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ARSENIC REMEDIATION OF MAINE DRINKING WATER

by

Austin Steward

A Thesis Submitted in Partial Fulfillment
Of the Requirements for a Degree with Honors
(Biomedical Engineering)

The Honors College

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May 2019

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ABSTRACT

Arsenic, a metalloid, is one of the most prominent toxins in Maine drinking water. There are approximately 86,500 Maine citizens exposed to water containing arsenic over the maximum contamination level causing adverse effects including nausea, multiple cancers, and a reduction of full scale IQ and executive function. In drinking water, arsenic arises both by the natural leaching from bedrock and from the use of chemicals such as pesticides, embalming fluids, and wood preservatives. Although there are many known arsenic water remediation techniques, finding a method compatible for multiple arsenic isotopes is challenging. In this work, we test the low-energy and low-cost technique coupling ferric chloride pre-treatment coagulation with liquid-gated membrane filtration. We find that flocs are formed under specific conditions and can be filtered out of the water, bringing the arsenic with it. We were additionally able to determine the size of these particles using dynamic light scattering and associated pH changes during pre-treatment steps. This work provides evidence that liquid-gated membrane filtration can be used to effectively filter out arsenic containing flocs. These experiments lay the groundwork for a new approach to arsenic remediation of Maine drinking water using membrane filtration, in a low-cost, self-cleaning system.

ACKNOWLEDGMENTS

I would like to take this opportunity to acknowledge everyone who has played a critical role in the actualization of this Honors Thesis. I would like to start by acknowledging my Advisor Dr. Caitlin Howell, without whose support this project may have never existed and without her constant guidance would not have manifested as the thesis it is today. I would like to thank Jonathan Overton for being a role model and a guide when I first entered the world of student research, and for training me on membrane filtration. Also I would like to extend my appreciation to the entire Howell Lab group who has provided feedback and guidance across many presentations and iterations for the past two years; especially Chloe Lilly for helping me with the faucet.

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INTRODUCTION

As early as 1993, the World Health Organization recommended that the Maximum Contamination Level (MCL) for arsenic (As) in drinking water should be lowered to 10 µg/L, but it wasn't until 2001 that the United States officially lowered the MCL from 50 µg/L[1]. In comparison iron (Fe) and magnesium (Mg) have current MCLs of 200 µg/L and 50 µg/L respectively, despite the fact that arsenic has a 100 times higher cancer risk than any other water contaminant with an MCL. Today, approximately 13 million US citizens are exposed to drinking water over the 10 µg/L limit[2].

Studies conducted on Maine wells have determined there is still much improvement to be made in the way of our water remediation methods and drinking water quality. Bedrock wells account for providing water to nearly 50% of Maines population with 12-13% of those same wells having a MCL over 10 µg/L [3]. Looking particularly at the watershed in Northport, Maine, studies were conducted to make conjectures about Maine and overall New England water quality. When looking at both bedrock wells and drift wells, bedrock wells were found to have higher contamination levels with a greater variance, whereas drift wells consistently had contamination levels below the MCL and a lower variance. The study found 69% of all bedrock wells tested exceeded the MCL and one cluster of bedrock wells that had an arsenic contamination level of 1810 µg/L. This finding, combined with studies of soil components in correlation to water contamination, concluded that most arsenic levels in Maine are naturally occurring from the bedrock and not human influence. Additionally this study found no correlation between the concentration of arsenic in the bedrock and that of the water, suggesting that hydrologic controls such as pH, reduction potential, temperature, and flow rate come into play. To this end, samples taken upgradient had a much lower concentration of arsenic then those taken downgradient in the watershed.

Over 50 towns in the state of Maine were found to contain private wells with an arsenic level of 100 µg/L, with the highest concentration at 3,000 µg/L [4]. Bedrock wells provide water to nearly 50% of Maine's population, with 12-13% of those same wells having a MCL over 10 µg/L. In other words, roughly 86,500 Maine citizens are currently exposed to unacceptable drinking water quality[3]. Another study conducted with Maine school-aged children examined the neurological effects from consuming drinking water contaminated with arsenic. The data collection included in home interviews of parents and children, as well as test results for full scale IQ and Wechsler Preschool and Primary Scale of Intelligence. During analysis, adjustments were made for maternal education and IQ, the particular school district, and the number of children in the household. For the children exposed to a water arsenic concentration of above 5 µg/L there were significant reductions in full scale IQ (5-6 points), working memory, perceptual reasoning, and verbal comprehension[5]. There was no significant difference in the study of water concentrations above 5 µg/L, or those below, effectively making it a threshold. In adults (above 30) with a mean water arsenic concentration of 6.3 µg/L, there was a reduction in cognitive skills, processing speed, executive function and memory[5]. Considering the prevalence of arsenic contamination in Maine, and the absence of predictive measures, the availability and effectiveness of arsenic remediation technology is of upmost importance[3].

OBJECTIVE

Previous results suggest that a two-step system of pre-treatment followed by membrane filtration would yield the most effective results[6–9]. Nano- and ultra- filtration with membranes had success of arsenic removal without any required pretreatment, removing effectively 100% and 50% As(V) As(III) respectivly[6]. However, with micro filtration membranes a pretreatment of ferric chloride ($FeCl_3$) was used create arsenic complexes prior to filtration. In the literature, these complexes were able to be successfully removed and remained intact over a pH range of 6-9. The experimental design outlined below is based on the optimal conditions stated in the aforementioned literature, tested on a range of 0-25 mg/L ferric chloride with 0.1-1.2 μm filters[6]. In addition to this pretreatment process the samples will be filtered via micro filtration with filters altered with a liquid gating. Adding a liquid-gating layer to membranes can alter the properties of flow through them and have applications in improving filtration[10].

In this experiment there were three main questions to be answered. First we wanted to find out how much arsenic could be removed from water pretreated with coagulant and filtration via a 1 μm membrane, compared to the same membrane that was treated with a fluorinated gating liquid. Secondly, we wanted to quantify the volume of water that could be filtered through treated and untreated membranes, both in samples that had pretreatment with coagulant and those that had not, over a set period of filtration. Lastly, we wanted to measure the size of the complexes remaining in arsenic doped water post filtration. The accumulation of these results will allow us to determine the efficiency of our system and optimize our filtration conditions, resulting in an improved, scalable arsenic remediation technique for Maine drinking water.

While there is a real need for this technology in Maine as well as a potential for significant positive impacts on its communities, the applications stretch far beyond. Arsenic contamination is a problem globally, and as commercial usage of chemicals increases so does the risk of a major contamination of our limited drinking water resources. On an even larger scale, if NASA were to discover water sources on other planets there is low probability that it would be naturally safe for consumption. Having technology that is easily transportable while also low-cost and energy efficient would be of the upmost importance for human longevity in any such atmosphere.

LITERATURE REVIEW

Arsenic can have a multitude of effects on the human body including, physical and mental, short and long term, as well as immediate and delayed. Which effects ultimately manifest, hinges upon an individual's rate of exposure. Most commonly health effects can be classified as either acute or chronic. Acute arsenic exposure is caused by ingesting large quantities over a short period of time. High dosages are in the range of 0.04 mg/kg/day (or higher), with effects such as stomach pain, nausea, shock, coma, and in severe cases even death, though these effects are usually reversible[11]. Chronic arsenic exposure is defined as consistently ingesting contaminated water over a large exposure period. The effects of chronic exposure are not typically reversible, and can include hypertension, diabetes mellitus, as wells as cancer or diseases of the lungs, bladder, kidneys, liver, uterus, and skin. Skin lesions have been observed with a small of a range as 5-10 µg/L, as the skin is particularly sensitive[11]. All living organisms have slightly different metabolic pathways for metabolizing arsenic, but a general pathway is as follows: phosphate transporters uptake arsenic, As(V) is reduced to As(III) via arsenate reductases, and then finally As(III) is either extruded from or sequestered within the body[11]. Figure 1 illustrates the various mechanisms by which arsenic can enter the body, and be transformed as well as excreted.

