Sorption Study of Cu^{2+} Using Alginate as a Gel Matrix

Honors Project

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By

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ABSTRACT

In this study, alginate beads were tested to determine the ability of the beads to remove copper (II) ions from drinking water. The alginate beads were tested by passing a prepared copper solution through a chromatography column packed with alginate beads while collecting eluent samples. The samples collected were tested using atomic emission spectroscopy to determine the amount of copper that passed through the column. The alginate beads' sorption ability was tested against sepharose-iminodiacetic acid (sepharose-IDA), a known chelating agent of metal ions used in water purification. The alginate beads were successful in the removal of copper ions from solution, but further research is needed to improve the sorption ability of the alginate beads.

TITLE: SORPTION STUDY OF CU^{2+} USING ALGINATE AS A GEL MATRIX

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Introduction

The use of metals near and in water supplies is common throughout the United States and throughout the world. The use of metals can be dangerous to living organisms if the metal ions become concentrated in the water supplies. One metal commonly found in water supplies is copper since copper piping is used in water distribution supply systems and as the copper piping is corroded, copper ions (Cu^{2+}) are released into the water supply.[1] Copper ions in water are harmful to all life, especially aquatic life, and can cause harmful side effects in humans if they consume the contaminated water over an extended period of time.[1] As copper ions are introduced into the body, there is no harm as long as the copper ions become bound to ceruloplasmin, which is an enzyme found in blood plasma that binds copper.[2] However, as the amount of copper ions in the body increases, the ceruloplasmin is unable to bind all of the copper ions, and the unbound copper becomes "free" copper.[2] The presence of "free" copper in the body then presents a problem; as it circulates throughout the body, it can react with amyloid β peptides which results in the formation of plaques in the brain, which can cause cognitive impairment and Alzheimer's Disease.[2]

Filtration through alginate is a possible solution to the problem of metal ion contamination of water supplies. Alginate is a naturally occurring polysaccharide that is composed of mannuronate and guluronate which are linked by β 1, 4- and α 1, 4- glycosidic bonds.[3] Alginate can be used in the removal of metal ions from water because of its carboxylate functional groups which can bind the positively charged metal ions.[3] The use of alginate in the removal of metal ions from water is ideal because it is biodegradable, inexpensive since it is found in seaweed,[3] and can easily be formed into a gel due to its carboxylate functional groups, which can then be transformed into solid spherical beads.[3] The ability of the carboxylate functional group to bind metal ions is due to the strong intermolecular interactions than occur between the metal ions and carboxylate group.

The use of chitosan in the removal of metals from water has also been proposed due to the binding ability of the amine group present in chitosan. The amine group binds to the metal ions by intermolecular forces which allow the chitosan to remove metal ions from solution. This process has been researched, but the ability of chitosan to bind metals such as copper has not been proven yet. There is also a need to analyze the use of chitosan bound to the surface of alginate as a possible agent for metal removal.

The removal of metal ions from solution is a simple task for ethylenediaminetetraacetic acid (EDTA) which is able to bind metal ions to its 4 carboxylic acid groups. EDTA has been used in medicine for the treatment of heavy metal poisoning by removing metal such as mercury from the blood. EDTA can be harmful to human health, however, because the carboxylic acids are also able to bind free calcium ions found in the blood. EDTA, though is safe to humans in small concentrations, and is commonly used in fruit juice as an additive. Half of an EDTA molecule is also useful in the binding of metal ions, for this reason iminodiacetic acid (IDA) is also used for the removal of metal ions from solution. IDA has two carboxylic acid groups which bind to metal ions due to intermolecular interactions. Based on IDA's ability to bind metal ions it has been bound to the surface of sepharose which is a gel form. Sepharose-IDA is a commercial sold gel which is used in the removal of metal ions from water.

To determine the concentration of metal ions in solution atomic emission spectroscopy (AES) is used. AES works by heating the solution containing metal ions until the solution becomes a plasma which emits electromagnetic radiation (ER) at a certain wavelengths. Elements give off a specific wavelength which can be identified. For copper the wavelength of light released is around 324 nanometers (nm). The intensity of the light emitted at a certain wavelength is then used to determine the concentration of the element in solution. This method produces accurate results which is why it is commonly used to determine the chemical composition of solutions.

