

9-1-2013

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Molecular Imprint Polymerization for Caffeine Removal from Water Samples

Jake Letsinger and Dr. Jennifer Zemke

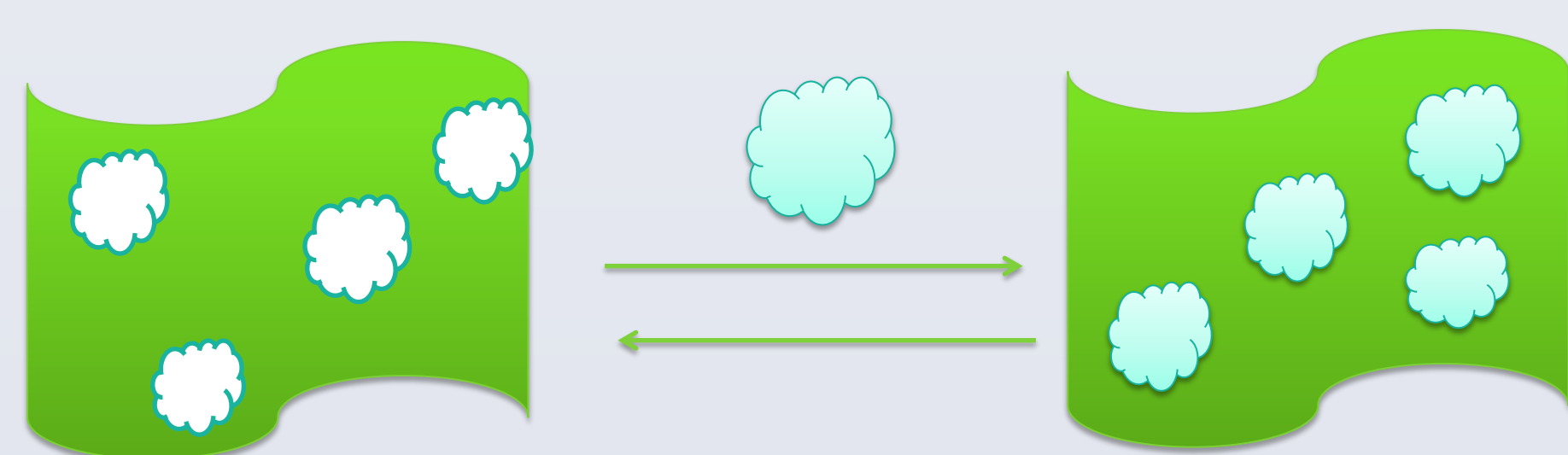
Department of Chemistry, Winona State University, Winona, MN 55987

Purpose

The purpose of the research project is to successfully polymerize a MIP with a caffeine template. Once this is completed the goal is to have the ability to efficiently bind caffeine back onto the MIP. This can be used in wastewater applications.

Background/Introduction

Molecular Imprinted Polymers (MIPs) are very cheap and easy to produce. MIPs have many attractive qualities such as being stable and versatile. The main principle behind MIPs is that a functional monomer and a cross-linker are combined and copolymerized with the presence of template molecules. This forms the cavities that are arranged with the template molecules. The monomer and cross-linker that formed bonds help to position the functional monomer around the template. After the polymerization is complete the template can be removed from the structure and this will produce binding sites that have size, shape and chemical functionality that are complementary to the structure².



Materials and Methods

Chemicals:

Caffeine, Acrylamide, Ethylene Glycol Dimethacrylate (EGDMA), Azobisisobutyronitrile (AIBN), Acetonitrile, methanol, acetic acid and ethanol are to be used during this experimental research project.

Polymerization:

The caffeine polymer is polymerized by mixing 0.165 g of acrylamide, 1.70 mL of EGDMA, 0.21 g of caffeine and 0.1 g of AIBN to a 60 mL solution of acetonitrile. After being mixed this solution needs to be purged with nitrogen gas for 10 minutes while cooling in an ice bath. After being purged it is then heated to 50 C for 6 hours, then the temperature is increased to 60 C for 24 hours. The final increase of temperature is at 85 C for 6 more hours. The product is a white, some what clumpy powder similar to that of powdered sugar.

Extraction:

To extract the caffeine the MIPs go through soxhlet extraction process. A thimble is placed in the soxhlet extractor and is filled with the MIPs. A RBF is placed on the bottom and contains a mixture of methanol and acetic acid while a condenser is placed on top. As the methanol and acetic acid start to heat up the vapors rise and then condense dropping back down to the area the thimble is held. The methanol and acetic acid solution extract the caffeine from the MIPs through the permeable thimble and then reach a level where the solution drips back down into the RBF and the cycle repeats. This process takes approximately 12 hours for total caffeine extraction.