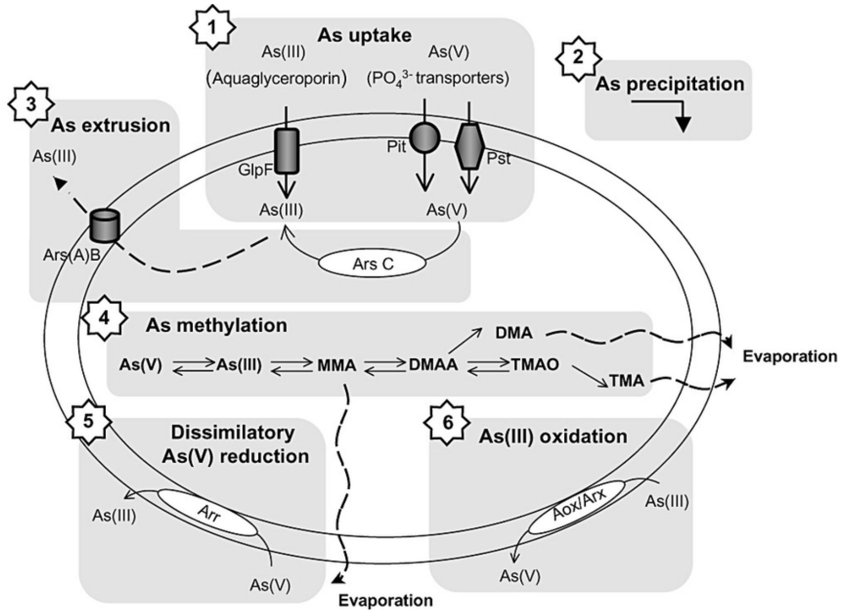

Figure 1: Arsenic pathways entering/in/exiting the body [10].

In studies conducted with inorganic arsenic, it was found there was no methylation threshold i.e. no limit to how much arsenic can be consumed before methylation can no longer detoxify it. Rather, the opposite was found to be true: the methylation process increases the carcinogenic effects of arsenic. Genotoxic effects were measured in the tissues of subjects after consuming 50 µg/L of arsenic contaminated water. The mortality rate for 50 µg/L of arsenic was found to be as high as 1/100, and as high as 1/10 for 500 µg/L [1]. Table 1 shows, the approximated cancer risk for various levels of arsenic exposure (assuming chronic exposure).

Table 1: Cancer Risk correlated to As levels in water. For reference, 1 ppb is equivalent to 1 μg/L [1].

Arsenic Level in tap water and cancer risk	Reproduced from Ref [1]
Arsenic Level in tap water (ppb)	Approximate total cancer risk (assuming 2 L consumed/day)
0.5	1 in 10,000
1	1 in 5,000
3	1 in 1,667
4	1 in 1,250
5	1 in 1,000
10	1 in 500
20	1 in 250
25	1 in 200
50	1 in 100

When talking about arsenic it is important to consider how it appears naturally in the water that is being studied. Dissolved arsenic molecules have a size of approximately 150 Daltons. In a pH range of 5-8 the two isotopes of arsenic usually appear as anionic Arsenate [As(V)] and neutral Arsenite [As(III)]. These isotopes react differently with the body, as well as with remediation techniques. Most commonly an oxidized form of As(V) is found in groundwater[6]. Once consumed by the body, As(V) typically cuts off the bodies processes that act to generate energy, while As(III) inhibits protein function, respiratory processes, and forms free radicals which can cause gene damage[11]. With remediation techniques As(III) filtration is typically more successful within a neutral pH range, while successful filtration of As(V) typically requires the water to be raised to a higher pH for remediation but then lowered again before consumption is possible.

The particular arsenic remediation methods examined in this literature review are; nano zero valent iron filtration binding, ferruginous manganese ore filtration binding, and membrane filtration including $FeCl_3$ as a flocculent.

Nano Zero-Valent Iron Binding Flocculation

One common method used for arsenic remediation of drinking water is flocculation using Nanoscale Zero-Valent Iron (nZVI)[9,12]. Due to an average size smaller than 30 nm [9], these nanoparticles they can be suspended in aqueous solutions with behavior similar to colloids and as size decreases, the surface area of intractable particles in the suspension increases. In general, nanoparticle technology aims to hit four main factors when working with polluted water sources: a high level of reactivity with contaminants, mobility of the source through the media, a significant reactivate longevity, and a low toxicity effect on the source[12]. The application of nZVI to remove toxins from drinking water is usually on a large scale involving an injection of the aqueous suspensions into the underground aquafers and wells of a town or city.[12]

Costs associated with nZVI are correlated with the adjustments required for each specific location[12]. Technicians gather samples of water to determine the ratio of nZVI that should be injected, and determine its duration at that location. Additionally, environmental impact plays a role in these determinations; in locations that have a high mobility range of water and contaminants, a lower mobility nZVI species is selected and vice versa[13]. These determinations are conducted through lab-bench testing and serve to prove that nZVI could be used even when scaled down, and potentially into water filters. A component of these laboratory analyses is a determination of the size of nZVI molecules to use. Borohydride reduction with ferrous salts generates particles on the scale of 10-1000 nm limiting applications due to potential agglomeration as well as the costly reagents necessary to achieve such sizes. Filtering particles by size is important in determining the optimal reactivity-to-longevity ratio. The smaller in size these particles are the larger the surface area as a whole there is, increasing reactivity but reducing longevity. In large-scale usage the balance between effective contamination treatment, and minimal maintenance is critical[12].

When the nZVI particles are introduced to water, dissolved oxygen and water are the primarily components readily available for corrosion reactions[14]. A primary product of these reactions is Fe^{2+}, which can further undergo oxidative transformation, as:

$$2Fe^0{}_{(s)} + 4H^+{}_{(aq)} + O_{2(aq)} \rightarrow\ 2Fe^{2+} + 2H_2O_{(l)} \quad E^0 = +1.67\,V \qquad (1)$$

$$2Fe^0{}_{(s)} + 2H_2O_{(l)} \rightarrow\ 2Fe^{2+} + H_{2(g)} + 2OH^-{}_{(aq)} \quad E^0 = -0.39\,V \qquad (2)$$

$$2Fe^{2+}{}_{(s)} + 2H^+{}_{(aq)} + \tfrac{1}{2}O_{2(aq)} \rightarrow\ 2Fe^{3+} + H_2O_{(l)} \quad E^0 = +0.46\,V \qquad (3)$$

$$2Fe^{2+}{}_{(s)} + 2H_2O_{(l)} \rightarrow\ 2Fe^{3+} + H_{2(g)} + 2OH^-{}_{(aq)} \quad E^0 = -1.60\,V \qquad (4)$$

Reducing conditions are far from equilibrium, including an induced increase in pH. Arsenic and heavy metals are treated by nZVI via surface reactions with particles, leaving them in an immobile state[15]. In these large scale situations there is no way for the nZVI and immobilized contaminants to be removed from the system, so there is the threat that remobilization of contaminants is possible over time[12,15].

In studies looking into the difference between nZVI remediation of As(III) an As(V), As(III) was found to be removed using 10% of the iron that As(V) systems required[9]. Additionally, it was found that in systems with nZVI, As(V) was reduced down to As(III) within 90 days. At pH levels between 3 and 7 the rates of removal were all above 90%, optimized at a pH of 6.5. After a pH of 7 there was an exponential decrease in removal. Figure 2 illustrates percent adsorption in comparison to different dosages of nZVI for As(V)-doped samples[9].

