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Utilization of Electrodeionization to Separate and Concentrate Cellobionic and Gluconic Acid

Andie Veeder

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Andie Veeder, Undergraduate Researcher

Dr. Jamie Hestekin, Faculty Research Mentor, Department of Chemical Engineering

University of Arkansas

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Abstract

Biofuel production is currently an expensive and inefficient process with many drawbacks. It is water and land intensive, competes with food production, and requires large energy inputs decreasing its relative sustainability. This paper explores the use of electrodeionization (EDI) to improve the biofuel process by separating and concentrating large, organic sugar acids that are important materials for the production of bioethanol. An EDI device was assembled for the purpose of separating and concentrating gluconic, cellobionic and lactobionic acid. Several trials were conducted and samples were analyzed to determine the success of this experiment. The results for the separation and concentration of gluconate were slightly successful, seeing a complete depletion of gluconate in the dilute stream and an increase from 0 g/L to 0.92 g/L of gluconate in the concentrate stream. It is hypothesized that gluconate was lost to the rinse streams, since there is about 2 g/L of gluconate unaccounted for. The results from the lactobionic acid trial were inconclusive due to equipment failures and contamination of samples. Future steps will be taken to improve the overall process of electrodeionization, and figure out how different combinations of important variables can achieve the greatest level of separation and concentration of large molecules.

Background

Biofuels

Biofuels are renewable fuels produced from organic matter such as crops, algae, and waste. They have recently gained popularity due to their lower carbon footprint and potential to reduce reliance on fossil fuels. However, like any fuel source, biofuels have their advantages and disadvantages.

The most positive aspect of biofuels is that they are renewable. Unlike fossil fuels, which are finite, biofuels can be produced indefinitely as long as there is a steady supply of organic matter. They also produce significantly lower amounts of greenhouse gas emissions compared to fossil fuels. While burning fossil fuels releases carbon that has been sealed away for millions of years, biofuels are produced from organic matter that has recently absorbed carbon from the atmosphere. As a result, using biofuels can help to reduce overall carbon emissions. Also, many countries already have a steady supply of organic matter that can be used to produce biofuels, therefore, biofuels can be produced locally, reducing reliance on imported fossil fuels and promoting energy independence [1]. The biofuel industry also has the potential to create jobs in farming, production, and distribution; this would have major positive economic effects on local communities. Finally, biofuels produce fewer air pollutants, which can lead to improved air quality and better respiratory health for people living in areas with high levels of air pollution [1].

On the other hand, there are some drawbacks to biofuel production. One of the biggest criticisms of biofuels is that they can require large amounts of land and water to produce. This can lead to deforestation and change in land use, which can have negative impacts on biodiversity and ecosystems. Their production can also compete with food production, leading to

higher food prices and potential food shortages. With them being fairly water-intensive, it can lead to competition for water between different sectors, like agriculture and urban use [2]. This also leads to an incentive for farmers to grow crops for biofuel production instead of food, which can exacerbate this problem. Lastly, the production of biofuels requires energy inputs, such as the use of fossil fuels for transportation and processing [2]. The energy required to produce biofuels can sometimes be greater than the energy they produce, which can reduce their overall sustainability. All of these factors are important to consider when evaluating the overall potential of biofuels to be a sustainable energy source.

Bioethanol is a type of biofuel that is produced by the fermentation of sugars or starches derived from biomass, such as corn, sugarcane, or wheat. The process of producing bioethanol typically involves five steps, 1) preparation of the feedstock, 2) conversion of the sugars or starches to glucose, 3) fermentation, 4) distillation, and 5) dehydration [3]. After the biomass is harvested, it must be processed to extract the sugars or starches that will be fermented to produce ethanol. Then, through a process called saccharification, enzymes break down the sugars and the starches into glucose [3]. After that, the glucose is then fermented using yeast or other microorganisms, converting it into ethanol and carbon dioxide. Next, the resulting mixture of ethanol and water is then separated through distillation, where the ethanol is evaporated and then condensed to be collected as a liquid [4]. Lastly, the ethanol is further purified through dehydration to remove any remaining water to get the highest purity ethanol possible.

