REDUCTION OF WATER HARDNESS USING SULFONATED POLYSTYRENE SUBJECTED TO VARIOUS CONDITIONS

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ABSTRACT

Water hardness is a prevalent unwanted physical characteristic in water such as scales forming in water pipes, which cause precipitates to form yellow rings on the edges of bathroom and kitchen fixtures. It also causes water to taste and smell foul and for soap not to produce lather well. Water hardness is caused by the excessive amounts of calcium and magnesium ions in the water. A previous study determined that incorporating sulfuric acid and polystyrene or Styrofoam, forming sulfonated polystyrene, reduces the hardness in water due to the ion-exchange properties of the sulfonated polystyrene being used as a resin. When hardness in water is being reduced, this is called softening. This study aimed to determine the water hardness before and after filtration using sulfonated polystyrene subjected to various conditions. The various conditions are the following; temperature of sulfonation (40°C, 60°C, 80°C, 100°C), time of sulfonation (1, 2, 3, 4 hours), and concentration of sulfuric acid (40%, 60%, 80%, 100%). Each combination of each condition was performed. There was a total of 64 set ups. The results show that the sulfonated polystyrene significantly increased the hardness of water. This was due to the circumstance that normalization of the resin with NaOH was not performed.

Keywords: Water Hardness, Sulfonated Polystyrene, Ion-Exchange, Resin, Softening, Filtration, Sulfonation, Normalization

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF APPENDICES

Chapter 1
INTRODUCTION

Background of the Study

There is a prevalence of unwanted physical characteristics in water. Such characteristics include scales forming in water pipes. These scales cause precipitates in water to form yellow rings on the edges of bath tubs, toilets, sinks, and other bathroom and kitchen fixtures. This also causes the water to taste and smell foul. Soap also does not produce lather well.

Also, when the water is used for bathing and such, the calcium and magnesium clogs pores in the skin, which usually cause bacterial growth and therefore cause the formation of pimples in the skin.

According to the 2010 Provincial Profile of the Province of Iloilo, Metro Iloilo Water District (MIWD) stated that the hardness of raw water is 48. Water that has a hardness of 48 would mean that the water is slightly hard. After water is processed, the hardness becomes 44 but is still slightly hard. The ideal range of hardness should only be 0 to 17.1 for it to be considered as soft.

The cause of these unwanted physical characteristics and pore clogging is due to the hardness of water. Hardness of water or water hardness is caused by the excessive amounts of calcium and magnesium present in the water. This water is then called hard water. This water usually comes from groundwater wells. When a certain area's soil is rich in calcium and magnesium ions, these ions present in the soil can seep into the groundwater, which is taken by users through the wells.

Hard water can be treated using different processes. These processes include ion exchange, reverse osmosis, nanofiltration, and lime softening. The frequently used method is the ion exchange method, which uses resins that exchange calcium and magnesium ions for sodium ions.

Some of these processes, such as ion exchange and lime softening, produce an undesirable change in pH and/or salinity.

Also, a problem with the ion exchange method is that the installation and maintenance can be too complicated for domestic use. Most homes do not treat their water because present treatments either include the use of chemicals, which makes it non-renewable, or are not readily available, such as the machineries and equipment used.

Bekri-Abbes, Bayoudh, and Baklouti have researched on the removal of hardness of water using sulfonated waste plastic. Their study investigated the possibility of waste polystyrene to remove the hardness of water.

Other studies have also investigated on polystyrene. They use different values for the properties of sulfonated polystyrene. These properties are those during sulfonation and properties of the polystyrene (e.g. temperature and time duration of sulfonation, size of the polystyrene).

This study developed sulfonated waste polystyrene as filter medium. The study also determined if manipulating the sulfuric acid concentrations, temperature of sulfonation, time duration of sulfonation, polystyrene size or the surface area, and the sulfonating agent will affect the water hardness treatment.

The study concentrated on maximizing the potential of the sulfonated polystyrene. This led to the manipulation of the variables of the medium.

Statement of the Problem

This study aimed to determine the water hardness before and after filtration using sulfonated polystyrene subjected to various conditions.

Objectives

a) To measure the hardness (ppm) of water before and after filtration

b) To calculate the percent removal of the water hardness using sulfonated polystyrene subjected to various conditions.

Hypothesis

Sulfonated polystyrene will reduce the hardness of the groundwater. Manipulating the properties of the medium's variables; concentration of the sulfonating reagent (sulfuric acid), time duration of sulfonation, and temperature of sulfonation will greatly affect the potential of the sulfonated polystyrene to reduce the hardness of the ground water after the filtration.

Significance of the Study

The research study was dedicated to treating water to be fit for household use. There is an evident problem on the unwanted physical characteristics that are present in water from groundwater wells. These characteristics include scales forming in pipes and soap not being able to create lather. This water is called hard water. Hard water is due to the presence of calcium and magnesium ions present in the water.

When scales form in pipes, these damage the pipes and cause the water to have some more unwanted characteristics when the water passes through it such as foul odor and taste, yellowish color, and precipitates forming on the edges of bathroom and kitchen fixtures.

When soap is not able to create lather, tons of detergents and cleaning materials are wasted since you would need to use more of the cleaning materials to make them work.

The study treated the hard water to fix the problems mentioned, and other problems.

The study manipulated the following variables: sulfuric acid concentrations, temperature of sulfonation, duration of sulfonation, polystyrene size or surface area, and sulfonating reagent to be used.

Scope and Delimitation

The study dealt with the maximization of the potential of the sulfonated polystyrene as a medium to reduce water hardness. The study manipulated variables such as sulfuric acid concentrations, time duration of sulfonation and temperature of sulfonation. Also, the study determined the hardness of the hard water before and after the filtration.

Definition of Terms

Groundwater is the water within the earth especially that supplies wells and springs (Merriam Webster Dictionary). In this study, a hard water solution will be made to substitute the groundwater.

Hardness is the presence of calcium and magnesium ions in the water (Craun and others). In this study, hardness will be treated through filtration.

Hard water is what water is called once there is a presence of an unwanted range of calcium and magnesium ions in the water (Heidekamp and Lemley 2005). In this study, hard water will be filtered to result in a desired range, which is suitable for domestic use.

Ion exchange capacity in general terms, the capacity of an ion exchange resin can be expressed as the quantity of ions that can be taken up by a specific volume of the resin. This would be expressed in quantity-per-unit volume, such as kilograins per cubic foot (Kgr/ft3), milli-equivalents per milliliter (meq/mL), which also equals equivalents per liter (eq/L). For the record, for a softener, 1 eq/L = 21.87 Kgr/ft 3. 1.0 grains per gallon = 17.1 ppm of substance expressed as calcium carbonate (Michaud 2011). In this study, the ion exchange capacity will determine the removal capacity of the filter medium, sulfonated polystyrene.

pH is a measure of acidity and alkalinity of a solution that is a number on a scale on which a value of 7 represents neutrality and lower numbers indicate increasing acidity and higher numbers increasing alkalinity (IDC Technologies). In this study, pH will be determined to check if the sulfonated polystyrene has an effect to the pH of the water.

Polystyrene is a polymer of styrene. It is a rigid transparent thermoplastic that has good physical and electrical insulating properties and is used especially in molded products, foams, and sheet materials (Pond J.). In this study, the polystyrene will be sulfonated to be used as the filter medium for the filter.

Sulfonation is defined as a substitution reaction used to attach the $-SO_3H$ group on a molecule of an organic compound via chemical bond to carbon or, less frequently, to a nitrogen atom of the organic compound. Compounds such as H_2SO_4, SO_3, and its complexes, such as acyl and alkyl sulfates and chlorosulfonic acid, are commonly used as sulfonating agents (Kucera and Jancar 1998). In this study, the polystyrene will be processed through sulfonation in order to get its water hardness removal capacities.

Sulfonating reagent is able to add a sulfonate group on aromatic rings or to sulfate a hydroxyl group. In both cases the resulting sulfonate or sulfate increases the hydrophilicity of the polymer and can turn it water soluble (Salager 2002). In this study, the sulfonating reagent will be used during sulfonation. It will be where the polystyrene will be immersed.