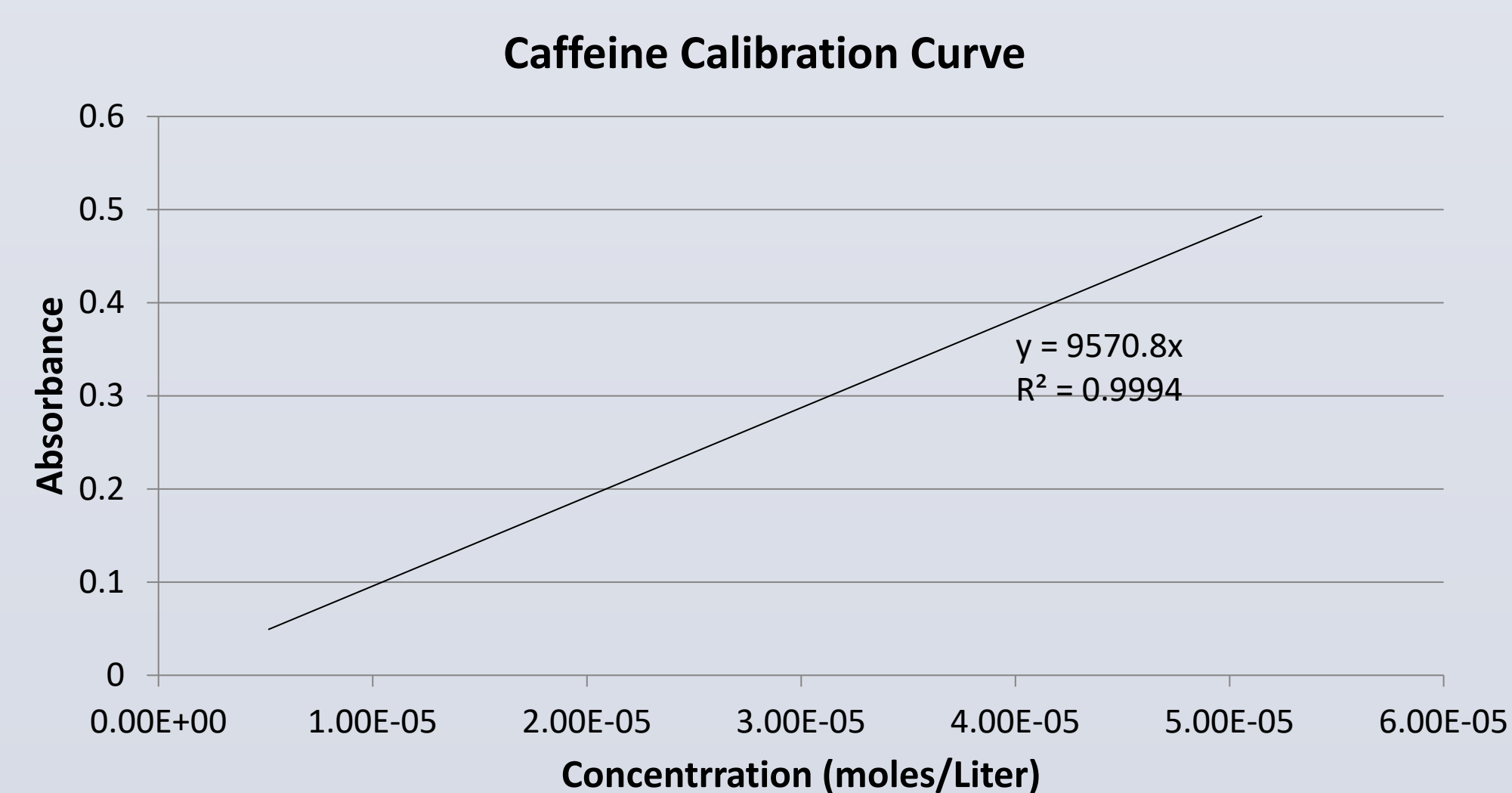
Testing:

After the caffeine has been extracted, the MIPs are placed in caffeine standard solutions of varying standards ranging from 5, 10 and 20 ppm. Three samples are prepared for each caffeine standard; each sample contains 0.02 grams of the caffeine extracted MIPs with 10 mL of their respected caffeine standard. The samples are shaken occasionally over a 24-48 hour period to ensure maximum exposure of MIPs to the caffeine standards. Next each sample is filtered and tested in the UV-Visible spectrometer that is set at a wavelength of 273.6nm and a range of 400-200nm.

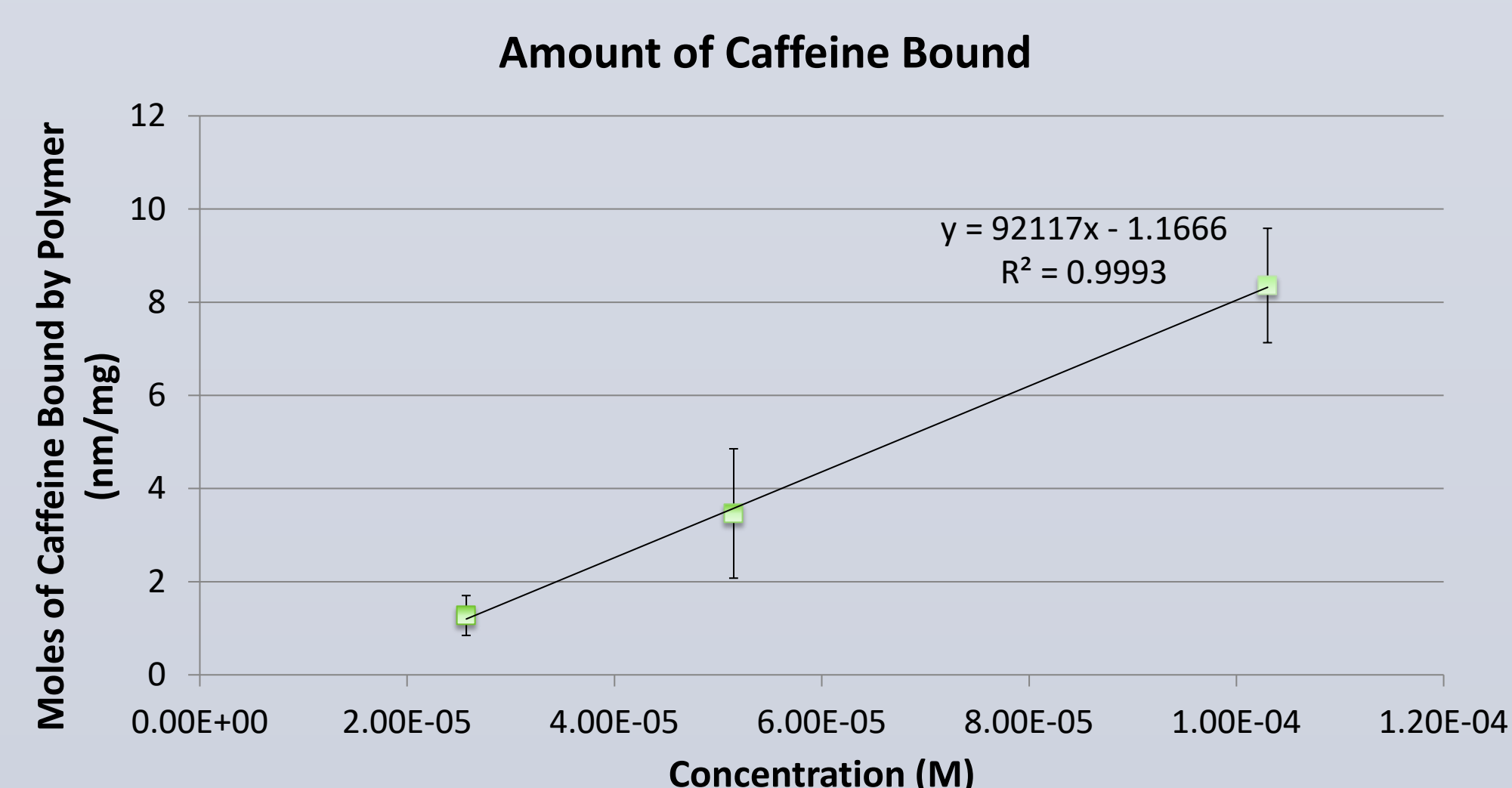


Results

The first results obtained were a caffeine calibration curve of our standards. This can be seen on the graph below.