Experimental

Materials

Sodium alginate used for this experiment was purchased from Sigma Aldrich and was used without being purified. The 2-(N-morpholino)ethanesulfonic acid (MES) buffer used for this experiment was purchased from Sigma Aldrich in powder form and was not purified. Calcium chloride solutions were prepared using calcium chloride in distilled water. The copper solutions used were prepared using copper (II) sulfate pentahydrate in distilled deionized water. The sepharose-IDA used to compare to the effectiveness of the alginate beads was purchased from Sigma Aldrich and was used without purification.

Preparation of MES Buffer

For this experiment a 10 millimolar (mM) MES buffer was used for the formation of alginate beads. The 10 mM MES buffer was prepared by dissolving 1.672 g of MES powder in distilled water. After the MES was dissolved in the distilled water, the pH of the buffer had to be adjusted to 5.5 using 0.1 M hydrochloric acid (HCl).

Preparation of Alginate Beads

The alginate beads used in this experiment were prepared using a 1.75% alginate solution. The 1.75% alginate solution was prepared by dissolving 1.75 g of sodium alginate in 100 milliliters (mL) of 10 mM MES buffer. The alginate solution produced had high viscosity, and had to be stirred on a stir plate overnight using a magnetic stir bar to decrease the viscosity. When the alginate solution's viscosity was decreased, it was added to a burette to be added drop wise into a 2.5% solution of calcium chloride. The calcium chloride ($CaCl_2$) solution was prepared by dissolving 2.5 g of calcium chloride into 100 mL of 10 mM MES buffer. The alginate solution was dropped into the calcium chloride solution while being stirred by a magnetic stir bar on a stir plate. The beads were allowed to stir in the calcium chloride solution for a day to ensure the stability of the beads. After stirring in the calcium chloride solution for a day, the alginate beads were ready for use and were stable in multiple environments.

Preparation of Copper Solution

To test the ability of the alginate beads to remove copper from water, a 10 parts per million (ppm) copper solution was prepared by dissolving 0.0393 g of copper (II) sulfate pentahydrate in 990 mL of distilled deionized water and 10 mL of 1 m nitric acid (HNO_3). The 1M nitric acid was added to prevent the copper ions (Cu^{2+}) from being oxidized, and to ensure they are in a cation state.

Sorption Experiment

The ability of the alginate beads to remove Cu^{2+} was tested using a Bio-Rad chromatography column packed with alginate beads. The column was first loaded with 10 mL of the alginate beads, and then washed with over 60 mL of distilled deionized water to remove any calcium ions that were bound to the surface of the alginate beads. Once the beads were washed and the water was evacuated from the column, 25 mL of the 10 ppm copper solution was added to the column. The sample of elutant was collected as the copper solution passed through the column and out as elutant. X fractions were collected. To remove the bound Cu^{2+} ions trapped by the alginate beads in the column 25 mL of 10 mM Ethylenediaminetetraacetic acid (EDTA) was passed through the column to remove the copper. EDTA chelated the copper bound to the surface of the alginate beads with a high affinity allowing it to remove the copper from the chromatography column. The EDTA solution passed through the column was also collected in a 50 mL beaker as a sample to determine the amount of copper the alginate beads were able to remove from the 10 ppm copper solution. The samples collected from the column were then analyzed using atomic emission spectroscopy.

To determine the amount of copper present in the samples collected from the chromatography column containing the alginate beads, a microwave plasma atomic emission spectrometer (MP-AES) was used. The MP-AES worked by heating the solutions until they were vaporized into gas, light was then passed through the gas and the amount of light absorbed at a certain wavelength by the gas is used to determine the amount of copper present in the solutions. The MP-AES microwave plasma atomic emission spectrometer required standards with varying amounts of copper to determine the concentration of copper present in samples collected during research. For this experiment, standard solutions of 0, 2, 4, 6, 8, and 10 ppm Cu^{2+} were used in the MP-AES. The standards were prepared by doing serial dilutions of the 10 ppm copper solution that was prepared to be used in the chromatography column. These standards allowed for the preparation of a calibration curve using the atomic emission spectroscopy instrument which was used to determine the amount of copper present in samples.