Sulfonated polystyrene in this study is what you call the polystyrene that has undergone the sulfonation process.

Surfactant or surface active agent is a substance that, when dissolved in water, gives a product the ability to remove dirt from surfaces (Schramm 2000). In this study, surfactants will be determined to check if the sulfonated polystyrene also has an effect to it.

Chapter 2
REVIEW OF RELATED LITERATURE

A. Water Hardness

A.1. Description

Water hardness is characterized by the presence of calcium and magnesium ions in water. It is measured in terms of parts per million (ppm), grains per gallon, or milligrams per liter (mg/L). Water with an undesirable range of water hardness is called "hard water" (Water Stewardship Information Series 2007).

A.2. Cause of Hard Water

Excessive amounts of calcium and magnesium in the water cause hard water. This water usually comes from groundwater wells. When a certain area's soil is rich in calcium and magnesium ions, these ions present in the soil can seep into the groundwater, which is taken by users through the wells.

In groundwater, water hardness is usually naturally occurring from weathering of limestone, sedimentary rock and calcium bearing materials (British Columbia Ground Water Association 2007).

A.3. Effects of Hard Water

A.3.1. Advantages

When ingested, calcium in hard water contributes to the total calcium and magnesium amounts needed for the human diet (Cambridge Water Department, National Research Council).

A.3.2. Disadvantages

Hard water forms scales in water pipes. These scales cause precipitates to form yellow rings on the edges of bath tubs, toilets, sinks, and other bathroom and kitchen fixtures. Hard water tastes and smells foul.

When soap is used with hard water, it does not produce lather well. Hard water requires more soap and synthetic detergents for home laundry and washing.

When the water is used for bathing and such, the calcium and magnesium in the hard water clog the pores of the skin, which cause bacterial growth and therefore cause the formation of pimples in the skin.

Hard water interferes with almost every cleaning task. Cooking using hard water can be difficult because vegetables lose their color and flavor (Hairston and others 2001).

It also contributes to scaling in boilers and other industrial equipment (USGS).

A.4. Water Hardness determination

Water hardness is determined using Ethylenediaminetetraacetic acid (EDTA) titration (Neidig 1994).

A.5. Water Hardness treatment

Hard water can be determined using different processes. These processes include ion exchange, reverse osmosis, nanofiltration, lime softening, and using sulfonated polystyrene (Heidekamp and Lemley 2005).

A.5.1. Ion exchange

Ion exchange is a process where resins are used as a medium to exchange ions. Ion exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them. These exchanges take place without any physical alteration to the ion exchange material. Ion exchangers are insoluble acids or bases, which have salts, which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers).

Using resins containing sodium cations softens the water but which bind with calcium and magnesium more strongly than sodium. As the water passes through the resin, the resin takes up calcium and magnesium and releases sodium making “softer” water. The process has some disadvantages in that there are substances occurring in some water, which can foul the resin, but in general the advantages of the process outweigh the disadvantages (Alchin, D).

A.5.1.1. Resins

Resins are small round beads about 0.5 to 1.0 mm in diameter. These resins are used for the ion-exchange process where its sodium ions are exchanged for calcium and magnesium ions. An example of a commonly used resin is zeolite. Zeolites are crystalline microporous minerals (Lobo 2005) that usually consist of aluminum and silicon. Zeolites have large exterior areas where most reactions occur. Zeolite structures consist of silicon (Si^{4+}) and aluminum (Al^{3+}) cations, which are tetrahedrally coordinated by four oxygen anions (O^{-2}), thus forming a macromolecular three-dimensional framework in such a way that uniform voids and channels are created in the crystals (Lobo 2005). The negative charge is compensated by additional non-framework cations like sodium (Na^{+}) (Lobo 2005).

There are also other known synthetic or natural resins or zeolites such as Clinoptilolite, chabazite, mordenite, erionite, ferrierite, phillipsite, MCM-41, H-Beta, H-ZSM-5, H-ZSM-58, H-MCM-22, MCM-22, PSH-3, and SSZ-25. In the Philippines, natural zeolites can be found in the Sulu Sea.

A.5.2. Nanofiltration

Nanofiltration utilizes pressure to effect separation of contaminants from water streams. It uses semi-permeable membranes that have the ability to hold back (reject) dissolved and/or suspended solids from a water stream containing these contaminants.

A.5.3. Reverse osmosis

The reverse osmosis process uses a reverse osmosis membrane. A reverse osmosis membrane has a thin microporous surface that rejects impurities, but allows water to pass through. The purity of the product water depends on the purity of the inlet water. The purity of the reverse osmosis product water is typically 95% higher than the purity of the feed water. Reverse osmosis requires external pressure to reverse natural osmotic flow. Pressure is applied to the more concentrated (feed water) side of the membrane (Williams 2003).

A.5.4. Lime softening

Lime softening, also referred to as cold lime process, is often used to reduce the hardness of water and sometimes to enhance clarification prior to filtration. Lime is added to water to reduce bicarbonate hardness by precipitation of calcium alkalinity as calcium carbonate and magnesium alkalinity as magnesium hydroxide.

A.5.5. Using sulfonated waste polystyrene

Polystyrene such as Styrofoam, coffee cups, and insulators are sulfonated to create a resin that can be used to soften hard water.

After sulfonation, the sulfonated polystyrene will be converted to its Na+ form for the ion exchange. The resin will be placed in the hard water sample and agitated for two hours under room temperature.

I. Bekri-Abbes, S. Bayoudh, and M. Baklouti conducted the study on the removal of hardness of water using sulfonated waste plastic. Their results showed that the value of the exchange capacity of the sulfonated polystyrene are close to the exchange capacities of membranes, slightly higher than natural organic exchangers such as smectite clays and lower than the commercial organic exchange resin.

In the last part of their paper, they mentioned their intent to study in further research the possibility of regenerating the resin after exchange.

B. Polystyrene

B.1. Definition

Polystyrene is produced from styrene through free radical vinyl polymerization. It is composed of a long chain of hydrocarbons with a phenyl group attached to every other carbon atom. Polystyrene products are 5% styrene while the rest is air.

Polystyrene can be an electron donor or acceptor. Therefore, it can be polymerized by cationic, anionic, and radical mechanism or by coordination propagation step. Polystyrene can be used as food containers for thermal insulation. It is also used in furniture, packaging, appliances, automobiles, construction, radios, televisions, toys, house ware items, and luggage (Rodriguez and Ferdinand 2003).

B.2. Properties

B.2.1. Size/Surface area

Diameter also determines surface area of a particle Small-diameter spheres present more surface area per unit weight, while larger spheres present more surface area per bead. Size also effects ease of handling, process considerations (such as the method used for separations [centrifugation, dialysis, filtration]) and the amount of reagent needed for coating (Polysciences, Inc).

B.2.1.1. Determination of size/surface area

Using this equation: Surface area = 4(pi)r^2

The unique form of the polymer complicates the determination of the surface area of polystyrene spheres. These beads are made by the formation of many single chain polymers, which may be likened to a ball of wool. Thus, the surface area will be much greater than that predicted by the simple formula. This is particularly important for protein binding applications and charge calculations (Polysciences, Inc).

B.2.2. Water Capacity/Water uptake

The water uptake and IEC value of the sulfonated membrane increases as sulfonation is increased (Naim, Ismail, Saida, and Saion).

The increase in water uptake of membranes is essential to improve proton conductivity (Naim, Ismail, Saida, and Saion).

B.2.2.1. Determination of water capacity

The method to be used to determine water capacity is the Karl Fischer Method. The Karl Fischer Method or Karl Fischer Titration is a direct method that is almost specific for water. The method is especially useful for low moisture levels (<1%), and levels <0.01% are achievable. The Karl Fischer Titration method is especially useful for samples that may be high in sugar, or high in both reducing sugar and protein (Ruiz 2001).

Unlike gravimetric methods, the Karl Fischer titration does not provide a dried sample that may be used for further tests (Ruiz 2001).