Electrodeionization

Electrodeionization (EDI) is popularly used as a water purification technology that utilizes an electric field to remove impurities from water. It encompasses a combination of ion

exchange and electrodialysis technologies, and has been increasingly used due to its efficiency and ability to produce high-quality separations.

In general, it works by passing water through an ion exchange resin that has an electric field applied across it. The electric field causes the ions in the water to migrate towards electrodes of opposite charge, where they are removed. This process is known as deionization and helps reduce the levels of minerals, dissolved solids, and other impurities present in the solution [5]. The EDI process typically includes several steps, including pretreatment, ion exchange, electrodialysis, and polishing. Pretreatment is necessary to remove any large particles that could foul the ion exchange resin [6]. In the ion exchange step, the water is passed through resin beds that selectively remove ions based on their charge and size. The electrodialysis step applies an electric field to remove any remaining ions [7]. Finally, the polishing step removes any remaining impurities to produce the highest-quality water possible [7] [8] [9].

Ion exchange is a separation process that involves the exchange of ions between a solid phase (resin) and a liquid phase (solution) [10]. It is the key difference between electrodeionization and electrodialysis. In ion exchange, a resin is used to selectively remove or recover ions from a liquid solution based on their chemical properties. The resin is usually composed of small beads or particles with a high surface area that are functionalized with specific chemical groups that can selectively bind certain ions [10]. When the resin is brought into contact with a solution containing ions, the ions will diffuse into the resin and exchange with the ions already present in the resin. The ion exchange process can be either cation exchange (removal of positively charged ions) or anion exchange (removal of negatively charged ions), depending on the type of resin used. It also allows for the separation of much larger molecules, which electrodialysis cannot separate. This technique is desirable because ion exchange can be

highly selective, allowing for precise control over the separation of specific ions. It is also easily scaled up or down depending on the application, making it suitable for both small and large-scale processes [11]. The resins can also be regenerated and reused, making it cost-effective and sustainable for a continuous process.

Electrodeionization can further be used to concentrate desirable ions. Because the resin beds are separated by semi-permeable membranes that allow the passage of ions, but prevent the passage of larger molecules and particles, this technology can be used strategically to isolate particular ions. Depending on if cations or anions are needed as a final product, the EDI can be designed to isolate a particular ion from the feed. As these ions migrate through the resin beds, they are exchanged for other ions with opposite charge that are bound to the resin [10]. This process continues until the ion concentration has reached its desired level, or maximum potential. While in water purification, these ions are seen as a byproduct and part of a waste stream, there is an advantage to being able to separate these ions and concentrate them using the ion exchange resin to get ions that are necessary for other process, like biofuels.

Introduction

The main drawback of the biofuel production process is that currently it is very expensive and inefficient. It is possible that by utilizing techniques in the lab, like EDI, to concentrate the large organic sugar acids that are used to produce biofuels, the overall sustainability of biofuels can be improved and scaled to a reasonable size to make them a reliable source of fuel for the rest world. Less biomass would have to be harvested if EDI is exploited to increase the initial concentration of these desirable ions by using ion exchange resin beds.

A preliminary experiment was conducted at the University of Arkansas to utilize EDI in order to separate and concentrate large organic sugar acids that are important for the production of bioethanol. The EDI was designed to acidify potassium cellobionate and generate sodium hydroxide in the dilute stream. Figures 1 & 2 show that during the experiment, cellobionate was transported from the dilute stream to the concentrate stream, and sodium ions were generated in the dilute stream.