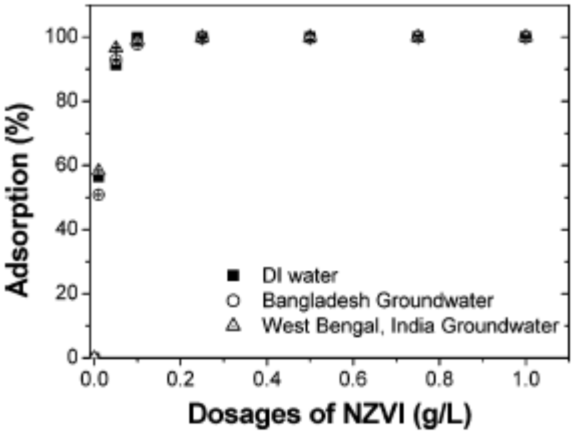

Figure 2: Sorption of As(V) using nZVI for Bangladesh and West Bengal groundwater samples; As(V): 1mg/L in 0.01M NaCl, NZVI: 0.1g/L, pH 7, 25°, reproduced from Ref [9]

Ferruginous Manganese Ore

Ferruginous Manganese Ore (FMO) flocculation is another successful method of arsenic remediation[2,7]. The major mineral phases in FMO are pyrolusite and goethite and once washed with deionized water both phases can be separated into particles sizes of 250, 150, and 75 µm. One major advantage of FMO is its availability and low cost; one metric ton can be obtained for as little as $50[11]. A general process for water remediation of Arsenic is as follows: adding a specific mass of FMO to a beaker of water for remediation, mixing in a wrist mixer for a set time followed by a set rest period, then filtration and analysis of the sample[7].

Various experiments have been conducted to find optimized conditions for the remediation of Arsenic from water[7]. For all phases of arsenic the ideal conditions occurred at 0.2g of 75 µm FMO, 5 minutes of mixing, and 1 hour of rest before filtration. For As(III) the samples were doped to 0.12ppm in 100mL, and for As(V) samples were doped to 0.19ppm in 100mL. These experiments resulted in a 72.58% reduction at pH 6.3 and 72.16% at pH 6.5 removal for As(III) and As(V) respectively. By increasing the FMO amount above 0.2g there was no change in percent removal for As(III) and only a 3% increase for As(V). In further analysis and fitting of isotherms, As(III) was found to have a better removal rate over a pH range of 2-8; even though both As(III) and As(V) can be successfully removed. In these same analysis it was determined that there was no desorption of arsenic from the FMO over the same pH range, leaving a safe residual sludge[7].

Over time As(III) can be oxidized to As(V) by manganese ore [2]. The presence of Ni^{2+}, Co^{2+}, and Mg^{2+} all increased the capability of the FMO to remove arsenic from water[7]. The presumed mechanism is that As(III) reduces the MnO_2 component of FMO to Mn^{2+}; this newly formed cation then generates more adsorption sites for As(V)[2], which can increase the percent absorption of arsenic by up to 14%. In tests performed with well water, all the samples had final concentrations of arsenic significantly below the MCL and some had near 100% removal. In these same samples changes in other contaminant levels were analyzed to determine the safety of FMO for drinking water. There was no change in the concentration of magnesium or manganese, showing that the FMO was not leaching or deteriorating. Additionally, there was a decrease in the iron levels to below the maximum allotted levels, and a decrease in phosphate. Lastly, there was a slight increase in the calcium levels of the water samples still leaving the treated water well below the MCL[7]. As a whole FMO is a promising and inexpensive method of arsenic remediation that is easily adaptable to a small-scale filtering process.

Membrane Filtration

Membrane Filtration has a wide variety of applications ranging from the first to final steps of the remediation processes. In the aforementioned FMO process, membrane filtration is used as a final step to separate the sludge from the water sample[7]. Other experiments have been performed to test the effectiveness of membranes in water remediation including reverse osmosis, nano, ultra, and micro filtration[6]. The selectivity of these membranes decreases from former to latter where micro and ultra filtration require mechanical filtration but nano filtration and reverse osmosis use capillary flow. Additionally the driving pressure of these filtration systems are directly correlated to their selectivity[6]. One major hindrance of membrane filtration is the high fouling rate but with technology such as liquid gated membranes[16], which allow for flux recovery after a passive resting period, these issues of the past may be able to be minimalized[17].

Liquid-gating is a bioinspired mechanism which brings the characteristics of natural systems coordinating multiphase transport without clogging, to membrane filtration[17]. In these studies[10,17,18], liquid gates were added to membranes and their characteristics and flow were analyzed. In the closed state a liquid-gated membrane the pores and filled and sealed, but when a critical pressure is reached the liquid enters the open state in which a non-fouling, liquid-lined pore is created[17]. The state of the gate is tunable and can be reversed depending on whether or not the critical pressure is reached, this critical pressure is depended upon the pore size, geometry, and surface tension of the liquid-gate[17]. Further studies[18] showed the ability of these liquid-gates to recover flux during a period of rest, even after becoming fully fouled. We hope to apply these properties to this thesis to harness a reduced pore size, reduction of fouling, and self-cleaning properties.

Tests on water samples doped with As(III) and As(V) with concentrations levels of 25.5 µg/L and 18.5 µg/L respectively, the effective removal with reverse osmosis, nano filtration, and ultra filtration. Reverse osmosis performed the best, with As(V) removal significantly close to 100% and the As(III) removal between 70-90%. Nano filtration was the next most effective, with As(V) removal approximately 100% and As(III) had removal rates between 20-50%. Ultra filtration was the worst of the three tested here, with a As(V) removal of just under 50% and an As(III) removal of 10%. For these experiments, two different water sources were doped with arsenic standards, each with different dissolved organic carbon (DOC) levels. The higher concentration was 11.1 mg/L and the lower concentration was 1.0 mg/L. Arsenic in the water samples with a greater DOC were consistently removed at a higher rate, leading the researcher to believe two possible mechanisms: one, arsenic was being co-rejected with humic materials found in high DOC water; or two, that a shielding effect was created at the membrane in low DOC water samples which reduced the electrostatic forces between arsenic molecules and the membrane. This latter mechanism brings in the idea of Donnen Exclusion to membrane filtration, which applies when an ionic solution is filtered through membranes with a fixed surface charge. In this scenario, any ions that share a like charge with the membrane can be inhibited, i.e. removed at a higher rate. In the case of arsenic remediation, arsenate rejection rates can be increased by selecting a membrane with a fixed negative charge[6].

The last membrane to be tested is micro filtration membranes, which have the largest pore size and therefore the lowest selectivity. Due to the poor selectivity and relatively large pore size compared to an arsenic molecule, ferric chloride ($FeCl_3$) was used as a flocculent in membrane filtration pretreatment[6]. The pilot test was conducted using well water that had a natural concentration of approximately 18 μg/L total arsenic. To compute how effective the ferric chloride was at flocculating the arsenic molecules, a series of experiments were conducted over a range of coagulant doses, membrane sizes, and pH levels. In Figure 3, the percent arsenic removal is compared to the coagulant dose for three different pore sizes. For pore sizes of 0.1 and 0.2 microns, a dose of 10mg/L seemed to be optimal as there was no significant increase in removal with higher doeses while being more successful than lesser doses. With a pore size of 1.2 microns, only a coagulant does of 25 mg/L had any significant removal, which was still under 20%. For all filter sizes, a pH range of 6-9 was tested in correspondence to arsenic removal. The result was a decrease in arsenic removal as the pH increased, in which the largest reduction occurred above 8.1[6].