B.2.3. Porosity

In the early work on ion-exchange resins, the space between the network chains in a swollen gel available for the transfer of solutes was defined as 'porosity' or 'molecular porosity'. However, this term is clearly misleading because the distance between the chains cannot be measured independently and it varies between zero and several nanometers depending on the external conditions (Okay 2000).

B.2.4. Ion exchange capacity

In general terms, the capacity of an ion exchange resin can be expressed as the quantity of ions that can be taken up by a specific volume of the resin. This would be expressed in quantity-per-unit volume, such as kilograins per cubic foot (Kgr/ft3), milli-equivalents per milliliter (meq/mL), which also equals equivalents per liter (eq/L). For the record, for a softener, 1 eq/L = 21.87 Kgr/ft 3. 1.0 grains per gallon = 17.1 ppm of substance expressed as calcium carbonate (Michaud 2011).

B.2.4.1. Determination of ion exchange capacity

The method used for measuring the ion exchange capacity is acid-base titration (Marek, Benes, and Jelinek).

The ion exchange capacity (with unit of mmol/g of dry polymer) of sulfonated polystyrene was determined by measuring the concentration of H^+ that was exchanged with Na^+ when acid-form of sulfonated polystyrene was equilibrated with NaCl solution.

Fischer's titration method was used to measure the ionic exchange capacity (Shin, Kim, Lee, and Suh 2004).

The method is a titration of water with an anhydrous methanol solution containing iodine, sulfur dioxide, and excess pyridine (Ruiz 2001).

C. Sulfonation

C.1. Definition

Sulfonation is defined as a substitution reaction used to attach the SO_3 group on a molecule of an organic compound via chemical bond to carbon, or less frequently to a nitrogen atom of the organic compound (Bukukyagci 2004).

Sulfonation is the process wherein the polystyrene will be introduced to a sulfonating reagent and an anionic mechanism would occur.

C.2. Factors that affect sulfonation

Studies regarding sulfonating polystyrene manipulate different factors during sulfonation. These include the concentration, the temperature, and others

C.2.1. Temperature

Different research studies use different temperatures when sulfonating polystyrene. Examples are as follows:

In the study conducted by Bekri-Abbes, Bayoudh, and Baklouti, they varied the temperatures in the sulfonation process; namely: 40°, 50°, and 60° Celsius.

In the study of Martins et al., the reaction mixture was maintained at 40° Celsius.

In the study of J.-P. Shin et al., the PS and PTFE was treated at 90° Celsius.

In the study of Lee W, Gil S, Lee H, and Kim H, the temperature during sulfonation was 60°.

It was also mentioned in the study of Bekri-Abbes, Bayoudh, and Baklouti that the time and temperature were varied when the sulfuric acid was left to react under agitation.

C.2.2. Time of sulfonation

Different research studies use different times of sulfonation when sulfonating polystyrene. Examples are as follows:

In the study conducted by Bekri-Abbes, Bayoudh, and Baklouti, they varied the periods of sulfonation; namely: 1.5 hours, 2 hours, and 4 hours.

In the study of Martins et al., the reaction was stirred for 2 hours.

In the study of J.-P. Shin et al., the PS and PTFE was treated for 12 hours under a nitrogen atmosphere.

In the study of Lee W, Gil S, Lee H, and Kim H, the time of sulfonation was 3 hours.

The results of Bekri-Abbes et al. have shown that the best values have been obtained for samples treated at 40°C for 4 h and 60°C for 1.5 h (respectively 16% and 17%).

C.2.3. Sulfonation Reagents

Sulfonation reagents

Increase of molar ratio of the sulfonating agent to polysulfone repeats unit lead to an increasing degree of sulfonation (Naim, Ismail, Saidi, and Saion).

Compounds such as H_2SO_4, SO_3, and its complexes, such as acyl and alkyl sulfates and chlorosulfonic acid are commonly used as sulfonating agents (Martins, Ruggeri, and Paoli 2003).

C.2.3.1. Sulfuric acid

The study of Bekri-Abbes, Bayoudh, and Baklouti used dense sulfuric acid in their experiments.

The study of Pentamwa, Thipthara, and Nuangon used dense sulfuric acid in their experiments in reference to the study of Bekri-Abbes et al.

C.2.3.2. Sulfur trioxide / Sulfuric anhydride

The studies of Noshay and Robeson, Johnson et al., O'gara et al., Arnold and Assink, Pintauro et al., all used sulfur trioxide in their experiments (Naim and others).

C.2.3.3. Triethylphosphate

The studies of Noshay and Robeson, and Johnson et al. sulfonated polysulfone with the use of sulfur trioxide with triethylphosphate (Naim and others).

C.2.3.4. Chlorosulfonic acid

The study of Abdel-Hady, El-Toony, Abdel-Hamed, and Hammam used chlorosulfonic acid and 1,2 dichloroethane with ratio of 1:1 in ice bath for interval times (hours).

The study of Quentin sulfonated polysulfone with chlorosulfonic acid (Naim and others).

The study of Sivashinsky sulfonated polysulfone with chlorosulfonic acid (Naim and others).

J.P. Shin et al. did their treatment with a solution of chlorosulfonic acid and dichloroethane.

C.2.3.5. Acetyl sulfate complexes

Matowski et al also prepared lightly sulfonated polystyrene by using acetyl sulfate complexes as sulfonation reagent (Martins, Ruggeri, and Paoli 2003).

The study of Lee, Gil, Lee, and Kim added freshly prepared acetyl sulfate to dichloroethane.

The study of Martins, Ruggeri, and Paoli, polystyrene was sulfonated with acetyl sulfate according to their patented procedure. The new procedure was similar to that of Matowski et al.

C.2.4. Size/surface area of the polystyrene

It has shown that degree of sulfonation increased intensively when dimension of particles decreased. In fact, by decreasing the dimension of particles, the efficiency of the contact between the polystyrene and the sulfonating agent can be remarkably increased (Bekri-Abbes, Bayoudh, Baklouti 2008).

Chapter 3
METHODOLOGY

Overview of the Study

The main purpose of this study was to determine what combination of temperature, time duration, and concentration of sulfuric acid during the sulfonation of polystyrene will give the most favorable hardness removal capacity of the sulfonated polystyrene. We manipulated the temperatures, time durations, and concentrations of the polystyrene during sulfonation.

Materials and Equipment

A. Sulfonation of the polystyrene

The materials and equipment used in the sulfonation of polystyrene are the following: 65 g of polystyrene balls/pellets, weighing scale, Grade 2294 filter paper, funnel, 50 mL, 100 mL, and 250 mL beaker, magnetic hot plate stirrer, pH meter, oven, and thermometer. mL beaker, a stir plate, a magnetic hot plate stirrer, a pH meter, an oven, and a thermometer.

The chemical reagents utilized are the following: 10 L sulfuric acid and 20 L of distilled water. We also used an extra 5 L of sulfuric acid.

C. Hard water sample preparation

The materials and equipment used in the hard water sample preparation are a 500 mL beaker and a magnetic hot plate stirrer.

The chemicals and reagents utilized were 150 mg of magnesium salt and 150 mg of calcium salt for every 1 L of distilled water. We prepared 10 L of the hard water sample.

D. Hardness determination

The materials and equipment used for the determination of hardness are as follows: 25 mL buret, 250 mL beaker, buret clamp, ring stand, stir plate, bar and retriever, pH meter and electrode, 125 mL Erlenmeyer flask, and a 25 mL pipet and pipet bulb.

The chemicals and reagents utilized are the following: Eriochrome black T indicator, pH 7 and 10 buffer, the hard water solution prepared, standardized 0.01 M EDTA, and distilled water.

Methods

A. Sulfonation of the polystyrene

One manipulation of the sulfonated polystyrene 0.60 grams of polystyrene balls/pellets. The pellets were then transferred into the beaker. It was subjected to manipulations of temperature, time duration of sulfonation, and concentration of sulfuric acid. The four manipulations of temperature were 40, 60, 80, and 100° Celsius. The four manipulations of time duration of sulfonation were 1, 2, 3, and 4 hours. The four manipulations of the concentration were 40, 60, 80, and 100% Sulfuric acid. The sulfuric acid was diluted to get the said concentrations. The manipulations' groupings were determined in the data table. After, 300 mL of the sulfuric acid was poured into the beaker then agitated for the specified number of hours while subjected to a certain temperature. After the reaction was complete, the slurry was then filtered with a funnel and the filter paper. The granules was then washed with six 250 mL portions of distilled water. The sulfonated resin was then dried in an oven at 100°C for 2 hours.