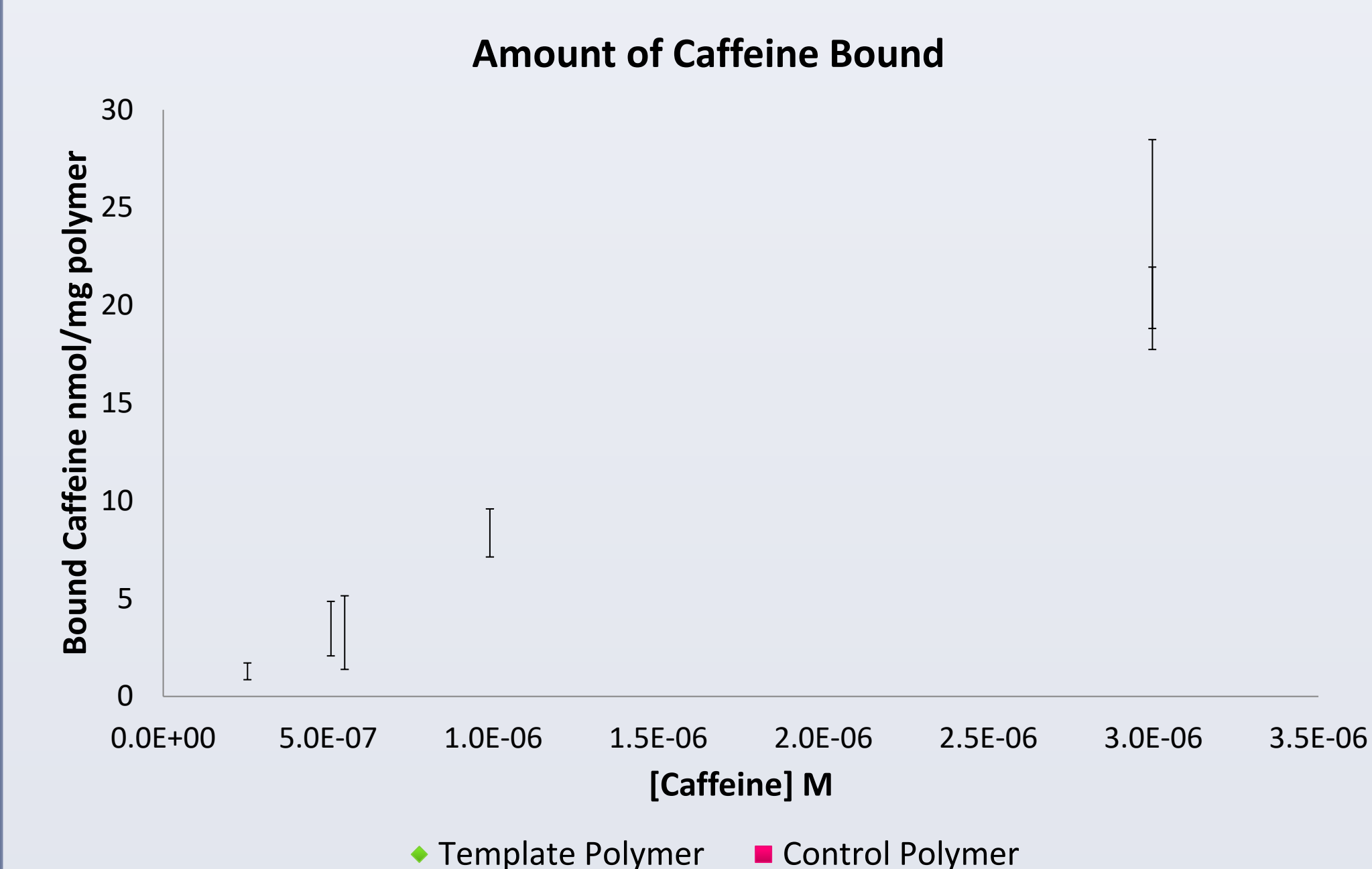


This calibration curve gives the molar absorbance value which is used to determine the concentration from the absorbance values that are obtained from the samples by using Beer's law ($A=\epsilon bc$).