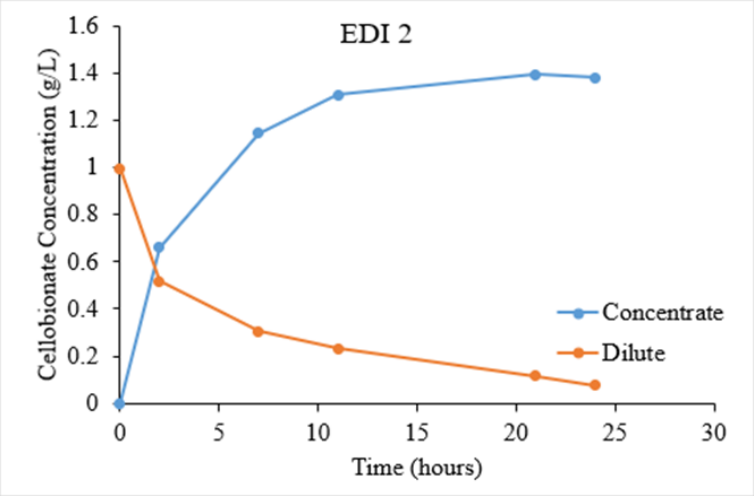

Figure 1. Cellobionate Concentration vs. Time

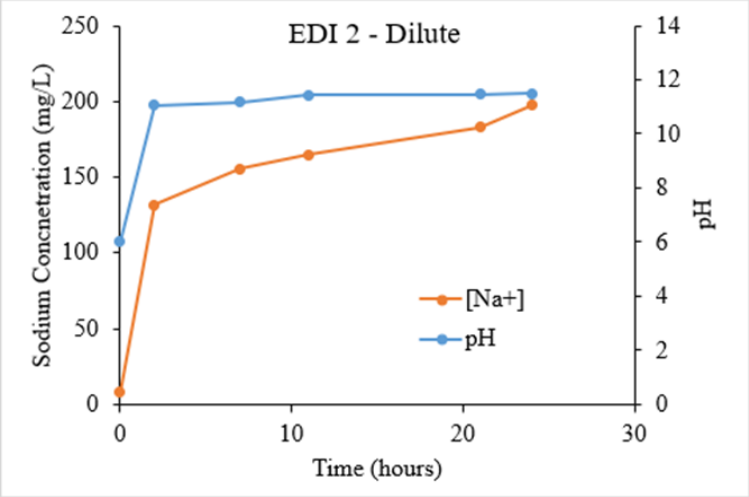

Figure 2. Sodium Concentration vs Time

These findings confirmed that the EDI was able to separate these ions and concentrate cellobionate from 1 g/L to almost 1.4 g/L. Once the feasibility of this process using EDI was confirmed, the next steps included figuring out what parameters should be changed to increase the separation and concentration of the desired ions, and what the size range of ions was that can be involved in this process.

Research Objectives:

The goal of this project was to explore the technique of electrodeionization for the use of separating and concentrating large, organic sugar acids. Gluconic acid and lactobonic acid are the two molecules that will be focused on throughout the duration of this process. I also wanted to become familiar with the experimental process, and learn how to prepare, set-up, and run an experiment by myself. It was important to plan out what samples needed to be taken, when they needed to be taken, and how much needed to be taken. I also wanted to understand what measurements were being taken for the samples, and what they tell us about the experiment. While I wanted to see successful data come out of these experiments, my main goal was to become confident in the research process and understand the steps taken to run these experiments.

Methodology

The EDI device can be designed in a variety of ways depending on what ions are being separated and how their individual properties will react within the system. The EDI used in this experiment was designed with multiple compartments separated by ion-exchange membranes and a resin wafer in the center, which helps overcome mass transfer limitations. The resin wafer

used in this experiment was composed of Amberlite IR120+ Na+ (which is a cation exchange resin), Amberlite HPR 4200 Cl- (which is an anion exchange resin), and low-density polyethylene. As seen in Figure 3, there are four inlet streams and four outlet streams within the device. Electrodes are placed on the extremities of the device so they can be hooked up to a machine that applies a constant electric current to the process.