A.1. Manipulations of the filter medium

Manipulations were done simultaneously but in different experiment set ups to save time since the method takes up a lot of time. There were 64 set ups of the sulfonated polystyrene.

A.1.1. Sulfuric acid concentrations

To manipulate the sulfuric acid concentrations, sulfuric acid was diluted with distilled water. The manipulations were 100% sulfuric acid, 80% sulfuric acid, 60% sulfuric acid, and 40% sulfuric acid.

For 100% sulfuric acid, the sulfuric acid was not diluted with water. For 80% sulfuric acid, 80 mL sulfuric acid was mixed with 20 mL distilled water. For 60%, 60 mL sulfuric acid was mixed with 40 mL distilled water. For 40% sulfuric acid, 40 mL sulfuric acid was mixed with 60 mL distilled water.

A.1.2. Temperature of sulfonation

The temperature manipulations were 100°C, 80°C, 60°C, and 40°C. The beaker was placed in a heat stove where the temperature was changed when the reaction is sulfonating. Each experiment round differed with the temperature of sulfonation.

A.1.3. Time duration of sulfonation

Time manipulations were 1, 2, 3, and 4 hours. This was be the time of sulfonation or the time while the sulfonated polystyrene was agitated in sulfuric acid.

B. Hard water sample preparation

The hard water sample was made by dissolving 150 mg of calcium salt and another 150 mg of magnesium salt in 1 liter of distilled water. This hard water was used to test the sulfonated polystyrene.

C. Softening

The hard water sample prepared was agitated in with sulfonated polystyrene for one minute in room temperature. This was done with all 64 set ups.

D. Hardness determination, Ethylenediaminetetraacetic acid (EDTA) titration

An Erlenmeyer flask was prepared with 20 mL of the hard water solution. A few drops of Eriochrome Black T indicator and buffer hardness was then be added to the solution. The solution was then titrated with standardized EDTA two drops at a time until the endpoint color turned to blue.

Data Analysis

The hardness concentrations (ppm) and other water quality parameters of the sample were determined before and after filtration. The concentrations were then calculated to come up with their removal percentage. Data was descriptively analyzed to show the most favorable results.

Safety Precautions, Handling, and Disposal

Since sulfuric acid, a hazardous chemical, was used for sulfonation, protective clothing such as surgical gloves and laboratory masks were used. The workplace was also be appropriate with adequate ventilation. Hands were washed before and after handling chemicals. Also, the researcher avoided direct contact with the chemicals. When handling the hazardous chemicals, the researcher avoided working near ignition sources. When disposing chemicals, the chemicals were disposed in their proper containers and resealed.

Chapter 4
RESULTS AND DISCUSSION

This study aimed to determine the water hardness before and after filtration using sulfonated polystyrene subjected to various conditions. The objectives of this study are to measure the hardness (ppm) of hard water before and after filtration and to calculate the percent removal of water hardness using sulfonated polystyrene subjected to various conditions.

A. Results

The tables below show the different hardness concentrations (ppm) determined from the treated hard water in different conditions (acid concentration (40%, 60%, 80%, 100%), temperature (40°C, 60°C, 80°C, 100°C), and time duration (1, 2, 3, 4 hours) of sulfonation). Another table also shows the removal capacity of the different conditions subjected to the polystyrene.

A.1. Hardness concentrations of water after filtration with sulfonated polystyrene

Generally, the results show that the sulfonated polystyrene causes the hardness of the water to increase ranging from 45 ppm as the lowest to 11500 ppm as the highest. The results also show that there is no significant pattern occurring in the different conditions of sulfonation. The two highest results from the data are from the two-hour, 100% concentration conditions (Table 2).

A.2. Hardness removal capacity of sulfonated polystyrene

To calculate for the hardness removal capacity of the sulfonated polystyrene, we used the following formula:

$$\text{percent removal} = \frac{\text{Initial hardness-hardness concentration after filtration}}{\text{initial hardness}} \times 100\%$$

Negative results show the percent increase of the hardness of the water while the positive results show the percent decrease of the hardness. Only three conditions decreased hardness while one condition maintained the hardness and left it unaffected.

The highest removal capacity recorded is the condition 2 hours, 80%, 40°C having a removal capacity of 24.20%. The highest percent increase of hardness is the condition 2 hours, 100%, 100°C having a percent increase of 49900% (Table 3).

A.3. Conditions

A.3.1. Sulfuric acid concentrations

The highest percent increase of hardness can be found within the 100% concentration condition. The highest percent decrease can be found within the 80% concentration condition although some percent decrease can also be found within the 40% and 60% concentrations.

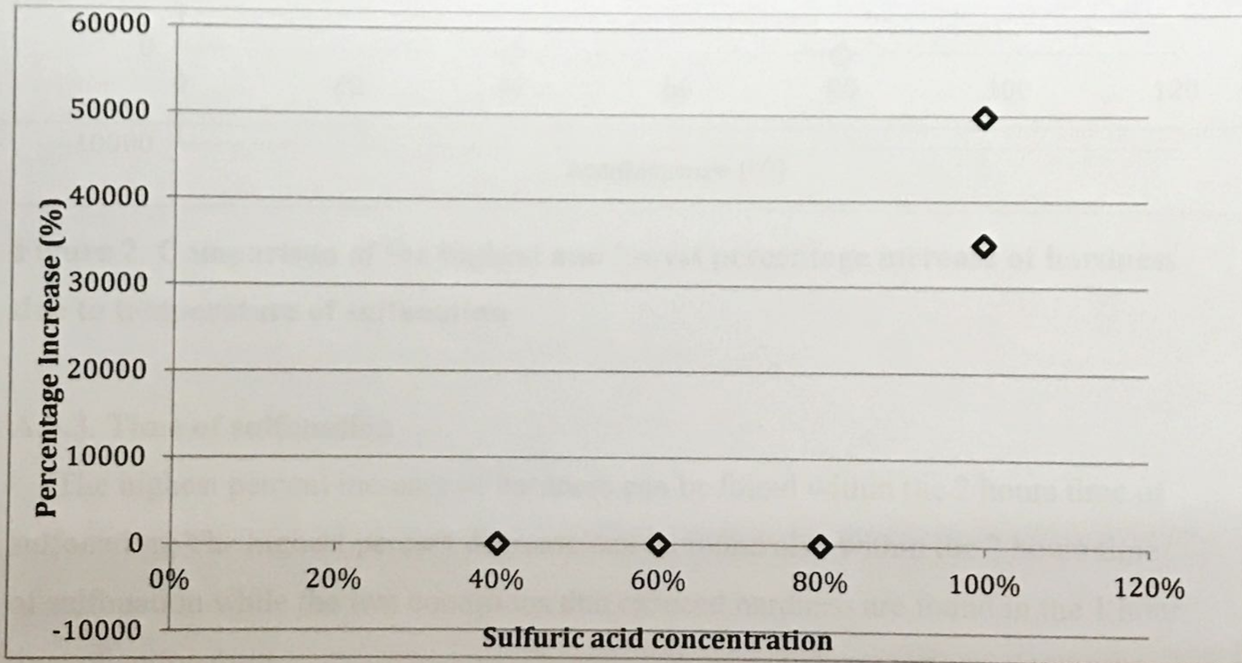

Figure 1. Comparison of the highest and lowest percent increase of hardness due to sulfuric acid concentration

A.3.2. Temperature of sulfonation

The highest percent increase of hardness can be found within the 100°C temperatures. The highest percent decrease can be found within the 40°C temperatures where the two conditions that decreased the hardness can be seen.