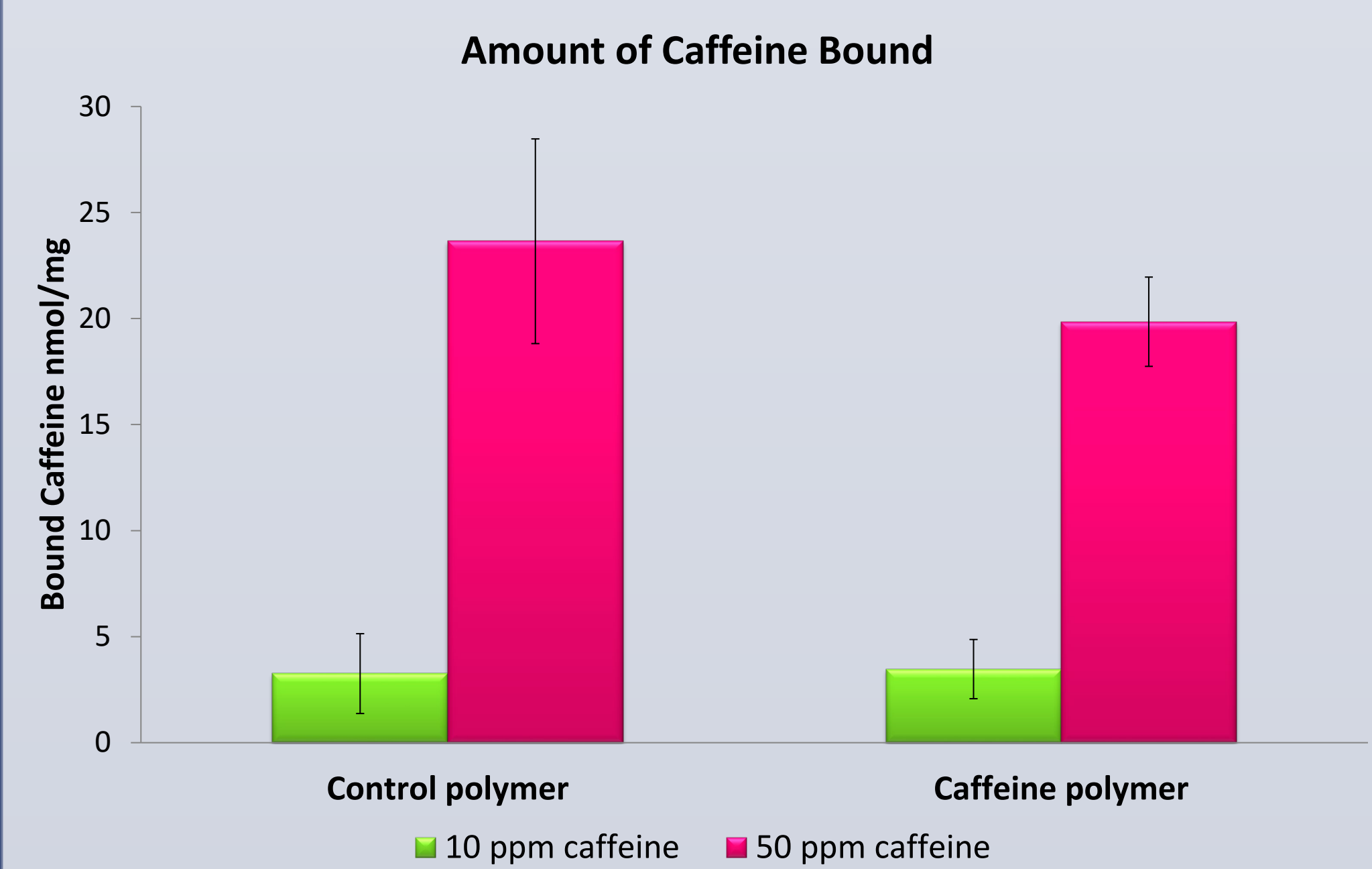


From the results on the graph at the bottom of the previous column we found that as the concentration of the caffeine standard increases so does the amount of caffeine bound onto polymer.

- Samples in 5 ppm standard had an average of 1.275 nm caffeine/mg polymer with a standard deviation of ± 0.428 nm caffeine/mg polymer.
- Samples in the 10 ppm standard averaged at 3.465 nm caffeine/mg polymer with a ± 1.396 nm caffeine/mg polymer.
- Samples in the 20 ppm standard had an average of 1.232 nm caffeine/mg polymer with a ± 1.232 nm caffeine/mg polymer.



This graph displays the amount of caffeine absorbed by the control polymer and by the template polymer. There is a linear trend for both as it was found that both polymers absorbed roughly the same amount of caffeine when placed in water samples. The reason for this is because of the low levels of caffeine concentration that were used in the water samples. Our prediction is that this linear trend will continue until each polymer is saturated with caffeine from absorption and then the trend will eventually level off. It is expected that the control polymer will reach saturation levels sooner and therefore level off sooner than the template polymer which should be able to absorb more caffeine than the control polymer.



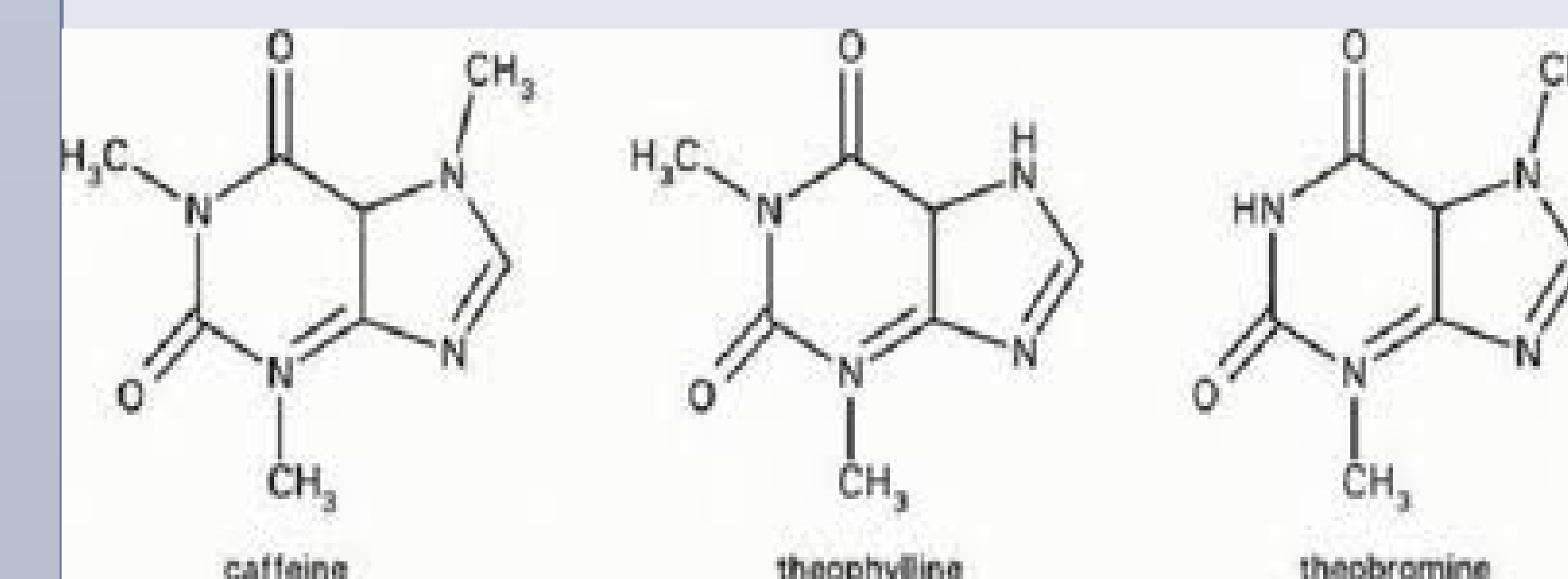
This is another representation of the previous graph as explained above. It displays that the caffeine polymer and control polymer bind roughly the same amount of caffeine.