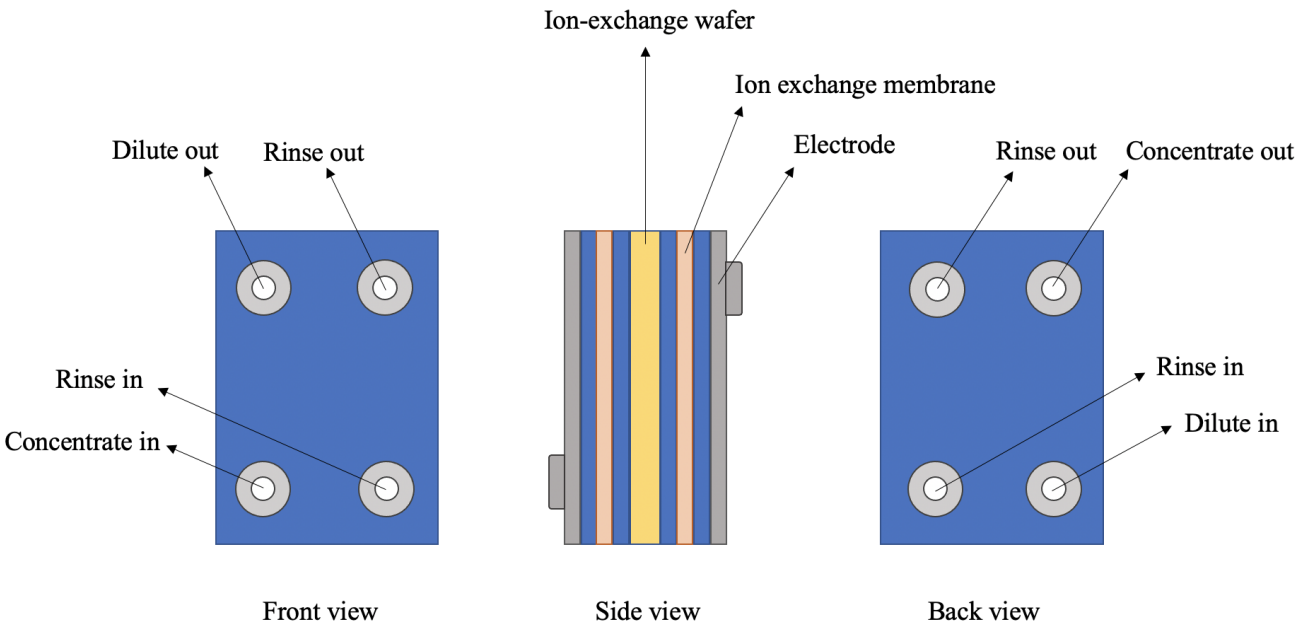

Figure 3. EDI Schematic

The device is assembled using small amounts of E6000 glue; it is placed in between every layer of the device, including the cation exchange membranes (CMX), anion exchange membranes (AMX), electrodes, rubber inserts, and plastic inserts to increase the structural integrity of the device. It is very important when assembling the device to make sure every section is positioned the right way, and lined up perfectly. If not, the solutions entering the device will not go to the right place, and it could cause a blockage or alter the results of the experiment.

Once everything is glued together, six screws are used to hold the layers together, and a 5-lb weight is placed on top of the device to ensure a tight seal as the glue dries. If there are any places where the glue does not adhere well, it could cause a leak when running the experiments, and the device will have to be completely disassembled and reassembled again. Figures 4 and 5 show the EDI device before and after it is assembled.

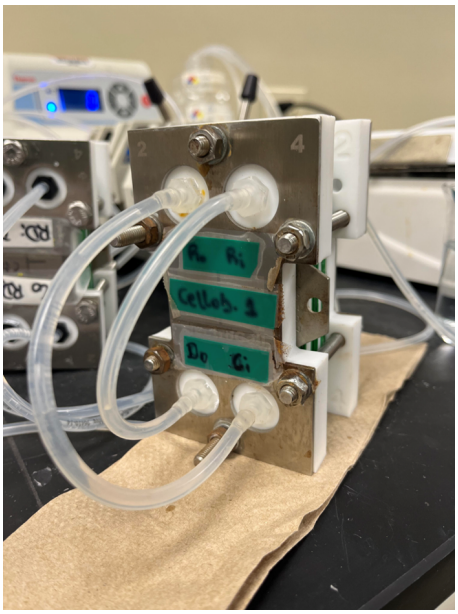

Figure 4. EDI Device Assembled

Figure 5. EDI Device Disassembled

Once the glue has thoroughly dried and it is ready to be used, tubing is connected to all four inlets and four outlets: inlet streams are situated to a pump that circulates the desired solutions, and each outlet stream is placed back into the original solution to be reused. Figure 6 shows the experimental setup with the pump situated in the middle.

Figure 6. Experimental Setup

In this experiment, the concentrate and dilute streams contain gluconic acid that is to be separated into gluconate, and the rinse streams are a solution of sodium sulfate. Before running the experiment, the EDI device is flushed with deionized water to wet the membranes and flush

out the system. After that, the tubes are placed in their respective containers and the solutions begin circulating. Next, cables are used to connect each electrode to a power supply, where a constant current of 0.02 A is applied to the device, as shown in Figures 7A and 7B. Through this applied current, positively charged ions and negatively charged ions are separated into their respective chambers after passing or being rejected by the ion-exchange membranes.