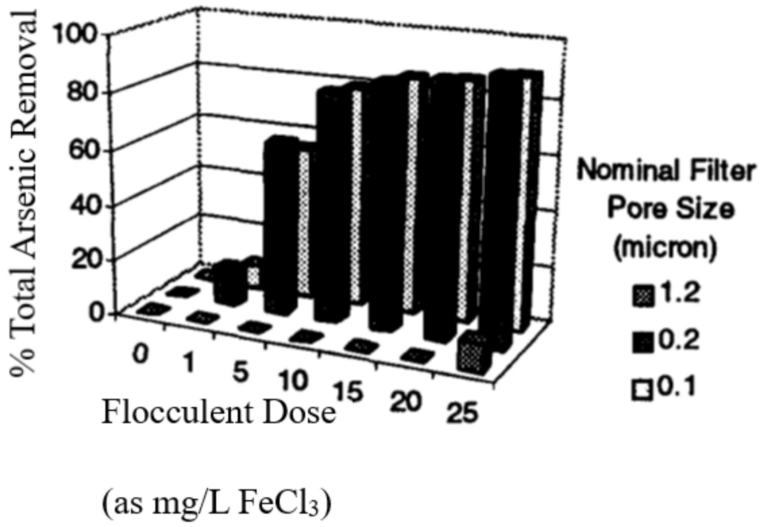

Figure 3: Percentage of total arsenic removed for various sized membranes, increasing the coagulant dose. Reproduced from ref [6]

When looking at the data for the 0.2 μm filter, in relations to coagulant doses, the least squares regression had a best fit to a hyperbolic relationship (r^2=0.975). The equation below was empirically found using this relationship and the pilot test as a guide. Where k=0.332 L/mg and the dose of $FeCl_3$ is measured in mg/L, with an upper boundary of 85% removal.[6]

$$\boldsymbol{Percent\ Arsenic\ Removal = \frac{k*Dose}{1+(k*Dose)} * 100\%}$$

EQUATION 1

This problem has still not been resolved, and overexposure to arsenic is an impending problem in the nation and in Maine. In this work, we will develop an arsenic remediation technique which produces a low-cost, low-energy solution to arsenic remediation here in Maine. Our approached focused on using this literature in parallel with equipment available on the University of Maine campus, and within the Howell Lab.

This technique will center around previously examined pretreatment flocculants paired with membrane filtration, with the unique and novel addition of a liquid-gated membranes which have not been examined previously.

METHODS AND MATERIALS

Arsenic Doping

A doped arsenic standard was created by diluting a 1,000 parts-per-million stock arsenic (SPEX CertiPrep, CL5-09AS) in Orono tap water to create a 100 ppb dilution (equivalent to 100 μg/L). Once the arsenic was added to the water, the container was shaken to ensure uniform mixing; each triplicate test mentioned below was performed using its own 100 ppb As standard solution. The concentration selected was high enough to record significant changes in arsenic levels, but is not beyond the scope of concentrations found in natural water samples in Maine[3].

ICP-MS

Arsenic-doped samples were validated by measuring in triplicate from multiple dilutions and analyzed via Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In ICP-MS (Finnigan ELEMENT2) a radio-frequency coil is oscillated between electric and magnetic fields at the end of an argon torch. When sparks are applied the argon atoms from argon ions forming a plasma. At this point the sample is added to the ICP plasma in an aerosol form (via a variety of processes) and the sample is separated into gaseous atoms and is then further ionized. From here the sample leaves the ICP chamber at atmospheric pressure into a chamber of lower pressure (approximately 10^{-5} torr), via a sampler cone of 1 mm diameter, and then enters the mass spectrometry unit though a hole of similar diameter. The purpose of this is to only sample from the center of the ICP stream, and precautions are taken in the form of the "Shadow Stop" to block significant light from the argon flame. In the mass spectrometer, ions are separated by a mass-to-charge ratio, only allowing one mass-to-charge unit through at a time and calculating its percentage of the given sample. In this study samples were screened for arsenic and iron in a single run and the results are presented in µg/L to the nearest hundredth.

Floc Formation

Once the water samples had been doped with arsenic, they were pretreated for the formation of flocs. Flocs are cloudy suspensions of particles found in solution, and in the application of water remediation can be seen with the naked eye. During literature review FMO seemed to be the most practical coagulant, as it had a significantly high removal rate of arsenic, insignificant increases in other metals, and promises of being extremely cheap for mass amounts. This was found to not be the case, and no accessible supply of FMO could be located. With these setbacks, ferric chloride was chosen for the flocculant, as it was also cheap and had significant literature reviews on experimental tests which were applicable to the filtration setup selected[2]. Based upon this previous work, a FeCl concentration of 25 mg/L was selected for these experiments to optimize results. To further optimize the process of floc formation, the pretreatment process was designed using a paddle mixer, Figure 4.

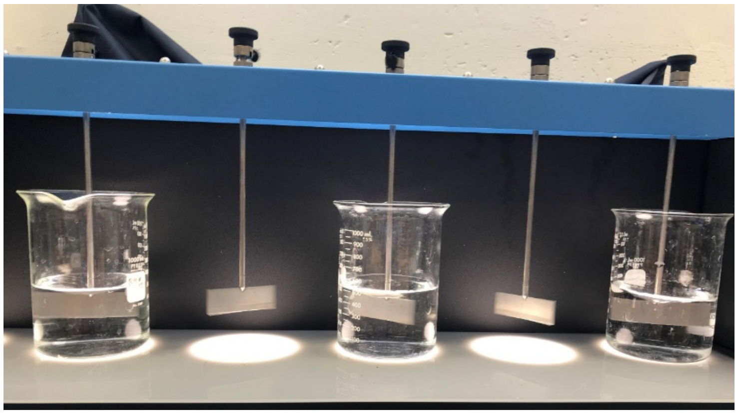

Figure 4: Experimental setup for mixing and floc formation.

Equations from Theory and Practice of Water and Wastewater Treatment[23] were then used to determine the optimal parameters for flock formation. These series of equations (Equation 2-5) have been leveraged to solve for the velocity gradient of the solution during mixing based upon the properties of water, mixer used, and the variable speed at which the mixing occurs.

$$\boldsymbol{Re = \frac{(\rho * \omega * r_p{}^2)}{\mu}}$$

EQUATION 2

Where Re is the Reynold's Number

ρ is density of water,

ω is the rate of paddle revolution,

r_p is the radius of the paddle,

and μ is the viscosity of water.

$$\boldsymbol{\phi = K * Re^p}$$

EQUATION 3

Where ϕ is the Power Number

K is the characteristic constant for the paddles geometry,

Re is the Reynold's Number,

and p is a constant representing either laminar or turbulent flow.

$$\boldsymbol{P = \phi * \rho * \omega^3 * r_p{}^5}$$

EQUATION 4

Where P net power in the mixer

ϕ is the Power Number,

ρ is density of water,

ω is the rate of paddle revolution,

and r_p is the radius of the paddle.

$$\boldsymbol{G = \sqrt{P/_{\mu * V}}}$$

EQUATION 5

Where G is the velocity gradient of the solution
P is the net power in the mixer,
μ is the viscosity of water,
and V is the volume of the sample.

A Mathcad sheet with these equations and constants is presented in Figure A3. The target conditions were a velocity gradient of 700-1000 s^{-1} for 1 minute and then a velocity gradient of 10-60 s^{-1} for 30 minutes. We found that a speed of 120 rpm would achieve a velocity gradient of 725 s^{-1}, followed by a speed of 30 rpm to achieve a velocity gradient of 90 s^{-1}. To test that the presence of various metals would improve the formation of flocs, these mixing conditions were tested on both arsenic-doped DI water samples and arsenic-doped tap water samples. Samples that went through this floc formation process will be refered to as "treated" samples in the remainder of this thesis. Once mixing was completed samples were collected and analyzed for pH, floc size, and composition of arsenic before being filtered.

pH Testing

The water samples were tested using a pH probe (Accument AB150). The pH probe was calibrated using 4, 7, and 10 standards, and all readings were taken in triplicate. The purpose of this analysis was to determine the effects on pH that both the As doping and ferric chloride treatment had on the water samples. As stated previously, the success of most flocculation methods occurs within specific pH ranges[19], and the final filtered sample must fall within certain metal concentrations for safety[20].