Use of Sepharose-IDA

To compare the results of the alginate beads' ability to remove copper from water sepharose-Iminodiacetic acid (sepharose-IDA) was also tested because it is known for its ability to remove metal ions from aqueous solution. The sepharose-IDA was tested by adding 10 mL of it in gel form to a Bio-Rad chromatography column and then passing 25 mL of the 10 ppm copper solution through the column. The elutant from the column was collected. Then, 25 mL of 10 mM EDTA was passed through the column to remove the Cu^{2+} ions that were bound by sepharose-IDA, and the elutant from the column was collected to be tested using atomic emission spectrometer?. The results of the atomic adsorption of sepharose-IDA was then compared to those of the alginate beads to determine the efficiency of the alginate beads to remove Cu^{2+} ions compared to a known chelating agent.

Results

Sorption of Alginate Beads

The copper solution eluted from the chromatography column with alginate beads contained 5.26 ppm of Cu^{2+} ions based on the MP-AES microwave plasma atomic emission spectrometer analysis (Figure 1).The goal of the research was to remove all Cu^{2+} ions from the solution, meaning no copper should have been present in the elutant. The 25 mL of EDTA sample passed through the column was found to contain 1.22 ppm of Cu^{2+} ions (Figure 1). The column was tested a second time to determine the ability of the alginate beads in the column to be reused, and the atomic adsorption of the elutant of the copper solution was determined to be 5.47 ppm of Cu^{2+} ions (Figure 1). The concentration of Cu^{2+} ions in the elutant from the column following rinsing with 25 mL of 10 mM EDTA was 1.49 ppm (Figure 1).