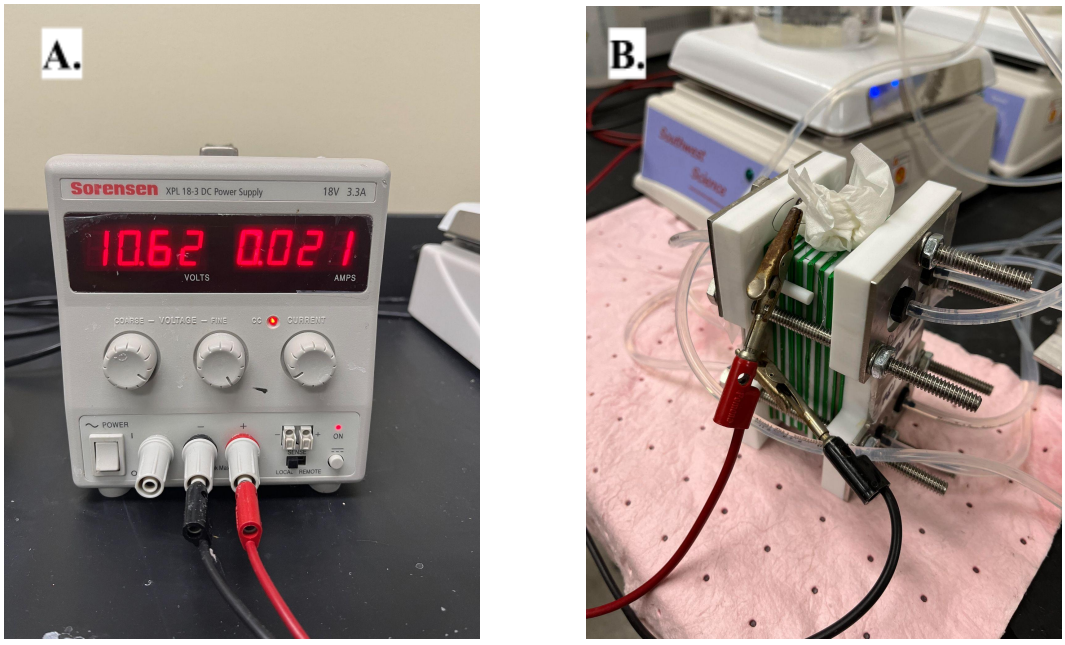

Figure 7. Power Supply

The device was allowed to run for 10 hours, with samples being taken at 0, 5, and 10 hours of each stream. The pH, conductivity, and temperature were measured and recorded for each sample after it was taken.