Dynamic Light Scattering

Dynamic Light Scattering (DLS) (Malvern Zetasizer) is a process that can be used to determine particle size in solution; in this case we wanted to measure the size of arsenic-ferric chloride complexes in the samples. This process works by shining a laser though cuvette samples, and analyzing the speckled pattern and intensity that becomes projected. The machine's software allows users to impute parameters based upon the suspended material and the solution's respective refractive index. Alongside this, users can manually change the number of measurements and runs taken by the machine; to best analyze a particular substance within its stated parameters. The data output by this program allows you to determine the size of particles in suspension, as well as the percent of the total volume which they make up. We set the analysis of each sample to be tested in triplicate, with each triplicate consisting of 10 scans. The samples chosen for analysis were treated DI water samples doped with arsenic pre-filtration, and treated tap water samples doped with arsenic post-filtration from both liquid-gated membranes and non-liquid-gated membranes.

Filtration

Once flocs were successfully formed and analysis of control groups was completed, the water samples were be filtered. The experimental setup for filtration can be seen in Figure 8, which consists of a vacuum pump pulling through a pressure gauge and across the 1.0 micron membrane (Sterlitech PTFE Unlaminated Membrane, 25mm). At this point the flocs settle to the bottom of solution, which is still clear in color. The pump is run for 45 minutes to warm up before it is used for filtration. The filters used experiments were composed of Polytetrafluoroethylene (PTFE), a straight-chain polymer which provides characteristics such as high maximum temperature, low coefficient of friction, and hydrophobicity. To increase the efficiency of remediation in this filtration process, some filters were also treated with Krytox (a widely used machine oil) to create

Liquid-Gated Membranes (LGM). Krytox is a long-chain perfluoronpolyether liquid, sold as the Krytox^{TM} series by DuPont; where the chain length determines the viscosity. This technique was first introduced by Hou et al.[17], and in our lab was further studied by Jonathon Overton[10]. It has been found that LGMs reduce entry pressure for DI water; when a critical pressure is reached the infused Krytox moves to the walls of the pores and when this pressure is lost it reinfuses back across the pore[17]. Figure 5 illustrates this phenomenon in action. The reinfusing of the pores allowed the membranes to have self-cleaning properties which could reduce fouling without the use of additional chemicals or procedures[18].

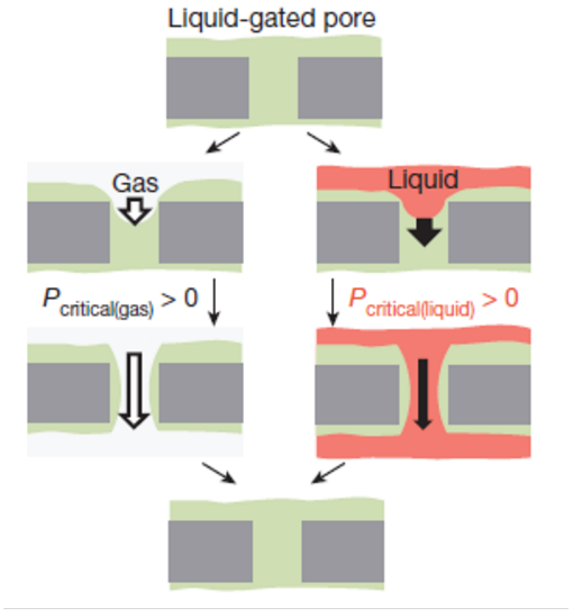

Figure 5: Figure 5: LGMs when the critical pressure is applied, reproduced from Ref [16].

One goal of this study is to determine if LGMs increase the remediation of arsenic from the flocked samples, working under the hypothesis that we can reduce the effective size of the pores. To create the LGMs, 200 µL of Krytox 105 (having a viscosity of 522 cSt [21]) was applied to the PTFE filter. After a minute of saturation the filter was suspended vertically for 15 seconds and gently wiped on a paper towel to remove any excess lubricant. Saturation of the membranes was visually apparent by a change from opaque to transparent, which can be seen in Figure 7(B). The saturation of membranes was always performed immediately before loading them into the filtration setup for use to improve consistency and prevent the membranes from drying out. Krytox was selected because of its use in the previously cited studies[10,17,18]. Krytox's highly fluorinated nature allows it to penetrate and saturate the PTFE filters.

A standard filtration time of three minutes was selected for each of the samples. This time was selected based upon previous trials, as sufficient amounts of sample can be filtered for analysis and the membrane will not be fouled from the flocculent. We wanted to study the effect LGM had on the flux and the percent of As and Fe removed from the solution. To successfully achieve this, samples of DI water were filtered using both LGM and Non-LGM in triplicate as a control. Next, the flocked samples were filtered in triplicate using both LGM and Non-LGM. The filtration setup and an engineering schematic can be found in Figure 6. The volume of filtered solution was collected, and the sample was analyzed using both DLS and ICP-MS. The filtration setup was carefully cleaned with DI water in between each filtration.

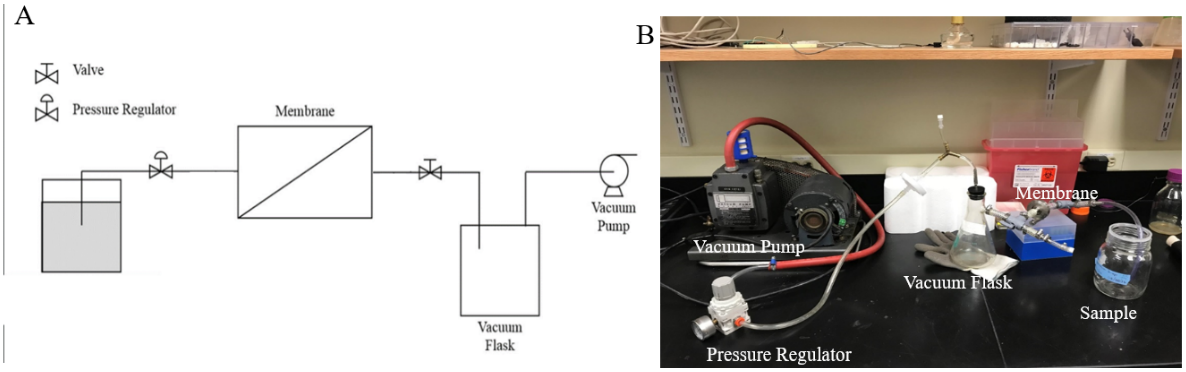

Figure 6: (A) Engineering schematic of filtration setup. (B) Experimental filtration setup.

RESULTS AND DISCUSSION

Selecting a source of water with a constant level of arsenic was of paramount importance when designing these experiments. Orono is reported to have under 1 parts-per-billion (ppb) of arsenic in it's water supply[22]. Previous work using FMO to remove arsenic[7] determined that the presence of nickel, cobalt, and magnesium aided in the formation of flocs, informing the decision to use a tap water source as opposed to DI water from the lab.

Does the presence of LGMs have a significant impact on the volume of sample filtered?

The results for the volume of sample filtered over three minutes for each of the methods is displayed in Figure 7(A). Each filtration methods was statistically analyzed and compared using both a F-test for variance and a t-test, the results of which can be found in Tables A6-A9 in the Appendix. The trends that appeared out of this data were that on average the control groups were able to filter more of the sample, and the Non-LGM filters appeared to have a larger filtration volume than the LGMs. The variance between the samples analyzed was always found to be equal and the only samples that had a significant difference in volume were the LGM Control and the Non-LGM control, with a P-value of 0.04645. From this we can assume that the presence and size of flocs has a larger impact on the rate of filtration than the presence of a liquid gate on the membrane. In the process of filtration there is always a period right as the pump is turned on, before the critical pressure is reached, where no sample flows through the filter. The average time for this period was 45 seconds for LGM and 20 seconds for the Non-LGMs. These averages are not significantly different from each other, but if the three minutes of filtration was aligned to start once this period ended the total volumes filtered may have had less variation. The membranes for these experiments are displayed in Figure 7(B).