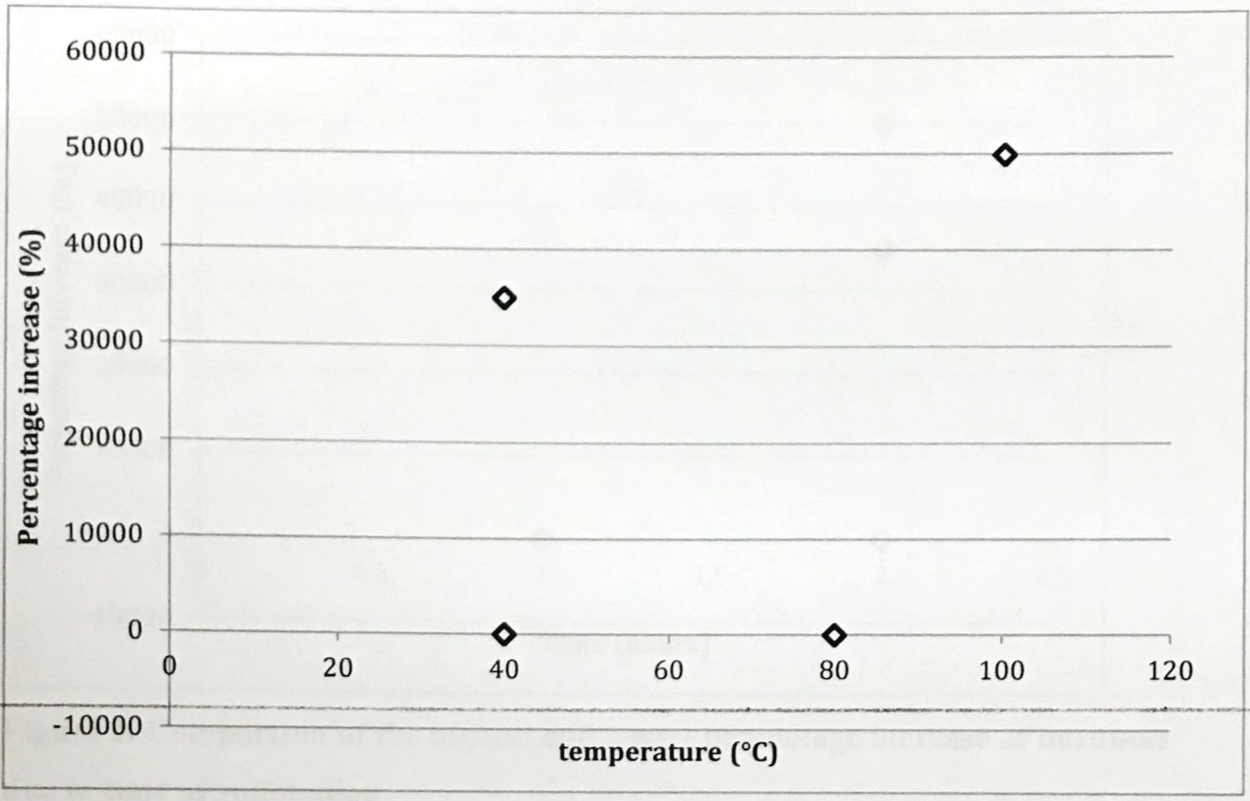

Figure 2. Comparison of the highest and lowest percentage increase of hardness due to temperature of sulfonation

A.3.3. Time of sulfonation

The highest percent increase of hardness can be found within the 2 hours time of sulfonation. The highest percent decrease can be found also within the 2 hours time of sulfonation while the two conditions that reduced hardness are found in the 1 hour time of sulfonation.

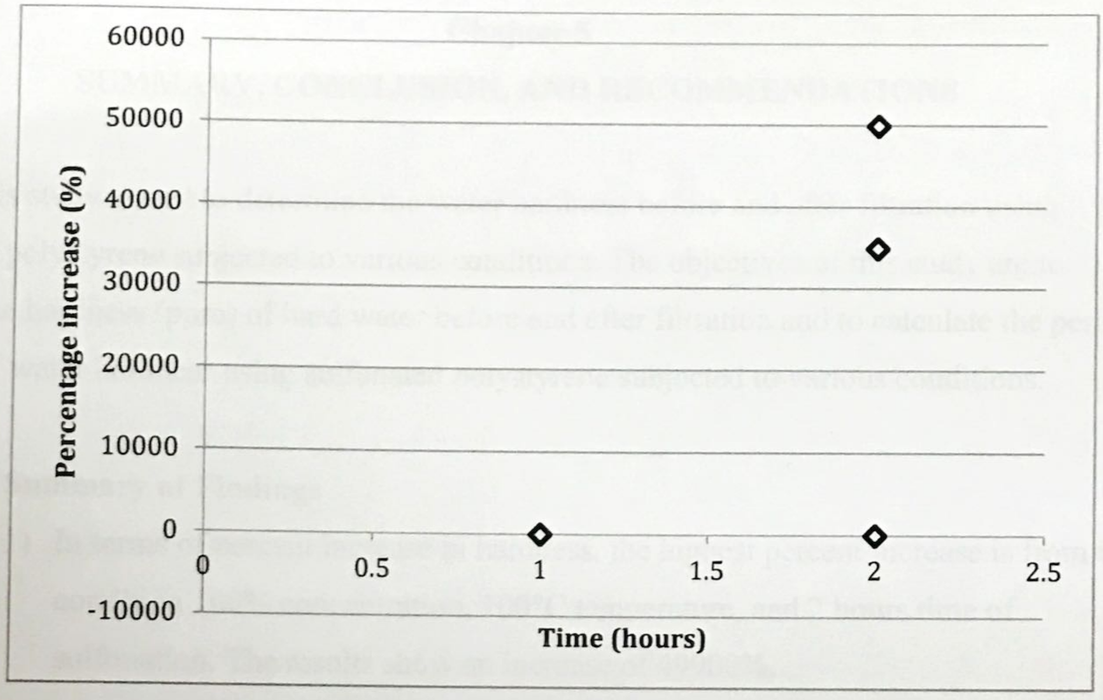

Figure 3. Comparison of the highest and lowest percentage increase of hardness due to time of sulfonation

Chapter 5

SUMMARY, CONCLUSION, AND RECOMMENDATIONS

This study aimed to determine the water hardness before and after filtration using sulfonated polystyrene subjected to various conditions. The objectives of this study are to measure the hardness (ppm) of hard water before and after filtration and to calculate the percent removal of water hardness using sulfonated polystyrene subjected to various conditions.

A. Summary of Findings

1) In terms of percent increase in hardness, the highest percent increase is from the condition 100% concentration, 100°C temperature, and 2 hours time of sulfonation. The results show an increase of 49900%.
2) The highest percent decrease in hardness was shown in the condition 80% concentration, 40°C temperature, and 2 hours time of sulfonation. The results show a decrease of 24.20%.
3) The highest increase of hardness can be seen within the 100% concentration, 100°C temperature, and 2 hours time of sulfonation separately.
4) The highest decrease of hardness can be seen within the 80% concentration, 40°C temperature, and 1 hour time of sulfonation separately.
5) Generally, the results show that the sulfonated polystyrene increases the hardness of water significantly.
6) It was also found that the normalization process, which should have included the use of NaCl, should have been performed in order for the ion-exchange process to have taken place.
7) The H_2SO_4 might have had increased the pH of the hard water solution, therefore requiring more EDTA solution to be added.

B. Conclusion

Since the normalization process was not performed, it can be concluded that the H_2SO_3 must have added to the pH of the solution, therefore indirectly increasing the EDTA requirement for the solution to change from red to blue. The increase in the hardness of the water was due to the lack of Na^+ and Cl^- ions to interact with the calcium and magnesium ions.