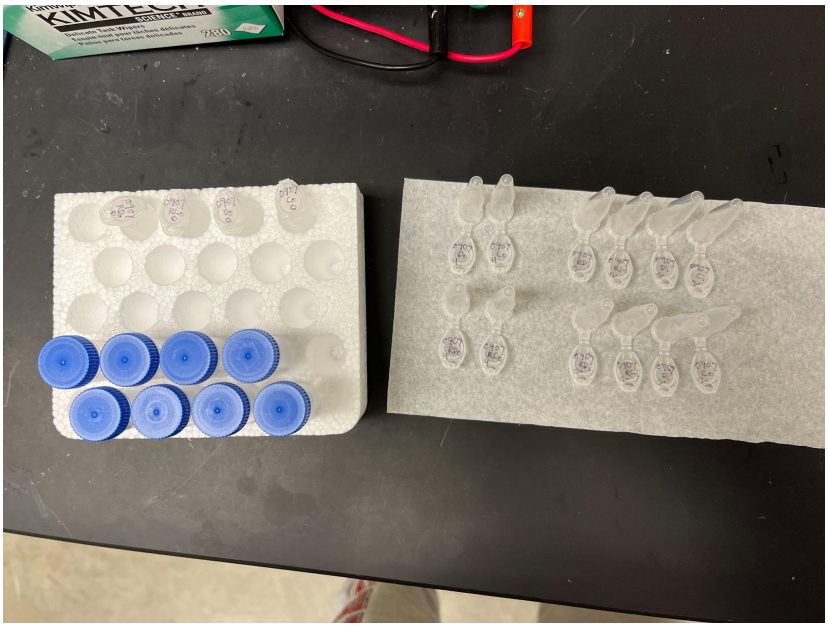

Figure 5. Prepared Samples

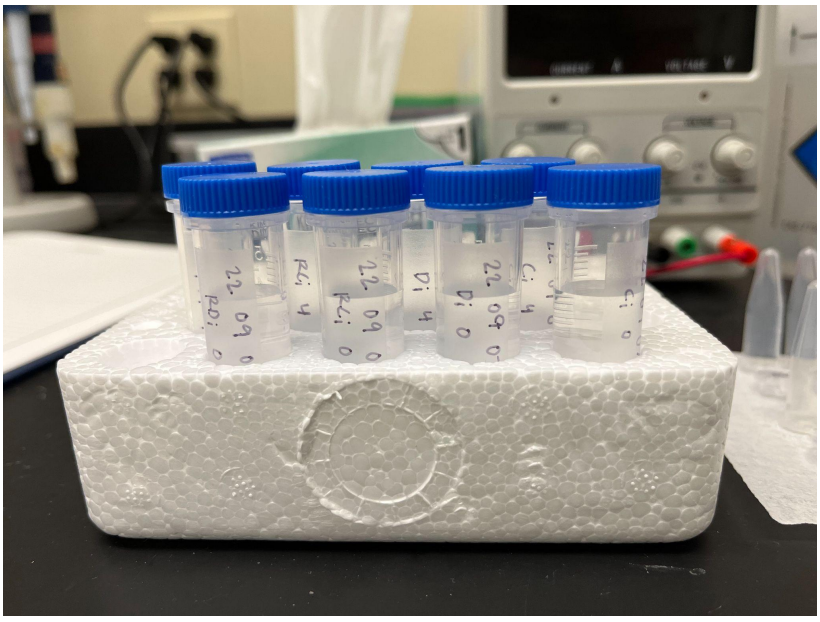

Figure 9. Gluconic Acid Separation Samples

Results:

Three trials of the gluconic acid experiment were conducted, and after the samples were collected, they were sent to the University of Califonia, Davis to have their compositions analyzed. Table 1 and Figure 8 show the average concentration of gluconate in the dilute and concentrate stream over the 10-hour period.

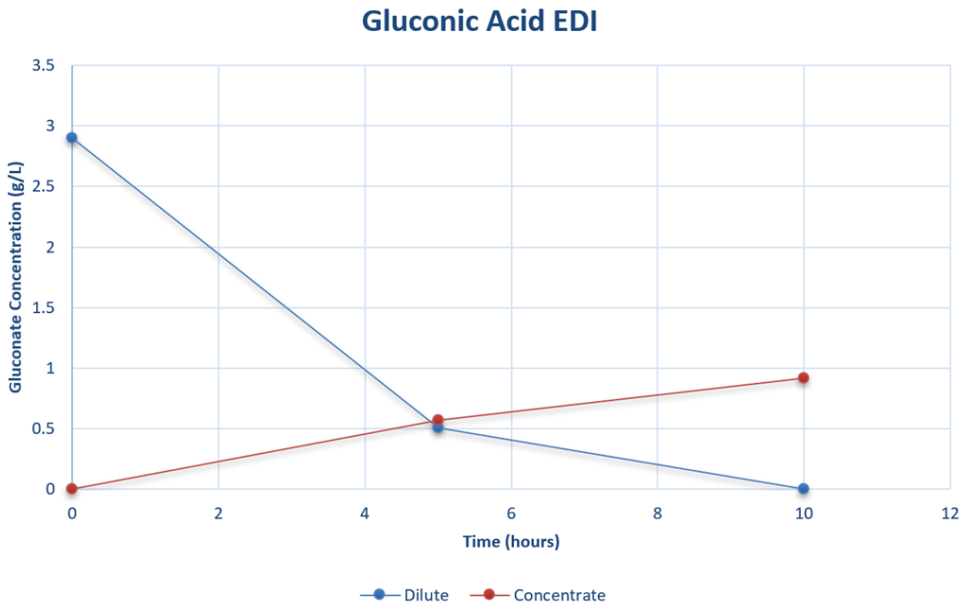

Figure 10. Gluconate Concentration vs. Time

Time (hours)	Gluconate Concentration in Dilute Stream (g/L)	Gluconate Concentration in Concentrate Stream (g/L)	Glucose Concentration in Dilute Stream (g/L)
0	2.9005	0	3.9898
5	0.5063	0.5703	2.1152
10	0	0.9171	2.3244