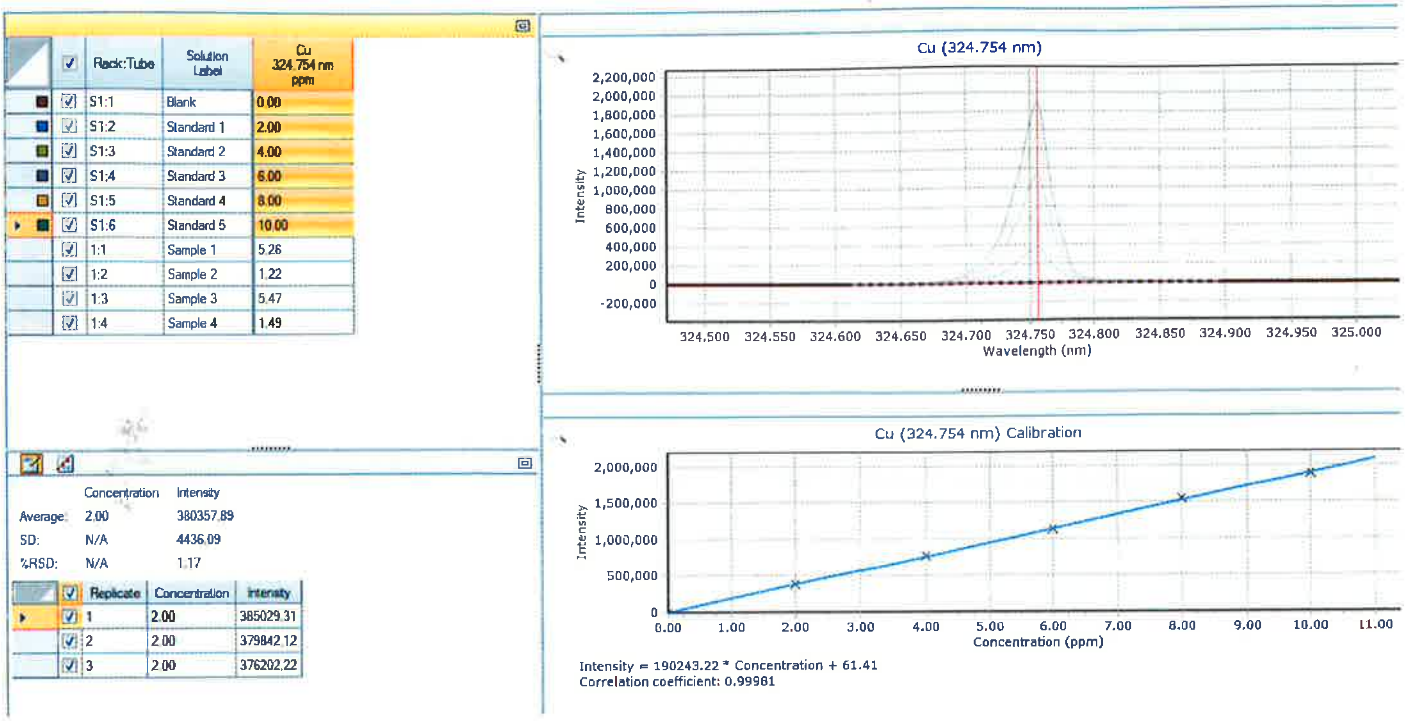
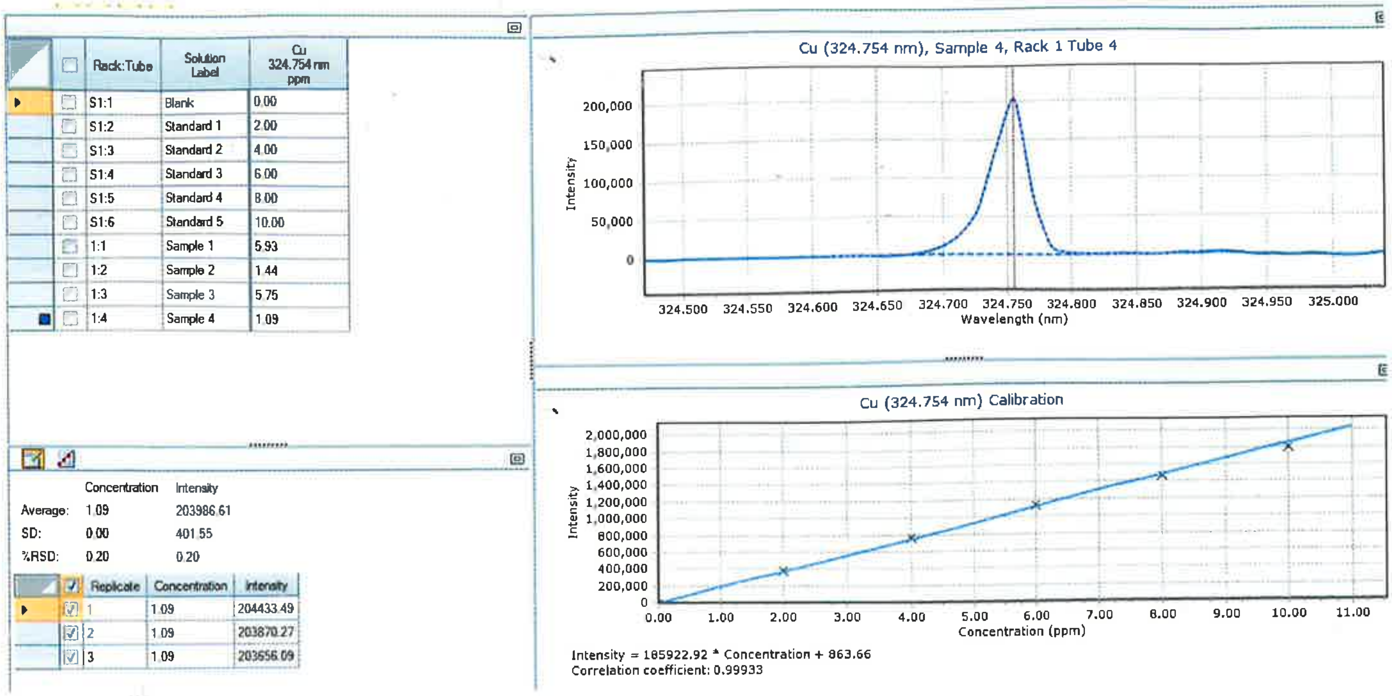


Figure 1: The sorption of Cu^{2+} by alginate beads. Sample 1 and 3 are samples collected after the 10 ppm copper solution was passed through the column. Samples 2 and 4 are the samples collected when 10 mM EDTA was passed through the column.

Sorption of Alginate Beads with Chitosan

Chitosan was added to the alginate beads to determine if it would increase the adsorption of the Cu^{2+} ions. To test the ability of alginate beads with chitosan two trials were conducted using 10 ml of the beads in a Bio-Rad chromatography column. In the elutant of the first sample of copper solution passed through the column was a Cu^{2+} concentration of 5.93 ppm (Figure2). The EDTA sample that was eluted from the column was determined to have a Cu^{2+} concentration of 1.44 ppm (Figure 2). In the second trial the sample collected from passing 25 mL of 10 ppm copper solution through the column resulted in a sample with a Cu^{2+} concentration of 5.75 ppm (Figure 2). The elutant from the column after passing 10 mM EDTA through was determined to have a Cu^{2+} concentration of 1.09 ppm (Figure 2).