C. Recommendations

Based on the observations and findings, the following are recommended for future studies, not in particular order:

1) To perform the normalization process
2) A follow-up study using a different acid instead of sulfuric acid
3) The use of hard water collected from wells or natural water sources
4) A study that would use an open flame oven instead of the typical heating oven to get the burnt silver color of the polystyrene
5) The use of coffee cups or Styrofoam packaging for sulfonation
6) The use of different sizes of polystyrene

LITERATURE CITED

Abdel-Hady EE and others. 2011. Grafting of styrene onto commercial PTFE membrane and sulfonation for possible use in fuel cell [internet]. [cited 2012 July 10]. Available from: http://www.physicsegypt.org/epc10/epc1026.pdf

Alchin, David. Ion Exchange Resins [Internet]. [Place of publication unknown]: [cited 2012 Feb 22]. Available from: http://nzic.org.nz/ChemProcesses/water/13D.pdf

Bekri-Abbes, Bayoudh, Baklouti. The removal of hardness of water using sulfonated waste plastic [Internet]. [Place of publication unknown]: [updated 2008; cited 2011]. Available from: http:// desline.com/articoli/9028.pdf

Brijmohan and others. Synthesis and Characterization of Cross-linked Sulfonated Polystyrene Nanoparticles [Internet]. [Place of publication unknown]: [updated 2005; cited 2012 Feb 12]. Available from: http://www.polyeng.uakron.edu/weisspublications/smita%20IECR%202005.pdf

Bruttel P, Schlink R. 2006. Water determination by Karl Fischer titration [internet]. [cited 2012 July 11]. Available from: http://www.metrohm.hu/DownloadDocs/mono_8_026_5013.pdf

Buyukyagci A. 2004. Synthesis and characterization of monoacetylferrocene added sulfonated polystyrene ionomers [ineternet]. [cited 2012 July 9]. Available from: http://etd.lib.metu.edu.tr/upload/3/1108026/index.pdf

DeLuca NW. 2008. Nafion blend membranes for the direct methanol fuel cell [internet]. [cited 2012 July 11]. Available from: http://idea.library.drexel.edu/bitstream/1860/2710/1/DeLuca_Nicholas.pdf

Fisher and others. Reverse Osmosis (R/O): How It Works [Internet]. [Place of publication unknown]: [cited 2012 Feb 22]. Available from: http://www.ag.unr.edu/walker/WebPublications/FS-05-08CSREES.pdf

Foster N. 1997. Sulfonation and sulfation process [internet]. [cited 2012 July 10]. Available from: http://www.chemithon.com/Resources/pdfs/Technical_papers/Sulfo%20and%20Sulfa%201.pdf

Geotechnical Engineering Bureau. Geotechnical Test Method: Test method for determination of pH value of water or soil [Internet]. [Place of publication unknown]: [updated April 2007; cited 2012 Feb 22]. Available from: https://www.dot.ny.gov/divisions/engineering/technical-services/technical-services-repository/GTM-24b.pdf

Hairston J. Typical Contaminants and Problems Water Hardness [Internet]. [Place of publication unknown]: [updated 2001; cited 2012 Feb 22]. Available from: http://www.aces.edu/pubs/docs/A/ANR-0790/WQ2.3.2.pdf

Heidekamp and Lamley. 2008. Water Bulletin [Internet]. [Place of publication unknown]: Cornell.edu; [updated 2008; cited 2012 Feb 22]. Available from: http://waterquality.cce.cornell.edu/publications/CCEWQ-50-HardWater.pdf

Lee W, Gil SC, Kim H. 2009. Improved mechanical strength of partially sulfonated polystyrene-poly(di methylsiloxane) block copolymer proton exchange membranes by nanoscale sequestration of thermally crosslinked silicone [internet]. [cited 2012 July 10]. Available from: http://www.cheric.org/PDF/MMR/MR17/MR17-6-0451.pdf

Marek J, Benes M, Jelinek L. Cation and anion exchangers from nanofibrous polystyrene for fast water treatment [internet]. [cited 2012 July 10]. Available from: http://www.elmarco.cz/upload/soubory/dokumenty/72-1-7-nanocon-roznov-09.pdf

Martins C, Rugerri G, De Paoli M. 2003. Synthesis in pilot plant scale and physical properties of sulfonated polystyrene [internet]. [cited 2012 July 2]. 14(5). Available from: http://www.scielo.br/scielo.php?pid=S0103-50532003000500015&script=sci_arttext

Naim R and others. Development of sulfonated polysulfone membranes as a material for proton exchange membrane (PEM) [internet]. [cited 2012 July 10]. Available from: http://eprints.utm.my/1037/1/Rosmawati2004_Developmentofsulfonatedpolysulfonemembranes.pdf

Okay O. Macroporous copolymer networks [internet]. [cited 2012 July 11]. Available from: http://www.kimya.itu.edu.tr/ookay/00review.pdf

Pentamwa P, Thipthara W, Nuangon S. 2011. Hardness removal from groundwater by synthetic resin from waste plastics [internet]. [cited 2012 July 10]. Available from: http://www.ipcbee.com/vol19/12-ICECS2011R00021.pdf

Ruiz R. 2001. Karl Fischer titration [internet]. [cited 2012 June 30]. Available from: http://www.nshtvn.org/ebook/molbio/Current%20Protocols/CPFAC/faa0102.pdf

Safe Drinking Water Foundation. Ultrafiltration, Nanofiltration and Reverse Osmosis [Internet]. [Place of publication unknown]: [cited 2012 Feb 22]. Available from: http://www.safewater.org/PDFS/resourcesknowthefacts/Ultrafiltration_Nano_ReverseOsm.pdf

Salager J. 2002. Surfactants types and uses [internet]. [cited 2012 July 10]. Available from: http://nanoparticles.org/pdf/Salager-E300A.pdf
Schramm L. Surfactants: Fundamentals and application in the petroleum industry [internet]. [cited 2012 July 11]. Available from: http://catdir.loc.gov/catdir/samples/cam032/99015820.pdf

Shin J, Chuang B, Kim J. 2004. Sulfonated polystyrene/PTFE composite membranes [internet]. [cited 2012 June 30]. Available from: http://infochem.hanyang.ac.kr/publications/pdf/JOMS_050128.pdf

Weiss RA, Turner SR, Lundberg RD. Sulfonated polystyrene ionomers prepared by emulsion copolymerization of styrene and sofium styrene sulfonate [internet]. [cited 2012 July 9]. Available from: http://www.poly-eng.uakron.edu/weisspublications/Turner%20Weiss%20Lundberg%20JPS%201985.p525.pdf

World Health Organization. 2011. Hardness in Drinking-water [Internet]. [Place of publication unknown]: [updated 2011; cited 2012 Feb 22]. Available from: http://www.who.int/water_sanitation_health/dwq/chemicals/hardness.pdf

APPENDIX A

RAW DATA

EDTA volume (mL) of water before filtration

	EDTA VOLUME (mL)			
1 HOUR				
	40%	**60%**	**80%**	**100%**
40°C	6.2	6.2	8.1	9.7
60°C	6.2	7.6	9.7	7.6
80°C	12.6	4.6	3.8	12.6
100°C	3.1	6.2	6.2	12.6
2 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	12.6	3.1	6.2	3.1
60°C	6.2	12.6	3.8	6.2
80°C	6.2	6.2	6.2	6.2
100°C	6.2	3.1	12.6	2.3
3 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	6.2	12.8	2.3	12.6
60°C	6.2	3.1	3.1	6.2
80°C	12.6	6.2	3.1	3.1
100°C	12.6	6.2	3.1	12.6
4 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	3.1	2.3	8.1	6.2
60°C	3.1	3.1	6.2	3.1
80°C	3.1	3.1	3.1	6.2
100°C	3.1		6.2	12.6

EDTA volume (mL) of water after filtration

EDTA VOLUME (mL)				
1 HOUR				
	40%	**60%**	**80%**	**100%**
40°C	18	5.7	11.8	9.7
60°C	8	17.6	9.9	8
80°C	12.1	7.1	4.5	234.6
100°C	317.6	9.4	16.1	76
2 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	22	866.2	4.7	1085.9
60°C	13.6	14.4	5.7	18.7
80°C	26.6	54.3	5.8	193
100°C	24	122.2	66.3	1150
3 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	22.4	32.1	5.6	129.2
60°C	10.2	58.3	7.8	78.1
80°C	16.8	22	8.3	6.2
100°C	111.9	21.2	9.2	17.1
4 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	8.2	108.6	14.1	145.8
60°C	7.8	10.5	6	133.3
80°C	9.7	13.7	224.6	143.9
100°C	12.2		55.1	149.9