Table 1. Concentration of Gluconate in Dilute and Concentrate Streams

Conclusion:

As seen in Table 1, the concentration of gluconate starts around 2.9 g/L in the dilute stream, and diminishes to 0 g/L after the 10 hours. As expected, the gluconate travels to the concentrate stream, where it increases from 0 g/L to 0.92 g/L after 10 hours. The results confirm that the gluconate anion was separated successfully over the course of the trial. However, since the concentration of gluconate fell from 2.9 g/L to 0.92 g/l, it can not be said that it was concentrated. The remaining gluconate must have been lost to the rinse streams duing this process and did not end up in the concentrate as hoped. This could have been because of several factors: the anion and cation exchange membranes were not fully successful at allowing and blocking the ions they needed to, the ion exchange resin wafer did not allow all the gluconate to pass through to the concentrate stream, there was a leak in one of the layers of the EDI where gluconate was lost to the rinse stream, etc. It is important to note these potential shortcomings and adjust accordingly for future experiments.

After running all the trials for the gluconic acid experiment, there were a few adjustments that I would have made for future trials. First, there were not enough samples taken. Instead of

taking only 3 samples at 0, 5, and 10 hours, there should have been samples taken every 2 hours, so 0, 2, 4, 6, 8, and 10 hours. This would produce a much more useful graph and allow for more statistical analysis to be done. It also could have possibly given us a better picture of where the gluconate was being lost to the rinse streams, and at what time the concentration dropped the most. The duration of 10 hours worked well though, because after 10 hours there was no gluconate left in the dilute stream which is the goal for these trials.

Unforeseen problems occurred when running trials for lactobionic acid. During 3 different occasions, the pump malfunctioned after about 5 hours, eating up the tubing connecting the concentrate stream to the EDI. It is hypothesized that one of the levers holding down the tubing for the pump became loose after a couple hours of shaking, and then caused the tubing to get sucked up into the machine because it was not properly secured. This prevented the solution from being circulated throughout the EDI and causing the results to be skewed. The issue was not caught early enough to be fixed quickly, so all 3 of those experiments were thrown out and not analyzed.

After the second round of trials had been run and samples were taken, orange specs were seen floating around in the samples after a few days. It is unknown where the particles came from, but the samples had been contaminated by another chemical at some point in the process. Because the solution had been constantly agitated from the beginning, these particles were not observed initially. It was not until the samples were allowed to rest for a few days that they were spotted. The unknown compound could have come from several places. A few possible sources of contamination include the original flask used to hold the lactobionic acid solution, the tools used to measure the lactobionic acid powder, the stir rods, tubing, beakers holding the dilute, concentrate, and rinse solutions, etc. Due to the contamination, the samples could not be

analyzed because of the unknown variable and how it would affect the results. In the future, all possible sources of contamination need to be properly cleaned and disinfected to avoid this problem.

Future Steps:

In the future, research could be done with several other large, organic sugar acids. The more we know about how these large molecules can be separated the more possibilities are unlocked. The ion exchange resin used in electrodeionization is a fairly new technology, and its limits are still being tested. This is likely the key to unlocking the separation of these large molecules that cannot be separated using traditional techniques. It is also desirable to determine the maximum separation level that these molecules have, so a known range can be documented for future experiments.

There are also endless combinations of electric current, anion and cation exchange membrane material, ion exchange resin, and EDI device layout that could be tested to see the potential of this experiment. Each of these variables needs to be tested against the others to see how they affect the level of separation achieved, and if they change any important factors. This process is highly adaptable and can be configured in multiple ways to achieve different results depending on the desired output. The chosen layout for the EDI device used in this experiment is not the only way to configure the device, and different combinations of device layouts should be tested to find the best configuration.

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