophobic PVDF was fabricated using the phase inversion technique and used in the bench-scale WWCCS. Compared to the commercial PFA membranes, the PVDF membranes significantly increased the DIC removal from the feed stream by 460%. Employing ZnO nanoparticles in PVDF polymer matrix

increased the membrane efficiency and removed 10% more DIC from the feed stream than the PVDF alone.

#### 4.2 Future Work

In this study, the effects of multiple physiochemical parameters on DIC removal, as well as the membrane modification to enhance the DIC removal efficiency, were investigated. Future studies can follow the existing project in two main directions.

Setup efficiency and configuration can enhance the ability of the WWCCS to remove and capture more DIC from waste streams. A hollow fiber membrane module would increase the interface area between feed and permeate sides and result in more captured DIC. Implementing multiple WWCCS in series and/or parallel with countercurrent flow in a closed system would maximize the driving force across the membrane. Although pressurizing the feed stream would be an energy intensive option for WWCCS, an optimized pressurized feed stream would create a substantial pressure gradient across the membrane and results in more DIC removal. Further investigation are needed to understand the tradeoff between added energy by pressurizing the feed and an increase in DIC removal. WWCCS also has the potential to be implemented in oceans, where CO<sub>2</sub> extraction from a greater source could have greater impacts on the global carbon cycle. In this scenario, to eliminate the energy intensive processes (e.g. pumping), co-location with desalination plants or using carbon-free electricity would likely be required.

Membrane modifications such as implementing nanoparticles in polymer matrix, facilitated transport membranes, the use of nanocomposite membranes, or

employing a CO<sub>2</sub> selective support layer would increase the membrane physical properties and removal efficiency. Common challenges in this area could be membrane wetting and membrane fouling. Applying an electrically conductive layer that generates an electrostatic repulsive force may prevent negatively charged foulants from attaching to the membrane surface. Hydrophilic coatings such as chitosan could decrease the chance of membrane wetting by low surface tension contaminants such as oil, alcohol, and surfactants.

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