Initial hardness of water (ppm)

INITIAL HARDNESS (ppm)				
1 HOUR				
	40%	**60%**	**80%**	**100%**
40°C	62	62	81	97
60°C	62	76	97	76
80°C	126	46	38	126
100°C	31	62	62	126
2 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	126	31	62	31
60°C	62	126	38	62
80°C	62	62	62	62
100°C	62	31	126	23
3 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	62	128	23	126
60°C	62	31	31	62
80°C	126	62	31	31
100°C	126	62	31	126
4 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	31	23	81	62
60°C	31	31	62	31
80°C	31	31	31	62
100°C	31		62	126

Hardness of water (mL) after filtration

HARDNESS (EDTA VOLUME - INITIAL HARDNESS) mL				
1 HOUR				
	40%	60%	80%	100%
40°C	11.8	-0.5	3.7	0
60°C	1.8	10	0.2	0.4
80°C	-0.5	2.5	0.7	222
100°C	314.5	3.2	9.9	63.4
2 HOURS				
	40%	60%	80%	100%
40°C	9.4	863.1	-1.5	1082.8
60°C	7.4	1.8	1.9	12.5
80°C	20.4	48.1	-0.4	186.8
100°C	17.8	119.1	53.7	1147.7
3 HOURS				
	40%	60%	80%	100%
40°C	16.2	19.3	3.3	116.6
60°C	4	55.2	4.7	71.9
80°C	4.2	15.8	5.2	3.1
100°C	99.3	15	6.1	4.5
4 HOURS				
	40%	60%	80%	100%
40°C	5.1	106.3	6	139.6
60°C	4.7	7.4	-0.2	130.2
80°C	6.6	10.6	221.5	137.7
100°C	9.1		48.9	137.3

Hardness of water (ppm) after filtration

HARDNESS (EDTA VOLUME - INITIAL HARDNESS) in ppm				
1 HOUR				
	40%	**60%**	**80%**	**100%**
40°C	118	-5	37	0
60°C	18	100	2	4
80°C	-5	25	7	2220
100°C	3145	32	99	634
2 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	94	8631	-15	10828
60°C	74	18	19	125
80°C	204	481	-4	1868
100°C	178	1191	537	11477
3 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	162	193	33	1166
60°C	40	552	47	719
80°C	42	158	52	31
100°C	993	150	61	45
4 HOURS				
	40%	**60%**	**80%**	**100%**
40°C	51	1063	60	1396
60°C	47	74	-2	1302
80°C	66	106	2215	1377
100°C	91		489	1373

Removal percentage of sulfonated polystyrene

Removal Percentage				
1 HOUR				
	40%	60%	80%	100%
40°C	-190.30%	8.10%	-45.70%	0.00%
60°C	-29.00%	-131.60%	-2.10%	-5.30%
80°C	3.97%	-54.30%	-18.40%	-1762.00%
100°C	-10145.00%	-51.60%	-159.70%	-503.20%
2 HOURS				
	40%	60%	80%	100%
40°C	-74.60%	-27842.00%	24.20%	-34929.00%
60°C	-119.40%	-14.30%	-50.00%	-201.60%
80°C	-329.00%	-775.80%	-6.50%	-3013.00%
100°C	-287.10%	-3842.00%	-426.20%	-49900.00%
3 HOURS				
	40%	60%	80%	100%
40°C	-261.30%	-150.80%	-143.50%	-925.00%
60°C	-64.50%	-1780.60%	-151.60%	-1159.70%
80°C	-33.33%	-254.80%	-167.70%	-100.00%
100°C	-788.10%	-241.90%	-196.80%	-35.70%
4 HOURS				
	40%	60%	80%	100%
40°C	-164.50%	-4622.00%	-74.10%	-2251.60%
60°C	-151.60%	-238.70%	-3.20%	-4200.00%
80°C	-212.90%	-341.90%	-7145.00%	-2221.00%
100°C	-293.50%		-788.70%	-1089.70%

APPENDIX B

CALCULATIONS

Solving the multiplying factor in determining hardness

given: 3.1 mL EDTA
0.02N EDTA
EDTA: 2 equivalents/mol
water sample volume = 100 mL

concentration of EDTA:

$$0.02\,N = 0.02\,\frac{\text{equivalents}}{L} \cdot \frac{\text{mol}}{2\,\text{equivalents}} = 0.01\,M$$

equation 8; equation 9; equation 10

$$\frac{(0.0031\,L)\left(\frac{0.01\,mol}{L}\right)\left(\frac{1000\,mmol}{1\,mol}\right)}{100\,mL}\left(\frac{1000\,mL}{1\,L}\right) = 0.31\,\frac{mmol}{L}\left(\frac{1\,mol}{1000\,mmol}\right) = 3.1\times10^{-4}\,\frac{mol}{L}$$

molecular mass:

$$\left(\frac{100\,g\,CaCO_3}{mol}\right)\left(\frac{1000\,mg}{1\,g}\right)\left(\frac{0.31\,mmol}{L}\right)\left(\frac{1\,mol}{1000\,mmol}\right) = 31\,\frac{mg}{L}$$

$$\left(\frac{31\,mg}{L}\right)\left(\frac{1\,L\,H_2O}{1000\,mL}\right) = 0.031\,\frac{mg}{mL}$$

equation 12

$$0.031\,\frac{mg}{mL}\left(\frac{1\,mL}{g}\right)\left(\frac{1\,g}{1000\,mg}\right) = 3.1\times10^{-5} \times 1\times10^{6} = 31\,ppm$$

density; million; basically multiplied by 10.