Conclusion

In conclusion it has been proven that the MIPs for caffeine that were polymerized have the ability to bind with caffeine. The MIPs can also be adjusted to meet the needs for binding of other small organic contaminants.

Future work

For future work will consist of testing how well the MIPs bind with caffeine in higher concentrated caffeine standards that will range from 50-100 ppm. There will also be more than three samples tested for each caffeine standard to obtain a better average and reduce the amount of standard deviation. Control caffeine MIPs will also be tested in the caffeine standards and used to compare with the extracted caffeine MIPs. In addition to caffeine the ability for the MIPs to bind onto naproxen, theobromine and theophylline. Naproxen will be used to test how selective the MIPs are in their binding abilities. Theobromine and theophylline are by products of the degradation of caffeine and are very similar in structure and they will also be tested to see if the MIPs can bind with similar compounds and how well the MIPs are able to bind with the two by products.



Acknowledgements

I would like to thank the WSU Student Research Grant for funding my research as there were many materials and chemicals that were needed in this research and the money they provided helped make my project possible. Also a thank you to Dr. Zemke for all of the guidance and direction she has provided me in the lab. She is a great mentor and it has been a pleasure working with her over the past year.

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RESEARCH / CREATIVE PROJECT ABSTRACT / EXECUTIVE SUMMARY
FINAL REPORT FORM

Title of Project

Molecular Imprint Polymerization for Caffeine Removal from Water Samples

Student Name Jacob LetsingerFaculty Sponsor Dr. ZemkeDepartment Chemistry

Abstract

Molecular imprint polymers (MIPs) have applications in wastewater treatment. The current focus of this research project is synthesizing MIPs that bind small molecule, organic contaminants with an emphasis on caffeine. The imprint polymer for caffeine is synthesized from a solution of acetonitrile, acrylamide, ethylene glycol dimethacrylate (EGDMA), caffeine, and Azo(bis)isobutyronitrile (AIBN) that is purged with nitrogen and polymerized and cross-linked in a variable-temperature oven for a period of time¹. The caffeine template is extracted from the polymer by Soxhlet extraction and then the imprinted polymer is then placed in various standard solutions of caffeine (10-30 ppm) for approximately 48 hours. The samples are analyzed by UV-Visible spectroscopy to determine the amount of caffeine the imprint polymer has absorbed. Both the control and caffeine MIP managed to absorb approximately 20 nanomoles of caffeine per mg of polymer.

The end product of this project in electronic format has been submitted to the Provost/Vice President for Academic Affairs via the Office of Grants & Sponsored Projects Officer (Maxwell 161, npeterson@winona.edu).

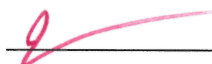
Student Signature



Date

5/8/14

Faculty Sponsor Signature



Date

5-8-14

Molecular Imprint Polymerization for Caffeine Removal from Water Samples

Individual Projects in Chemistry

CHEM 430

Spring Semester 2014

Winona State University

Chemistry Department

Dr. Zemke

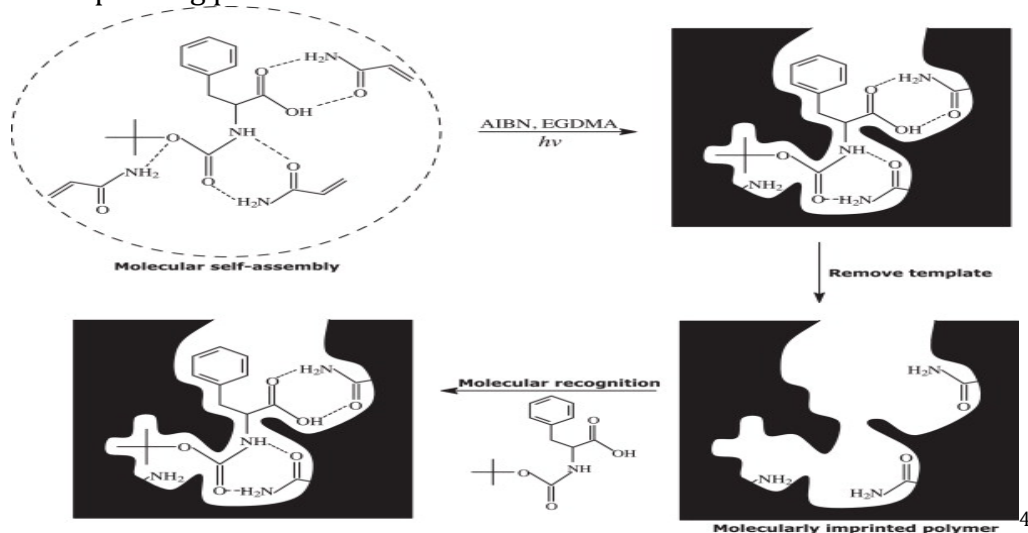
By: Jake Letsinger

Abstract: Molecular imprint polymers (MIPs) have applications in wastewater treatment. The current focus of this research project is synthesizing MIPs that bind small molecule, organic contaminants with an emphasis on caffeine. The imprint polymer for caffeine is synthesized from a solution of acetonitrile, acrylamide, ethylene glycol dimethacrylate (EGDMA), caffeine, and Azo(bis)isobutyronitrile (AIBN) that is purged with nitrogen and polymerized and cross-linked in a variable-temperature oven for a period of time¹. The caffeine template is extracted from the polymer by Soxhlet extraction and then the imprinted polymer is then placed in various standard solutions of caffeine (10-30 ppm) for approximately 48 hours. The samples are analyzed by UV-Visible spectroscopy to determine the amount of caffeine the imprint polymer has absorbed. Both the control and caffeine MIP managed to absorb approximately 20 nanomoles of caffeine per mg of polymer.

Background:

Molecular Imprinted Polymers (MIPs) are very cheap and easy to produce. MIPs have many attractive qualities such as being stable and versatile. The main principle behind MIPs is that a functional monomer and a cross-linker are combined and copolymerized with the presence of template molecules. This forms the cavities that are arranged with the template molecules. The monomer and cross-linker that formed bonds help to position the functional monomer around the template. After the polymerization is complete the template can be removed from the structure and this will produce binding sites that have size, shape and chemical functionality that are complementary to the structure. There are multiple factors that will affect the porous structure and surface area of an MIP. These factors include temperature, solvent, functional monomers, synthetic conditions, cross-linking density and template morphology and size. It has been shown that binding properties of a MIP and the molecule selectivity are influenced heavily by the functional monomers. Over the last 20 years most of the functional monomers studied have been in non-covalent imprinting. Also over this time period there has been an increase in different monomers used in the preparation of MIPs and this correlates to an increase in the number of functional monomers available for use^{1,3}.