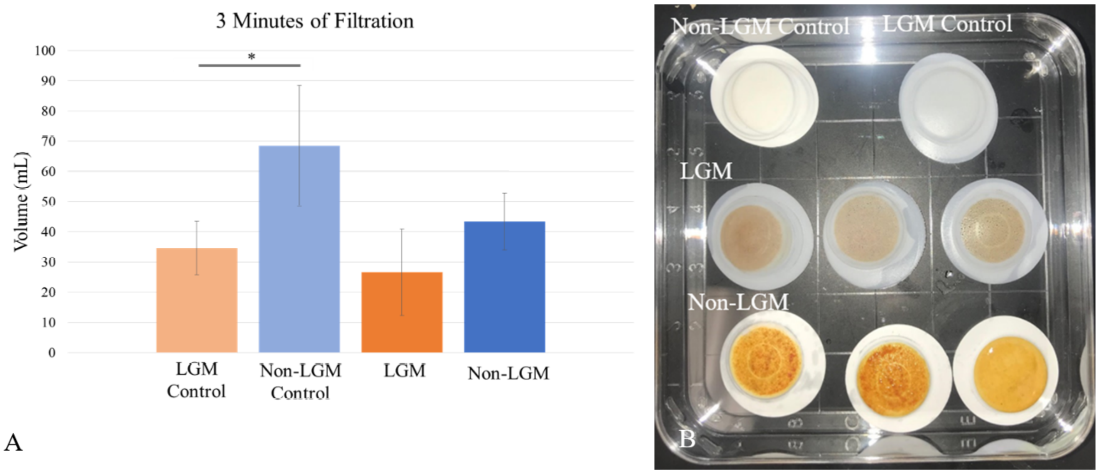

Figure 7: (A) Comparison of the volume of sample filtered over three minutes, across various filtration methods. (B) Membranes post-filtration.

Do LGM have a higher remediation rate of arsenic?

The results from the ICP-MS analysis on samples filtered with LGM and Non-LGM can be seen in Figure 8. The instrument was able to analyze the concentration of both arsenic and iron, and a percent removal was calculated by comparison to unfiltered samples that were also tested. A full report of each samples concentration can be found in Table A3. The same statistical test were run on these data sets as well and can be found in Tables A4-A5. The LGM removed an average of 80.06% of the As, which is significantly more than the 62.43% the Non-LGM removed (P=0.0267). Likewise, the LGM removed an average of 73.21% of the iron, which is significantly more than the 51.76% the Non-LGM removed (P=0.0471). The average concentrations of arsenic and iron in Orono Tap Water before doping, after doping, and after both filtration methods can be found in Table 2 . The average pH of the unfiltered As-doped sample with FeCl was 3.84.

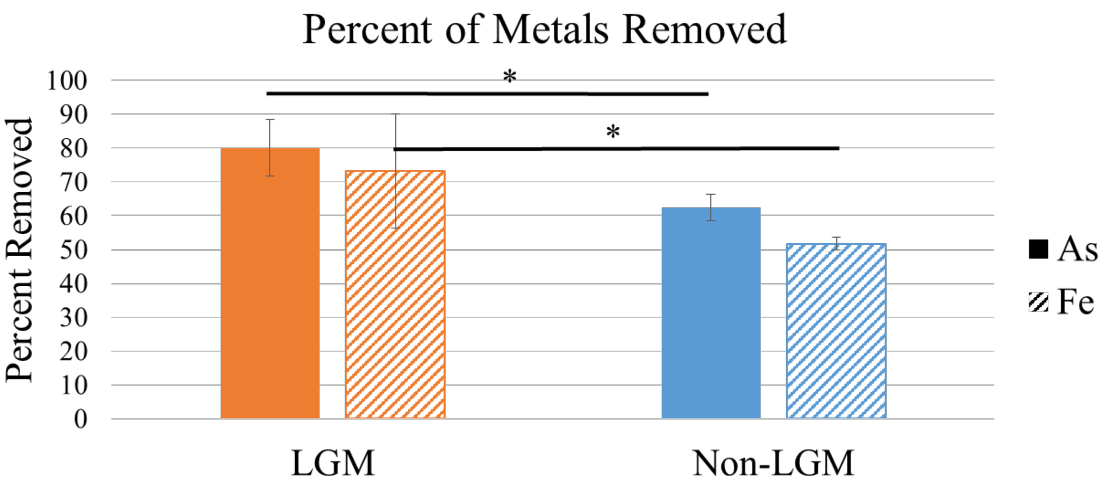

Figure 8: Percentage of As and Fe removed from LGM and Non-LGM filtrations.

Table 2: Concentrations of As and Fe in various samples.

	Orono Water	As Doped Sample	Non-LGM Sample	LGM Sample
As	< 1 ppb	106.62 ppb	37.57 ppb	19.94 ppb
Fe	< 0.5 ppb	3949 ppb	1905.01 ppb	1057.88 ppb

Does the presence of other minerals in water aid in the formation of flocs? How do the arsenic complexes sizes post LGM and Non-LGM filtration?

For the application of this method for practical use around the state of Maine, the water sample will not only contain As. For this reason we chose to dope Orono tap water instead of Deionized water, but we still wanted to compare the formation of flocs between these two water types. The same concentrations of chemicals and mixing conditions were used for both samples, DI and Orono tap. Figure 9(Ai) shows the clear formation of flocs from the Orono tap water while there are no visible flocs formed in the DI water of Figure 9(Aii), and in this sample the entire volume of water was tinted yellow. The DI water sample was tested with DLS before filtration, while the Orono water samples were tested after filtration. In Figure 9(B) it shows that there were small complexes formed, but each is only around 15% of the complexes found in the entire solution. It is assumed that these complexes would not be filtered out using our techniques, and that they most likely are FeCl complex that have not bonded with As. In Figure 9(C) it shows the complexes present in the Non-LGM filtered sample. There are peaks at diameters 220, 255, and 342 nm, each representing between 60-80% of the complexes in that sample. These complexes are assumed to be too small to be filtered out by the PTFE membrane and account for the roughly 40% of As that was not removed from these samples. In Figure 9(D) the complex size in the LGM filtered sample can be found. There was only 1 peak from all three samples tested, but it accounted for 100% of the complexes in that sample at a diameter of 141 nm. This is highly significant because the literature suggested a 0.2 micron filter[6], but our experimental setup uses a 1 micron filter. These data suggest that the LGM can effectively reduce the pore size below 200 nm and thus simulate a 0.2 micron filter.

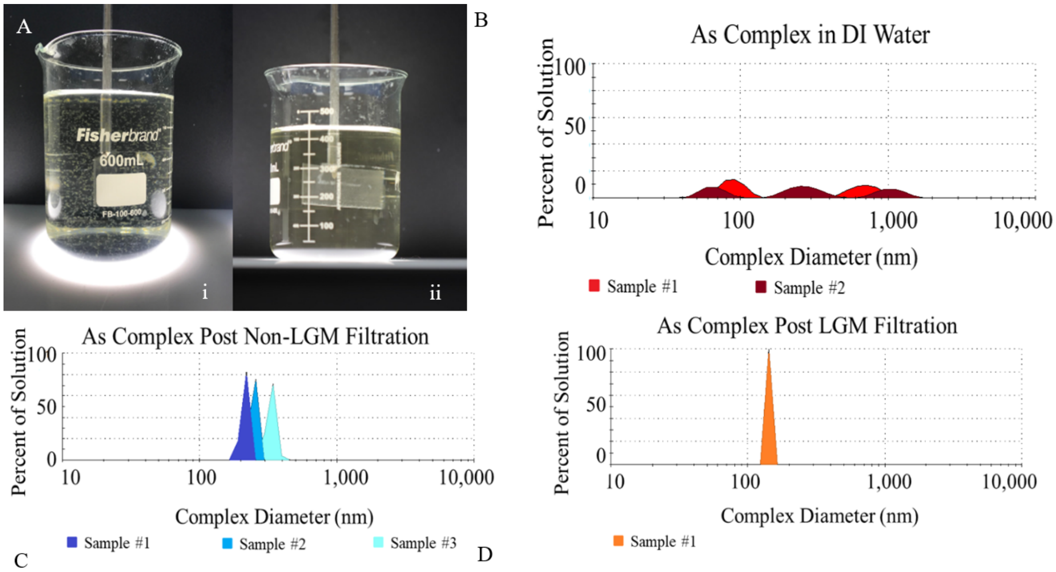

Figure 9: (A i) Ferric chloride mixed into arsenic-doped Orono water. (A ii) Ferric chloride flocs in arsenic-doped DI water. (B)DLS data for As complexes in DI Water samples, peaks at 58, 91, 255, 712, and 1106 nm. (C) DLS data for As complexes after Non-LGM.