APPENDIX C

PLATES

Plate 1. Preparation of the buffer hardness

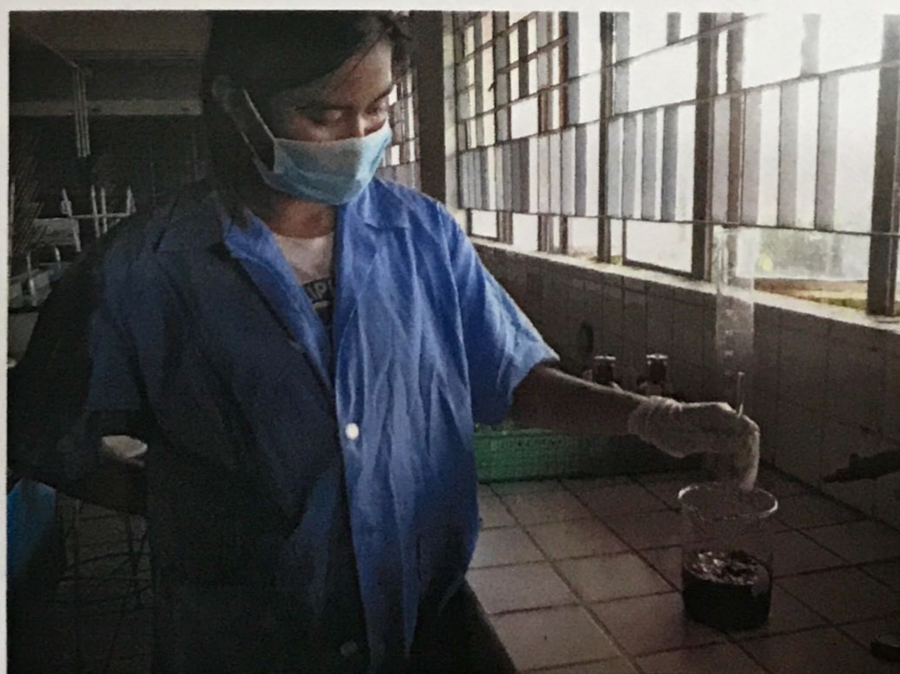

Plate 2. Preparation of the Eriochrome Black-T

Plate 3. Agitation of the set-ups, sulfonation

Plate 4. Oven-drying the sulfonated polystyrene

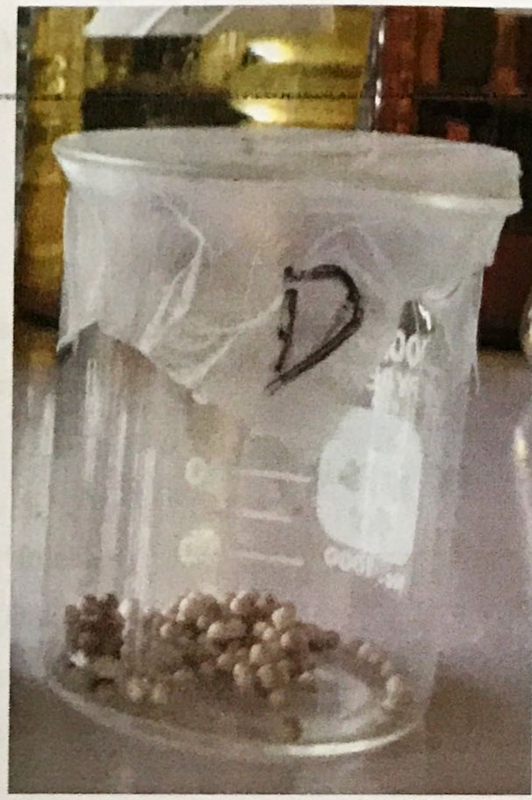

Plate 5. Sample of the sulfonated polystyrene

APPENDIX D

LIQUIDATION REPORT FOR THE PFIZER GRANT

Summary of Expenses

A. Materials	
1. Polystyrene pellets (Styrofoam)	359.00
2. Parafilm sealing tape	2,100.00
3. Filter paper	800.00
B. Chemicals	
1. Sulfuric acid (Unichem)	3,400.00
2. Sulfuric acid (Duksan)	3,200.00
3. Distilled water	1,200.00
C. Laboratory Set-up	
1. Burette clamp	480.00
2. Wash bottle	90.00
3. Glass stirring rod	45.00
4. 100 mL beakers	500.00
5. Aspirator	45.00

TOTAL: Php 12,219.00

List of Receipts

1. **Payee:** Harnwell Chemicals Corporation
   Date of Receipt: (no date – receipt no. 10863)
   Amount: Php 3,400.00
   Details: Four (4) x 2.5 L sulfuric acid (Unichem) @ Php 850.00 each

2. **Payee:** Harnwell Chemicals Corporation
   Date of Receipt: Dccember 28, 2012
   Amount: Php 3,200.00
   Details: Four (4) x 2.5 L sulfuric acid (Duksan) @ Php 800.00 each

3. **Payee:** Josmef Pharmacy
   Date of Receipt: March 19, 2013
   Amount: Php 45.00
   Details: One (1) Air syringe (aspirator) @ Php 45.00

4. **Payee:** Roest Marketing
   Date of Receipt: March 19, 2013
   Amount: Php 135.00
   Details: One (1) Stirring rod @ Php 45.00
   One (1) Wash bottle @ Php 90.00

Inv. No.	Amount	Discount Witholding Tax	Net
PAYMENT FOR			
4X2.5 LITERS SULFURIC			
ACID (UNICHEM)			

Cash ✓ P 3,400.00
Checked No. P
Total P

Princess and Me Enterprise Company
3272-D Kalayaan Ave. cor Zapote St., Makati City
100 Bklts. (50 x 3) 10001-15000
BIR Permit No. OCN8AU0000413116 2/15/10

HARNWELL CHEMICALS CORPORATION

(CEBU NORTH BRANCH) * ACCREDITATION A-32-019-85
USP Bldg., 220 Manalili St., Cebu City North
Tel. No. 253-2281 / 254-1339 FAX No. 254-3658
TIN 000-163-731-001 VAT

OFFICIAL RECEIPT № 10863

Date ...., 20 ...

Business Name / Style RECEIVED FROM BEA CUADRA
Address PHILSCI CAMPUS ILOILO
TIN:
the sum of Pesos THREE THOUSAND FOUR HUNDRED PESOS ONLY (P 3,400.00)

being payment (in full/on a/c) for our invoices listed.

TOTAL SALE
ADD VAT
LESS W/TAX
TOTAL PAYMENT

HARNWELL CHEMICALS CORPORATION

By: ....
Authorized Signature

HARNWELL Chemicals Corporation

USP BLDG., 220 MANALILI ST., CEBU CITY
NORTH CEBU 6000 (Branch)
ACCREDITATION A-32-019-85
Tels. 253-2281 ; 254-1339 Fax No. 254-3658
TIN : 000-163-731-001-VAT

SALES INVOICE

Nº 15527

#15527

SOLD TO: PHILIPPINE SCIENCE HIGH SCHOOL
ADDRESS: Iloilo City
BUSS. NAME/STYLE:

DATE: December 28, 2012
TERMS: 30 days
P.O. No.:
SALESMAN: ORVILLE
B/L No.:

SHIP TO: attn: MS. BEA CUADRA
TIN:

QUANTITY	UNIT	DESCRIPTION	UNIT PRICE	AMOUNT
4x2.5 lits.		Sulfuric acid, DUKSAN	₱ 800.00	₱ 3,200.00
		PESOS: THREE THOUSAND TWO HUNDRED ONLY. *		
			VAT SALES:	
			VAT EXEMPT SALE:	
			VAT ZERO RATED SALE:	
			TOTAL SALE:	2,857.15
			ADD. VAT	342.85

COMM. TAX No.	DATE	PLACE	TOTAL P	3,200.00

TERMS OR CONDITIONS

We/I hereby agree to pay the above amount at the date the terms specified. In case of default in payment at the time, we/I agree to pay interest at the rate of 1% per month from the date, and in case of suit for the collection of the amount and interest due. We/I agree to pay 25% of the amount due us for attorney's fees and cost of collection and that the suit shall be instituted in Cebu City, Philippines. Our responsibility ceases when merchandise is delivered to carrier in good order. Claims or loss and/or damage should be made against the transportation company. Returns for credit and/or adjustment claim must be made with 1 week after receipt of articles.

RECEIVED THE ABOVE GOODS IN GOOD ORDER AND CONDITIONS.

By: ______________________

CUSTOMER
SIGNATURE OVER PRINTED NAME

Princess and Me Enterprise Company
3272-D Kalayaan Ave., cor. Zapote St., Makati City
100 Bklts. (50x5) 15001-20000 BIR Permit No. 9AU0000413116 2/15/10

JOSMEF PHARMACY
Merly E. Ajayi - Prop.
Javellana - E. Lopez Street, Jaro, Iloilo City
TIN 183-772-161 VAT

CASH SALES INVOICE

No. 83486

SOLD TO: Bea cuadra   Date: 3-19-13
Bus. Name/Style
Address: TIN

DESCRIPTION	QTY.	UNIT COST	TOTAL
Air syringe	1	45	45

Gross Selling Price	45
VAT 12%	
Total Amount Payable	

SALES CLERK

ARMIX Copier Rentals, Services and Sales
Commission Civil Street, Jaro, Iloilo City
Auth. # 2AU0000750251 500bks. 50x2 75001- 100000 8/09/2012

ROEST MARKETING

ROMEO P. GRABATO - *Prop.*
Cor. E. Lopez - Mission Sts., Brgy. San Jose, Jaro, Iloilo City
Telefax 320-05-30 Tel. Nos. 329-25-80 ☎ 508-79-96 ☎ 509-3207
TIN 102-268-735 VAT

CASH SALES № 0014086

Date 3/19/13

Sold To: - Bea Cuadra

Bus. Name/Style: TIN:

Address: - La Paz IC

Qty.	Unit	ARTICLES	Unit Price	TOTAL
1	pc	Stirring Rod		45-00
1	"	wash bottle		90-00
			Gross Selling Price	120.53
			12% VAT	14.46
			Total Amount Payable ₱	135-00

MAKINAUGALINGON Printer & Bookbinder
251 Lopez Jaena St., Baluarte, Molo, Iloilo City
Auth. No. 2AU0000418524 1/7/10
200 Bks. 50x2 7,501-17,500

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Authorized Signature