Rack:Tube	Solution Label	Cu 324.754 nm ppm
S1:1	Blank	0.00
S1:2	Standard 1	2.00
S1:3	Standard 2	4.00
S1:4	Standard 3	6.00
S1:5	Standard 4	8.00
S1:6	Standard 5	10.00
1:1	Sample 1	5.93
1:2	Sample 2	1.44
1:3	Sample 3	5.75
1:4	Sample 4	1.09

	Concentration	Intensity
Average:	1.09	203986.61
SD:	0.00	401.55
%RSD:	0.20	0.20

Replicate	Concentration	Intensity
1	1.09	204433.49
2	1.09	203870.27
3	1.09	203656.09

Figure 2: The sorption of Cu^{2+} by alginate beads with chitosan. Samples 1 and 3 were the samples collected when the 10 ppm copper solution was passed through the chromatography column. Samples 2 and 4 were the samples collected when the 10 mM EDTA was passed through the column to elute the bound Cu^{2+}.

Sorption of Sepharose-IDA

The column containing 10 mL of sepharose-IDA was tested as a comparison since it is a known chelating agent that can remove metal ions from water. When the sample of elutant collected after passing 25 mL of the 10 ppm copper standard through the column was tested it was found to contain 0 Cu^{2+} ions (Figure 3). The sample of elutant collected after passing 25 mL of 10 mM EDTA through the column was found to contain 7.02 ppm of Cu^{2+} ions (Figure 3).