CONCLUSION

There appears to be a logical progression of experiments for future iterations of this project. Firstly we would like to replicate the experiments already conducted to increase the sample size and verify reproducibility of the results, mainly in regards to the number of peaks for post-filtration DLS. With more time for experimentation we would have run trials with lower concentrations of ferric chloride, analyzed the size of flocs formed in the mixing process, and compared the effectiveness of remediation. Additionally this would allow us to analyze the effect the filtration process as well as the remediation of arsenic and ferric chloride had on sample pH. In a similar vein, we would also have liked to compare the rate of arsenic removal in the samples we doped to be 100 ppb compared to a lower concentration that would more closely reflect the average levels in which these methods would be implemented. Lastly, as previously mentioned LGMs have been studied for their self-cleaning properties[10,17,18]. We would have therefore liked to run experiments to compare those results to the fouling rate of these flocs in the future.

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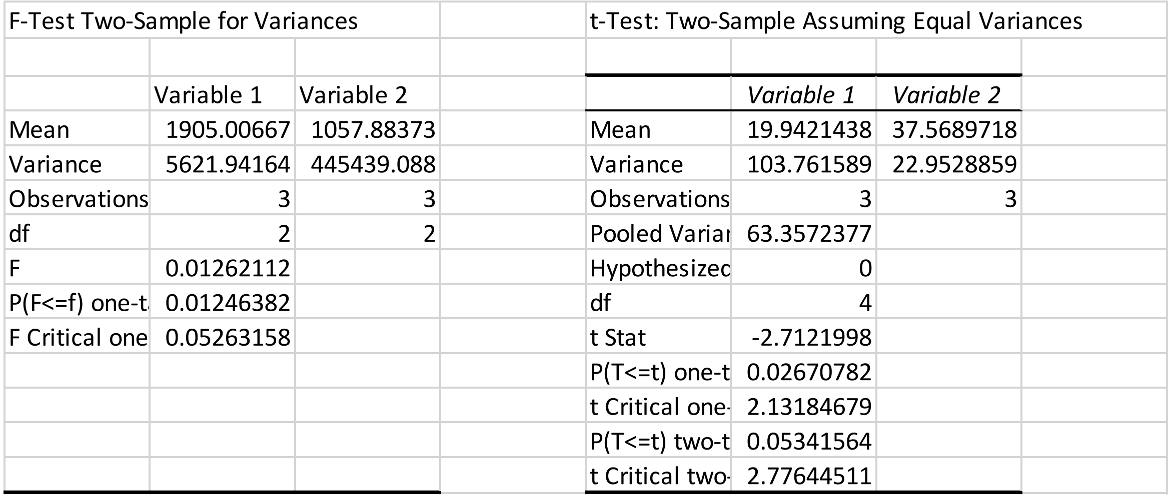
APPENDIX

Table A3: Full data set from ICP-MS. All values are reported as parts-per-billion.

Doped Standard [As]	**Pre-Filtration [Fe]**	**Post LGM Filtration [As]**	**Post Non-LGM Filtration [As]**	**Post LGM Filtration [Fe]**	**Post Non-LGM Filtration [Fe]**
94.07	3949.00	25.15	33.88	1708.91	1829.30
102.92		8.20	42.98	375.21	1979.24
110.27		26.47	35.84	1089.54	1906.48
61.73					
94.79					
99.95					
104.34					
117.00					
110.47					
110.60					
95.89					
114.67					
122.23					
126.92					
119.20					
120.81					

Table A4: Statistical analysis of LGM vs. Non-LGM for [As]



F-Test Two-Sample for Variances

	Variable 1	Variable 2
Mean	1905.00667	1057.88373
Variance	5621.94164	445439.088
Observations	3	3
df	2	2
F	0.01262112	
P(F<=f) one-t	0.01246382	
F Critical one	0.05263158	

t-Test: Two-Sample Assuming Equal Variances

	Variable 1	*Variable 2*
Mean	19.9421438	37.5689718
Variance	103.761589	22.9528859
Observations	3	3
Pooled Variar	63.3572377	
Hypothesizec	0	
df	4	
t Stat	-2.7121998	
P(T<=t) one-t	0.02670782	
t Critical one-	2.13184679	
P(T<=t) two-t	0.05341564	
t Critical two-	2.77644511	

Table A5: Statistical analysis of LGM vs. Non-LGM for [Fe]

F-Test Two-Sample for Variances				t-Test: Two-Sample Assuming Equal Variances		
	Variable 1	*Variable 2*			*Variable 1*	*Variable 2*
Mean	1905.00667	1057.88373		Mean	1057.88373	1905.00667
Variance	5621.94164	445439.088		Variance	445439.088	5621.94164
Observations	3	3		Observations	3	3
df	2	2		Pooled Varia	225530.515	
F	0.01262112			Hypothesize	0	
P(F<=f) one-t	0.01246382			df	4	
F Critical one	0.05263158			t Stat	-2.184688	
				P(T<=t) one-t	0.04712475	
				t Critical one	2.13184679	
				P(T<=t) two-t	0.0942495	
				t Critical two	2.77644511	

Table A6: Statistical analysis of LGM vs. Non-LGM for volume

F-Test Two-Sample for Variances				t-Test: Two-Sample Assuming Equal Variances		
	Variable 1	*Variable 2*			*Variable 1*	*Variable 2*
Mean	26.6667	43.3333		Mean	26.6667	43.3333
Variance	308.333	133.333		Variance	308.333	133.333
Observations	3	3		Observations	3	3
df	2	2		Pooled Variance	220.833	
F	2.3125			Hypothesized Mea	0	
P(F<=f) one-tail	0.30189			df	4	
F Critical one-tail	19			t Stat	-1.3736	
Variance is Equal				P(T<=t) one-tail	0.12076	
				t Critical one-tail	2.13185	
				P(T<=t) two-tail	0.24152	
				t Critical two-tail	2.77645	
				Means are Equal		

TableA7: Statistical analysis of LGM vs. LGM Control for volume

F-Test Two-Sample for Variances				t-Test: Two-Sample Assuming Equal Variances		
	Variable 1	*Variable 2*			*Variable 1*	*Variable 2*
Mean	26.6667	34.6667		Mean	26.6667	34.6667
Variance	308.333	116.333		Variance	308.333	116.333
Observations	3	3		Observations	3	3
df	2	2		Pooled Variance	212.333	
F	2.65043			Hypothesized Mea	0	
P(F<=f) one-tail	0.27394			df	4	
F Critical one-tail	19			t Stat	-0.6724	
Variance is Equal				P(T<=t) one-tail	0.26909	
				t Critical one-tail	2.13185	
				P(T<=t) two-tail	0.53817	
				t Critical two-tail	2.77645	
				Means are Equal		