Another way to look at molecular imprinting is a way of creating synthetic polymers with a biomimetic molecular recognition capability for templates used for their preparation. This means that before polymerization the complex is supposed to determine the formation of the imprint that will occur on the template. To achieve this there is "freezing" in the structures that occur because of molecular self-assembly and polymerization. In the self-assembly process the monomer molecules under-go functional group interactions around the template and then with the excess of cross-linker these become fixed by polymerization. Once the imprinted template is removed the binding sites are produced and are available for rebinding. The position and arrangement of the functional groups that go along with the binding sites forms an induced molecular memory. The picture below depicts the molecular imprinting process⁴.



In current research being done purified caffeine is trying to be absorbed to a MIP by placing the extracted caffeine polymer into a caffeine contaminated water solution. So far some caffeine has been purified but there is more that needs to be obtained otherwise commercial purified caffeine will have to be purchased and used. In research a method for synthesizing a MIP has been found and is in the process of being produced and characterized. An article related to our research was found and uses cellulose/silica as the MIP and caffeine as the template. The methods used to synthesize the MIP are very similar to the methods that are being used in our research. Not only is the synthesis of the MIP similar so are many other methods and is so close that this article may be comparable and assist in helping learn how to imprint our caffeine onto our polymer.

The experimental part of this method consisted of dissolving 0.48 mmol of caffeine into 25mL of distilled water. In a separate glass vial 4.8 mmol of TEOS was mixed with 9.6 mmol of 0.12 N HCl and stirred for 30 minutes. During the course of this experiment caffeine:TEOS:HCl(0.12 N) molar ratios of 1:10:20 were held constant. Two grams of pretreated cellulose were mixed with 30 mL of ethanol (200 proof) in a Teflon reactor. After being mixed the treated cellulose was added with the TEOS and HCl solution and this combination was stirred together for 30 minutes at room temperature. Then the solution was placed in an oven at 65°C, still in the Teflon reactor, and left at that temperature for 75 hours. Once the 75 hours was up the Teflon reactor lid was opened to allow the solution to air-dry in the 65°C oven for 5 hours. The dried product that was in the Teflon reactor was mixed with 80 mL of ethanol and left in the oven at 65°C to dry with occasional stirring. Two more extraction procedures were done with equal amounts of ethanol and drying times of two hours each to completely remove the template. After washing the product was filtered and the solids were dried in the oven at 110°C overnight. This dried solid is the final product and it being the MIP. To compare the how well the imprinted material worked an unimprinted or "blank" MIP was made. This time the same methods were used except the caffeine was not added.

The similarity of this experimental as compared to ours is the way that our polymer is produced. Both in this method and in our research methods heating and stirring at various temperatures for extended periods of time are used. Along with the washes by using ethanol and synthesizing a blank MIP to compare with one that is actually imprinted. In our research only a blank MIP has been synthesized and has yet to be analyzed to determine its properties. The caffeine used in this method was 99% pure commercial grade caffeine.

Experimental:

Caffeine Extraction:

For the first extraction 10.003 grams of Lipton loose tea was added to a 250 mL beaker that contained 100 mL of distilled water. After the tea was added the solution was stirred and brought to a gentle boil for 20 minutes. Over the course of the 20 minutes 30 mL of distilled water was added to compensate for water lost due to evaporation. Vacuum filtration was used to extract the concentrated tea. This was

not the most efficient process due to the loose tea covering the filter paper and preventing the vacuum from working. The tea was poured onto a beaker covered by a large filter paper to collect the liquid. After most of the liquid filtered through the paper by gravity the remaining loose tea was wrapped in the filter paper and squeezed by hand over the collection beaker to extract as much of the liquid tea as possible.

The collected tea was covered and placed in the fridge for storage. Three days later the extracted tea was taken out of the fridge and warmed at a low temperature on a hotplate. Once the tea had warmed up 2.502 grams of sodium carbonate was added and stirred until it was completely dissolved. After the sodium carbonate was dissolved the solution was taken off the hotplate and cooled to room temperature. After being cooled down 5.00 grams of NaCl was added and then the solution was placed in a separatory funnel. After being placed in the separatory funnel 15 mL of methylene chloride was added and inverted five times with occasional releasing of pressure.

There wasn't a clear organic layer to extract so 10 more mL of methylene chloride was added and again inverted. The organic layer (bottom layer) was extracted and two more washes of 15 mL methylene chloride were performed and the organic layers were collected. Not much separation occurred for each wash so a relatively large amount of distilled water was added and inverted to get separation. This was allowed to sit for an hour to get separation. After all of the organic layers were extracted it was set to dry in a fume hood for four days. After drying crude caffeine was left behind and weighed, it turned out to have a weight of 0.273 grams. A small amount of the crude caffeine was used to determine what type of solvent to use for purification. It was determined to use hexanes as the solvent. On a hotplate 120 mL of hexanes were warmed at low temperatures to dissolve the crude caffeine. After all the caffeine had dissolved it was cooled to room temperature and then placed in the fridge for recrystallization to occur. After being in the fridge the scratch method was used to get some fall out of crystals. The crystals were extracted by vacuum filtration and washed with a small amount of hexanes. The weight of the purified caffeine was found to be 0.049 grams¹.