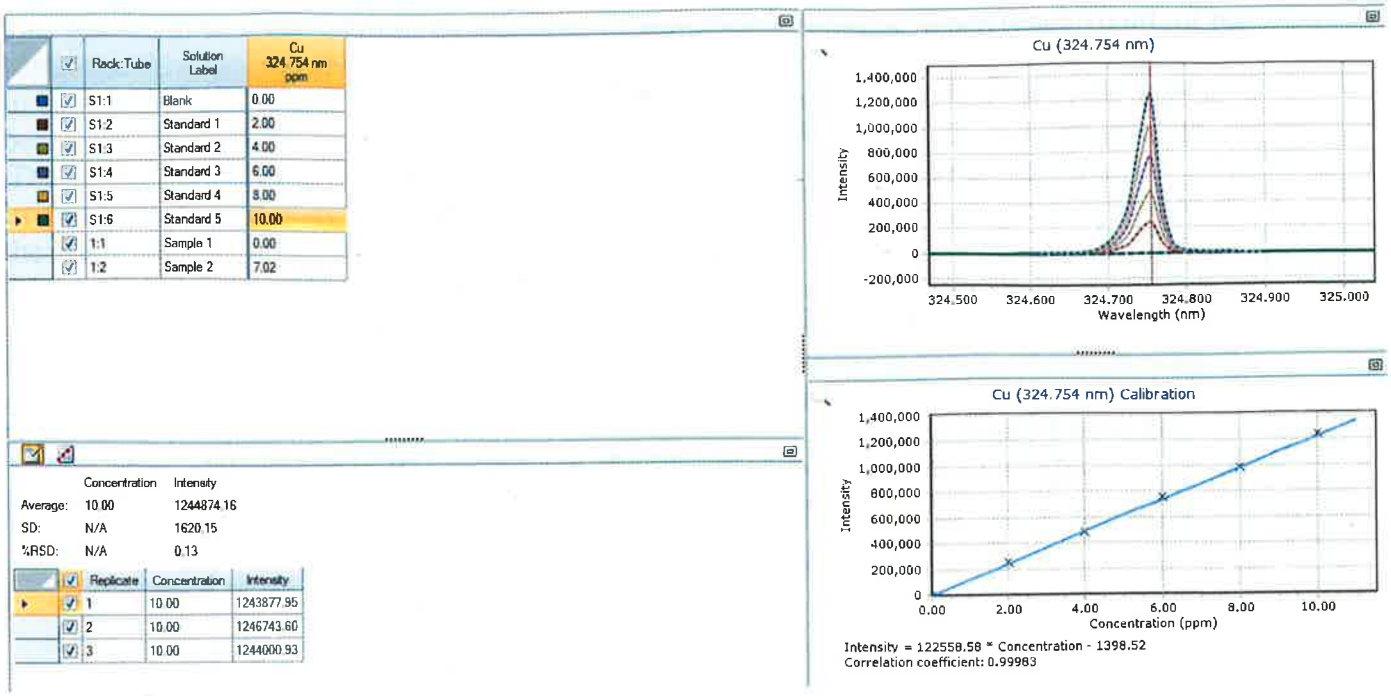


Figure 3: Sorption of Cu^{2+} by sepharose-IDA. Sample 1 was collected when the 10 ppm copper solution was passed through the chromatography column containing 10 mL of sepharose-IDA. Sample 2 was collected when 10 mM EDTA was passed through the column to elute the bound Cu^{2+} ions.

Discussion

In this study it was determined that alginate beads could be used for the removal of Cu^{2+} ions from drinking water. The binding of Cu^{2+} ions to the alginate beads was due to the two carboxyl groups on the single monomer of alginate which chelated the Cu^{2+} ions. The chelation of the Cu^{2+} by the carboxyl groups on the alginate beads removed the Cu^{2+} ions from solution decreasing the amount of Cu^{2+} present in the solution by 47.4%. In the second trial using the alginate beads in the column was only able to remove 45.3% of Cu^{2+} ions from water. The difference in the amount of Cu^{2+} ions remove from solution is due to the lack of rinsing which allowed ions to remain bound to the alginate beads which prevented them from binding additional ions.

The alginate beads were successful in the removal of Cu^{2+} ions; however, the beads were unable to remove all of the Cu^{2+} ions from the 10 ppm copper solution that was passed through the chromatography column. A possible solution to this problem is to bind another chelating agent to the surface of the alginate beads that could also bind Cu^{2+} ions as they pass through the chromatography column. Chitosan was added to the alginate beads to possibly improve the binding of Cu^{2+} ion by the beads. When the alginate beads containing chitosan were tested the sorption of the beads decreased. The decrease in the sorption of the beads illustrated that chitosan was not able to chelate the Cu^{2+} ions in solution, and the binding of chitosan to the surface of the alginate decreased the number of binding site on the surface of the alginate beads.

Sepharose-IDA is a known chelating agent of metal ions such as Cu^{2+}. For this reason sepharose-IDA is a commercially available gel used in water purification. As a comparison to the alginate beads produced in this study, sepharose-IDA was tested to determine the amount of Cu^{2+}

ions that could be removed from the prepared 10 ppm copper solution. When tested 10 mL of the sepharose-IDA gel was able to remove all Cu^{2+} ions present in the 10 ppm copper solution used in this experiment. When comparing the results of the sorption of sepharose-IDA to the alginate beads produced for this research, sepharose was able to remove more Cu^{2+} ions because of the IDA which is the chelating agent of the copper ions (Figure 4, 5). However, sepharose-IDA is an irritant to the human body and when sepharose-IDA is used in the treatment of drinking water, the water must be treated again to remove residue of sepharose-IDA before the water is safe to drink. Alginate is a natural occurring polysaccharide that is composed of glucuronate and mannuronate found in seaweed. Alginate is a naturally occurring polysaccharide which is not harmful to humans.[3] Water treated with alginate beads for the removal of Cu^{2+} is safe to drink if all of the copper is removed. A possible way to improve the sorption of Cu^{2+} ions by the alginate beads while retaining the safety to humans and other organisms would be to add IDA to the surface of the alginate beads. IDA contains half of the structure of EDTA which commonly used in orange juice and other fruit juices, and is not harmful to humans in small concentrations.