Table A8: Statistical analysis of LGM Control vs. Non-LGM Control

F-Test Two-Sample for Variances

	Variable 1	Variable 2
Mean	68.5	34.6667
Variance	594.75	116.333
Observations	3	3
df	2	2
F	5.11246	
P(F<=f) one-tail	0.1636	
F Critical one-tail	19	
Variance is Equal		

t-Test: Two-Sample Assuming Equal Variances

	Variable 1	Variable 2
Mean	68.5	34.6667
Variance	594.75	116.333
Observations	3	3
Pooled Variance	355.542	
Hypothesized Mea	0	
df	4	
t Stat	2.19758	
P(T<=t) one-tail	0.04645	
t Critical one-tail	2.13185	
P(T<=t) two-tail	0.0929	
t Critical two-tail	2.77645	
Means are not Equal		

Table A9: Statistical analysis of Non-LGM vs. Non-LGM Control

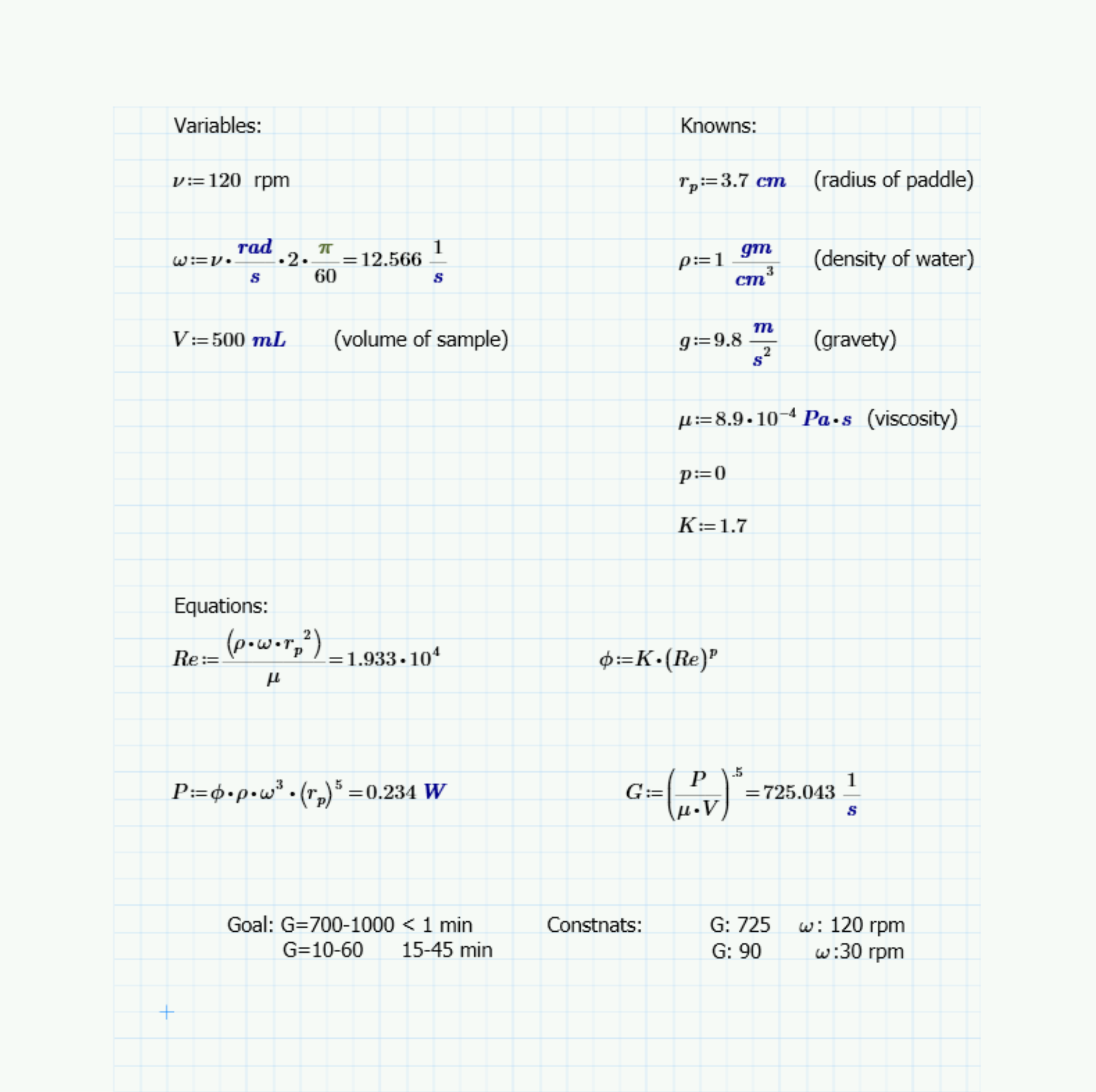
F-Test Two-Sample for Variances

	Variable 1	Variable 2
Mean	68.5	34.6667
Variance	594.75	116.333
Observations	3	3
df	2	2
F	5.11246	
P(F<=f) one-tail	0.1636	
F Critical one-tail	19	
Variance is Equal		

t-Test: Two-Sample Assuming Equal Variances

	Variable 1	Variable 2
Mean	43.3333	68.5
Variance	133.333	594.75
Observations	3	3
Pooled Variance	364.042	
Hypothesized Mea	0	
df	4	
t Stat	-1.6155	
P(T<=t) one-tail	0.09076	
t Critical one-tail	2.13185	
P(T<=t) two-tail	0.18151	
t Critical two-tail	2.77645	
Means are Equal		

Table A10: Mathcad sheet used for solving the series of equations correlating paddle speed to desired velocity gradient.



Variables:

$\nu := 120$ rpm

$\omega := \nu \cdot \frac{rad}{s} \cdot 2 \cdot \frac{\pi}{60} = 12.566 \ \frac{1}{s}$

$V := 500 \ mL$ (volume of sample)

Knowns:

$r_p := 3.7 \ cm$ (radius of paddle)

$\rho := 1 \ \frac{gm}{cm^3}$ (density of water)

$g := 9.8 \ \frac{m}{s^2}$ (gravety)

$\mu := 8.9 \cdot 10^{-4} \ Pa \cdot s$ (viscosity)

$p := 0$

$K := 1.7$

Equations:

$Re := \frac{\left(\rho \cdot \omega \cdot {r_p}^2\right)}{\mu} = 1.933 \cdot 10^4$

$\phi := K \cdot (Re)^p$

$P := \phi \cdot \rho \cdot \omega^3 \cdot \left(r_p\right)^5 = 0.234 \ W$

$G := \left(\frac{P}{\mu \cdot V}\right)^{.5} = 725.043 \ \frac{1}{s}$

Goal: G=700-1000 < 1 min
G=10-60 15-45 min

Constnats:
G: 725 ω: 120 rpm
G: 90 ω:30 rpm

AUTHOR'S BIOGRPAHY

Austin Wheeler Steward was born in Bangor, Maine on February 2nd, 1997. The Steward family lived in Readfield, Maine until 2008 when they relocated to Colebrook, New Hampshire. Austin excelled in his education at Colebrook Academy, but always stayed true to his Maine roots deciding to return and attend the University of Maine.

During his time at UMaine, Austin maintained a competitive GPA while being an active member of the community and plethora of organizations on campus. From the "*Hearty Maine Hello*" to Commencement Austin took on everything the University had to offer and fully embraced the College of our Hearts Always. The most influential opportunities were the Senior Skull Honors Society, Alpha Tau Omega, the InterFraternity Council, and Team Maine. Additionally Austin served as a Resident Assistant, Maine Learning Assistant, Sophomore Owl, V.P. of Dancer Relations for Black BearTHON, Director of Communications for UMSG Inc., member of the Campus Hype Initiative, and Summer Orientation Leader. In May of 2019 Austin graduated from the University of Maine with a Bachelor's Degree in Biomedical Engineering with a concentration on Pre-Medical studies and completion of the Honors Course of Study. After becoming a third-generation UMaine Alumni, Austin will attend Tufts School of Medicine and participate in their Maine Track MD program. Austin hopes to graduate from his program in four years, pursue a residency in Pediatrics, and one day return to practice in Maine.