A second extraction was performed using the same method as the first extraction. The only difference was the amounts of tea, sodium carbonate, and NaCl that were used, the solvent used to dissolve the crude caffeine and how the tea was extracted from the loose tea. This time 20.002 grams of Lipton loose tea was used in 100 mL of water that was brought to a gentle boil and stirred for 20 minutes. It was then cooled to room temperature. After being cooled down the tea was poured through a doubled-up cheesecloth that was stretch over a beaker to extract the liquid tea. Once again after most of the liquid was filtered through the cheesecloth the remaining loose tea was wrapped up in the cheesecloth and squeezed by hand over the beaker to extract the most tea as possible. The tea was then transferred to a separatory funnel to separate and extract the organic layer. This time instead of methylene chloride distilled water was used to get separation. Three washes of 20 mL of distilled water were done with inversions and after each wash the organic layer was collected. The organic layer was left in a beaker in a fume hood for a week to dry. The crude weight of the caffeine was 0.166 grams and this time instead of

hexanes 20 mL of 95% ethanol was used to dissolve all of the crude caffeine. It was still warmed on a hotplate at low temperatures to help the crude caffeine dissolve. After it dissolved the solution was cooled to room temperature and then placed in the fridge until the next lab session, which was a week later. Recrystallization had occurred over that one-week period and vacuum filtration was used to extract the purified caffeine. It was let to dry over the vacuum filtration and then weighed out to be 0.37 grams of purified caffeine¹.

A third caffeine extraction had to be performed. This time only 4.01 grams of Lipton loose tea was used. The tea was added to 300 mL of distilled water that was already boiling and stirred for only 10 minutes. It was cooled down until safe to touch where cheesecloth was still used to extract the tea from the loose tea into a separate beaker. The liquid tea was still warm so 1.001 grams of sodium carbonate was added and stirred in until all of the sodium carbonate was dissolved. This was followed by 1.0 grams of NaCl and stirred in until completely dissolved. The solution was then poured into a separatory funnel to begin the separation and collection of the organic layer. This time three washes and inversions of 30 mL methylene chloride were performed along with one wash of 30 mL of distilled water saturated with NaCl. The organic layer was collected into a separate beaker containing anhydrous sodium sulfate after each wash. The organic layer was then poured into another beaker and set to dry for a week. There was no crude weight recorded for the third extraction. It was dissolved in 5 mL of 95% ethanol while being warmed on a hotplate. It was cooled to room temperature and then placed in the fridge for an hour for recrystallization to occur. Vacuum filtration was used to extract the purified caffeine and then dried over the vacuum for a few minutes. The purified caffeine was found to have a weight of 0.026 grams¹.

Molecular Imprinting Polymerization:

For the control polymer 60 mL of acetonitrile was measured into a 100 mL RBF. Next 0.16 grams of acrylamide was added into the RBF along with 1.70 mL of ethylene glycol dimethacrylate (EGDMA). The final compound added to the RBF is Azo(bis)isobutyronitrile (ABIN). 0.1 grams of the ABIN was added. The solution was then purged with nitrogen while cooling in an ice bath for 10 minutes. After purging the RBF was placed on a heating mantle on top of a stir plate and was heated up to a constant 50°C and stirred gently. It took 45 minutes to adjust the heating mantle to stay constant at 50°C and during that time temperatures ranged from 30-55°C. Once it was stable at 50°C it was left to stir for two hours and 45 minutes. After the two hours and 45 minutes were up the temperature of the heating mantle was increased to 60°C and left over night. The next day the temperature was again increase to 85°C for six hours still stirring the entire time. Upon completion of the six hours the solution was taken off the heating mantle and allowed to cool to room temperature. A solid was suppose to form but none did but it was still placed on the rotovap and allowed to rotate until a brownie batter like sludge was formed. The product was taken out of the RBF and had a weight of 0.962 grams. A vacuum filtration was set up for the product and it was washed with 10 mL of acetonitrile and 10 mL of 95% ethanol. The final product was collected and placed in a vial for storage for characterization later on.

*May it be noted that the acetonitrile that was used in this first preparation of the control polymer was thought to be contaminated. When brought up to the research advisor it was agreed that it was contaminated by a dye from another colleague's research. The experiment proceeded anyways to see what results would occur².

For the second control polymerization the same method was used except with a few variations. The acetonitrile that was used was taken from the chemistry stock room to ensure it was not contaminated and an oven was used instead of a heating mantle. Again 60 mL of acetonitrile was used in a 100 mL RBF where 0.17 grams of acrylamide was added, followed by 1.7 mL of EGDMA and 0.1 grams of ABIN. This solution was purged for 10 minutes with nitrogen while cooling on an ice bath. It was then placed into the oven that was preset at 50°C for 6 hours and this time no stirring occurred. After the 6 hours was up the oven was increased to 60°C and the solution was left in the oven at that temperature for a little over two days. The oven was then increased to 70°C, which was the maximum temperature that the oven could achieve, and the solution was left in there for a day. A white solid powder had formed during the heating process and was taken out to cool. After cooling the product had a weight of 1.996 g.

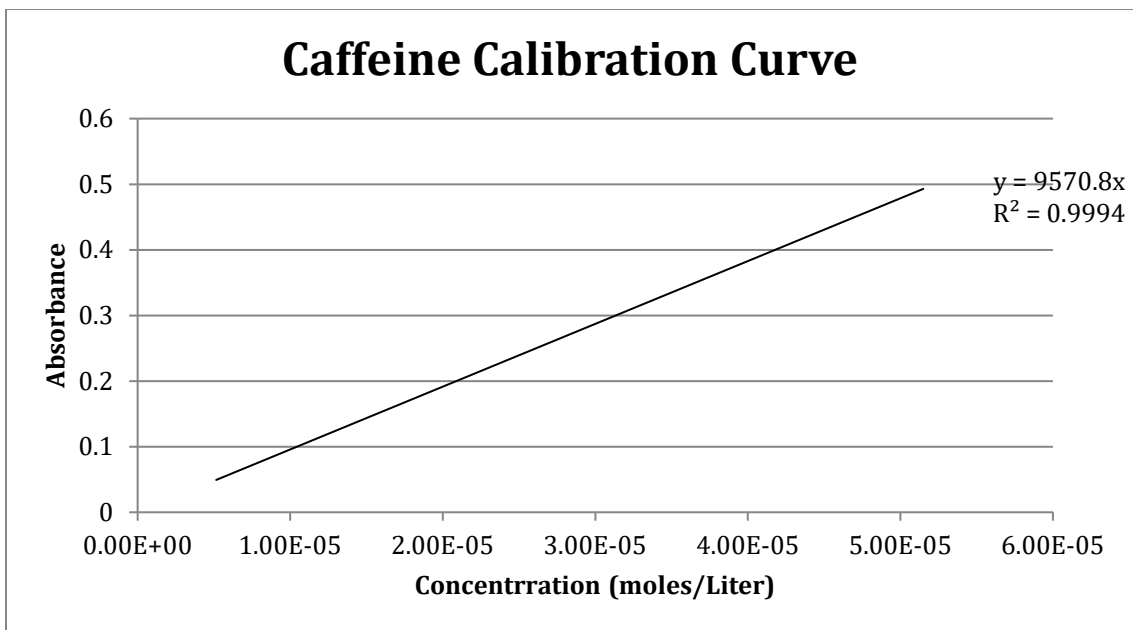
A third batch of polymer was made this time with caffeine to form caffeine MIPs. The process is the same as the previous method but this time 0.212 g of caffeine was added as well. After the MIPs were made the MIPs were placed in a Soxhlet extractor to extract the caffeine from the MIPs and to form the caffeine template. The Soxhlet extraction has a 9:1 mixture of methanol and acetic acid that heats up and condenses which in turn extracts the caffeine from the MIPs. The Soxhlet extraction process takes approximately 12 hours for complete caffeine extraction.