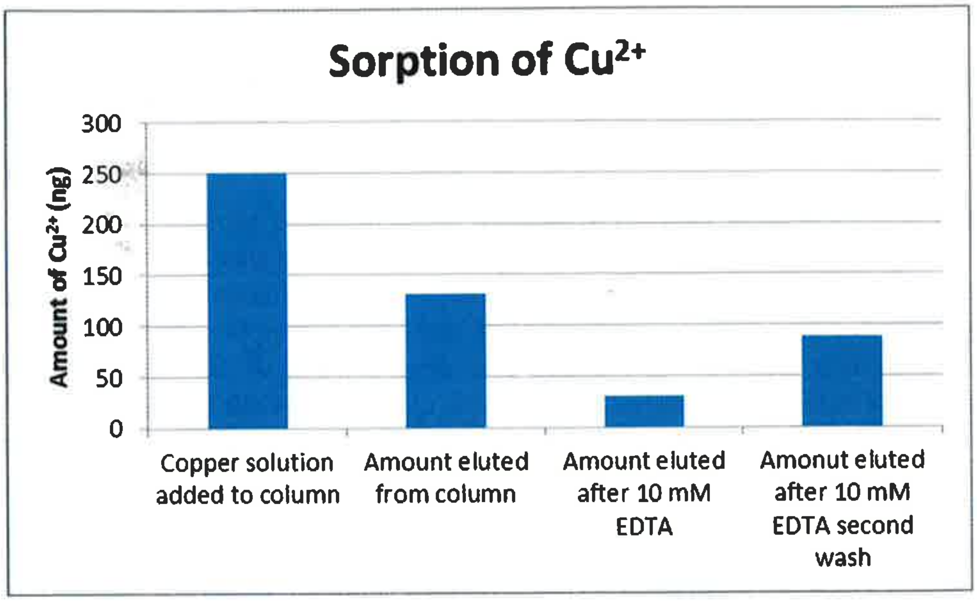


Figure 4: Sorption of Cu^{2+} by 10 ml of alginate beads in the chromatography column.

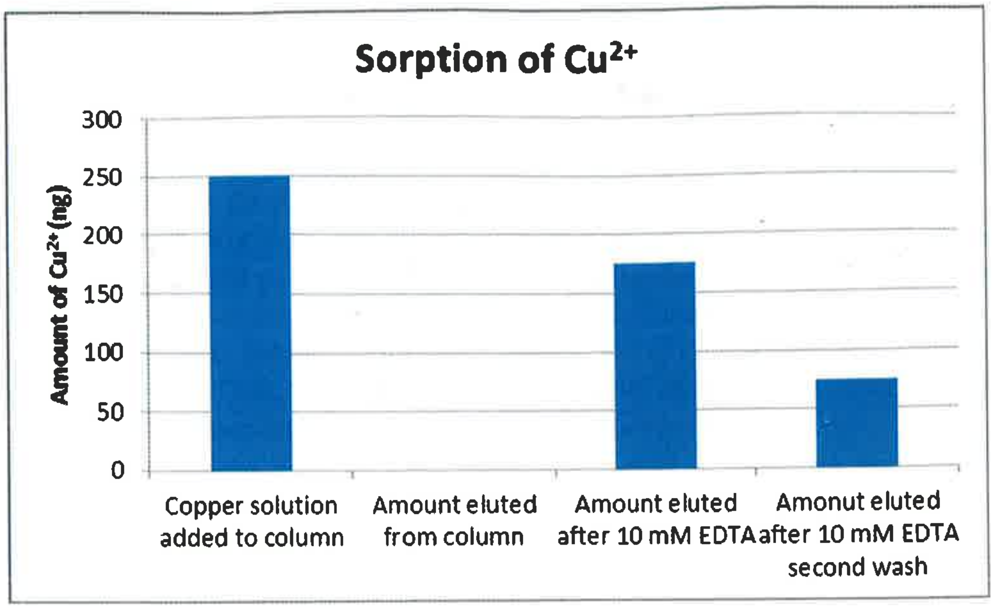


Figure 5: Sorption of Cu^{2+} by 10 mL of sepharose-IDA gel in chromatography column.

Conclusion

The alginate beads prepared for this experiment were successful in the removal of nearly half of the Cu^{2+} ions present in the 10 ppm copper solution used. The use of alginate beads for the removal of metal ions from drinking water, though, needs further research to develop a method which will produce alginate beads that have higher sorption affinity/efficiency? of metal ions such as Cu^{2+}. A possible method to improve the sorption of alginate beads is to attach IDA to the surface of the beads. When sepharose-IDA gel was tested in this study it was able to remove all Cu^{2+} ions present in solution. IDA contains half of the EDTA structure and since EDTA is a known chelating compound and is safe to humans in certain concentrations. EDTA is not suitable for use on alginate beads due to its large size, and the fact that it is free in solution which would cause it to become detached from the surface of the alginate beads. Alginate beads overall are a possible method of metal removal from drinking water that is safe and cost effective.

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