UV-vis testing:

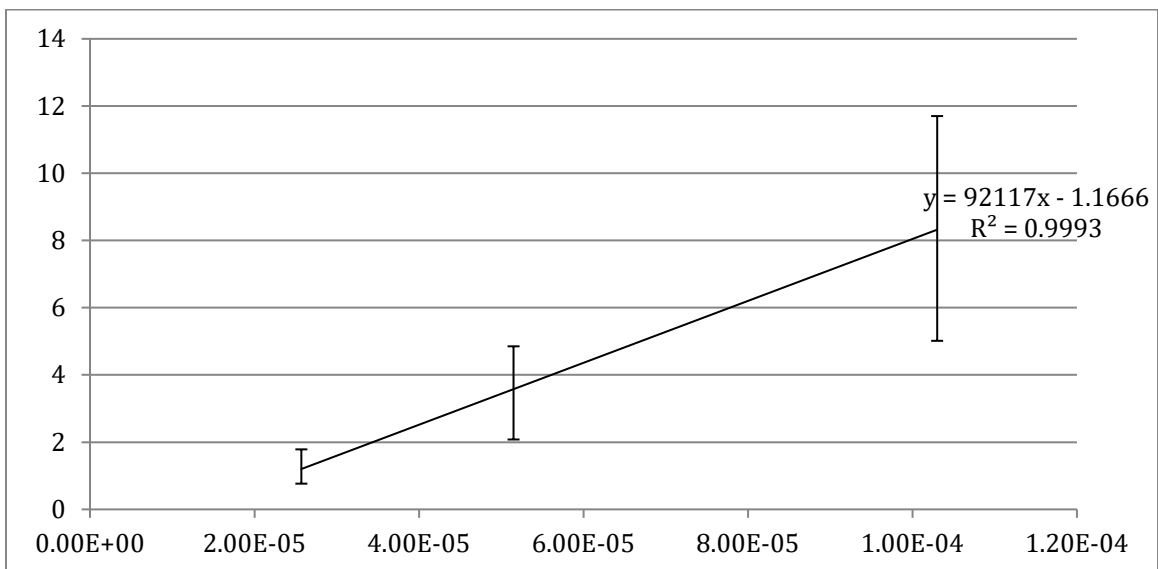
To determine how much caffeine bound onto the MIP three caffeine standards were made with the concentrations of 5, 10, and 20 ppm. For each standard three samples were prepped. In each sample it contained 20 mg of the extracted MIPs along with 10 mL of the 10 ppm standard. Once the samples were made over a period of 24-48 hours each sample was occasionally shaken to ensure maximum exposure of extracted MIPs to caffeine solution. The samples were filtered and measured in the UV-vis spectrometer at a wavelength of 273.6 nm and the absorbance values were recorded. Along with the extracted MIP, we tested the control in the same manner as stated above.

Results:

The first results obtained were a caffeine calibration curve of our standards. This can be seen on the graph below.



This calibration curve gives the molar absorbance value which is used to determine the concentration from the absorbance values that are obtained from the samples by using Beer's law ($A = \epsilon bc$) where $C = A/\epsilon b$ to find the molarity. From the molarity the value is multiplied by 0.01 L of water (amount per sample) to find the moles of caffeine that are left in each sample. To find the moles of caffeine bound by the polymer the moles of caffeine in each standard is subtracted from the moles of caffeine left in the water. These values are then converted to nanomoles and divided by the mg of MIPs in each sample. The nm of caffeine/mg of polymer are averaged out and the standard deviation is found to determine how accurate our data was. The results are shown in the graph below.



From the results we found that as the concentration of the caffeine standard increases so does the amount of caffeine bound onto polymer. It was found that the samples in the 5 ppm standard had an average of 1.275 nmoles caffeine/mg polymer with a standard deviation of ± 0.428 nmoles caffeine/mg polymer. For the samples in the 10 ppm standard the MIPs averaged 3.465 nm caffeine/mg polymer with a ± 1.396 nm caffeine/mg polymer. In the final samples in the 20 ppm standard they had an average of 8.358 nm caffeine/mg polymer with a ± 1.232 nm caffeine/mg polymer.

Conclusion:

In conclusion it has been proven that the MIPs for caffeine that were polymerized have the ability to bind with caffeine. However the standard deviations were rather large but that is attributed to the fact that the concentrations of the caffeine standards are low. For future work will consist of testing how well the MIPs bind with caffeine in higher concentrated caffeine standards that will range from 50-100 ppm. There will also be more than three samples tested for each caffeine standard to obtain a better average and reduce the amount of standard deviation. Control caffeine MIPs will also be tested in the caffeine standards and used to compare with the extracted caffeine MIPs. In addition to caffeine, the ability for the MIPs to bind onto naproxen, theobromine and theophylline will be tested. Naproxen will be used to test how selective the MIPs are in their binding abilities. Theobromine and theophylline are by-products of the degradation of caffeine and are very similar in structure and they will also be tested to see if the MIPs can bind with similar compounds and how well the MIPs are able to bind with the two by products.

Acknowledgements:

I would like to thank the WSU Student Research Grant for funding my research as there were many materials and chemicals that were needed in this research and the money they provided helped make my project possible. Also a thank you to Dr. Zemke for all of the guidance and direction she has provided me in the lab. She is a great mentor and it has been a pleasure working with her over the past year.

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