Entry to the Stockholm Junior Water Prize 2019

A Heavy Metal Extraction Process to Clean Contaminated Water Using Tannin-Embedded Biopolymers

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Abstract:

Throughout developing and developed countries, and especially locally in northern Ontario, the proliferation of mining and smelting operations continues to occur. This industry is crucial to the economic development and states of nations across the globe. This impact includes contamination of surrounding bodies of fresh drinking water with heavy metals. If accumulated in the human body, heavy metals can cause many health effects including irreversible organ damage. Exposure to heavy metals can also impact the rate of growth of plants. To scientifically address this concern, an eco-friendly biopolymer was embedded with mechanically isolated tannins from oak leaves. The biopolymer was then used to extract sample heavy metals from contaminated water. The results were measured using the change in mass, change in clarity, change in concentration of metal in water, and the effects on radish seedling germination. It was found that using a tannin-embedded biopolymer is an economically and eco-friendly way to remove heavy metals from water.

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Key Words:

tannins, biopolymers, heavy metals, mining, smelting, contaminated water, environment

Abbreviations & Acronyms:

World Health Organization/WHO

Tannin-Embedded Biopolymer/TEB

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Our research team would like to thank our teacher, Ms. Peterson, for not only developing our foundational empirical research skills, but also for honing our investigative laboratory skills in bio-chemistry. Ms. Peterson also assisted in the statistical analysis, which was greatly appreciated. Also, we would like to thank our Science Department at Widdifield Secondary School for allowing us to use the school laboratory equipment and space both before and after school hours. This enabled us to complete the laboratory research trials in a timely manner for our regional science fair. We wish to express our sincere gratitude to our Canada-Wide Science Fair 2019 delegate, Mrs. Page, for supporting us throughout the trip to Fredericton, New Brunswick.

Biography:

Emily Mah is a grade 11 student at Widdifield Secondary School in North Bay, Ontario. She has received recognition as a top ten academic student in high school each year, and, along with her partner, Jazlyn McGuinty, was awarded the gold medal in the North Bay Regional Science Fair. Emily is a volunteer at the North Bay Regional Health Centre and enjoys participating in the Peer Tutoring program at her high school. In addition to school, she is a top ranked Provincial level eight gymnast who has competed since she was seven years old. She has been fortunate to place second at the Provincial Gymnastics Championships and to qualify four years in a row. Emily's favourite subjects are math and science, and she would like to pursue these subjects in university. Along with her science fair partner Jazlyn, she got her inspiration for their project after reading about mining in northern Ontario, and how the water can become contaminated with heavy metals.

Jazlyn McGuinty is a grade 11 student attending Widdifield Secondary School in North Bay, Ontario. She published a research paper in the *Journal of Child and Adolescent Psychiatric Nursing* in 2018. She has presented two poster presentations at the 2018 Children's Mental Health Ontario Annual Conference and the Geneva Centre for Autism International Symposium, 2018. In addition, Jazlyn has been awarded the Top 10 Academic Average award consistently every semester since grade nine. Jazlyn enjoys volunteering at the North Bay Regional Health Centre Pharmacy, One Kids Place Children's Treatment Center, and Marina Point Retirement Home. Before moving to Canada, she participated in cleaning the ocean shoreline while living in Jeju-do, South Korea. Currently, she plays competitive badminton on the Provincial Team and received the MVP award for the 2019 season. Together with her science fair partner, Emily Mah, inspiration for the project was obtained after reading articles about mining and smelting in northern Ontario, and how heavy metal contamination can occur in surrounding bodies of water.

Introduction:

According to the World Health Organization and water.org, a world water crisis exists today where more than 844 million of the earth's people lack access to safe water. The WHO reported that by 2025, half of the world's population will be living in water-stressed areas. Canada has 7% of the world's renewable fresh water, which is an important domestic and global resource, according to the Government of Canada. So, protecting Canada's natural resources is not only of national importance, but is of global importance when considering our responsibility as a nation that possesses vast stores of fresh water.

Another category of national resources that includes minerals and metals makes up one of Canada's most important economic sectors (see The Mining Association of Canada). The Mining Association of Canada states that this industry employs more than 630 000 workers across the country and contributes nearly $100 billion to Canada's Gross Domestic Product each year. Northern Ontario, in particular, is a hotbed for the industry, where 30 of the 39 mines within that province exist. Environment Canada, a branch of the government that addresses the impact of mining on the environment, has an "Environmental Code of Practice for Metal Mines" that manages waste water and recommends environmental protection practices.

In 2024, a mining and smelting operation called the "Ring of Fire" will be developed across northern Ontario, Canada. This 3.3 billion dollar mining investment will cover 5 000 square kilometres. This new development has the potential of being a major environmental concern because it may pollute nearby ecosystems that include Canada's water systems. Like Canada, many developed and developing countries need both the metals and minerals produced from mining but face the consequences of contaminating water.

As a recommended environmental protection practice, this experimental research project focused on extracting metals (iron, zinc, copper) from contaminated water using a tannin-embedded biopolymer. Thus, this research project puts forth an economically viable solution to the conundrum of needing both natural resources within Canada and sets forth a real-world example of solving a potential economic-environmental problem. Additionally, a supportive and similar research project (Heredia and Martín, 2009), will be highlighted herein.

Heavy metals are toxic or poisonous at low concentrations in the water system (Lenntech, n.d.). Anthropogenic activities such as mining and smelting, industrial production, and use of metals can result in heavy metal contamination in nature and the human body (Tchounwou et al., 2012). Low levels of heavy metal exposure can cause adverse health effects, such as organ damage and hemochromatosis. Additionally, crop yields, biomass, fertility, and soil are affected by heavy metals, which causes a restriction in the growth of plants (Chibuike et al., 2014). Large amounts of heavy metals can cause metabolic disorders and growth inhibition. In fact, excess concentrations of some heavy metals in soils such as Cd (II), Cr (VI), Cu (II), Ni (II), and Zn (II) have caused the disruption of natural aquatic and terrestrial ecosystems (Peralta, 2000).

Tannins are bitter tasting, brownish organic substances found in high concentration in oak trees (Augustyn et al., 2016). The oak galls, bark, leaves and other tissues contain these substances. For this experiment, red oak leaves were used. The red oak leaves were harvested in the winter to insure an absence of chlorophyll. If chlorophyll had been present, the results of this study might have been impacted.

A biopolymer is a polymer made from organic substrates. There are several substrates used to make biopolymers including vegetable oils, cellulose, and starches (Rouse, 2014). Unlike conventional plastics, biopolymers are eco-friendly and can biodegrade into the earth. In addition, biopolymers are cost-effective and fairly simple to produce. In this laboratory experiment, the use of a biopolymer was necessary as it suspended the tannins. The heavy metals tested were iron (II) sulphate, copper (II) sulphate, and zinc sulphate. To further investigate this current laboratory experiment, the research team proposed a new model, called the TEB, with clinical applicability in the real world setting (using the tannin-embedded biopolymer in contaminated lakes and ponds).

Materials:

- Evaporating dish
- Red winter oak leaves
- Mortar and pestle
- Balance
- Glycerol
- Potato starch
- 5% acetic acid
- Hot plate
- Magnetic stirrer
- 1000 mL beaker
- Petri dishes
- Microscope
- Scoopula
- Erlenmeyer flask
- Filter
- Sodium bicarbonate
- Beakers
- Radish seeds
- Paper towel
- 0.1 M iron (II) sulphate
- 0.1 M copper (II) sulphate
- 0.1 M zinc sulphate
- Distilled water
- Drying rack
- Box
- Light
- Scotch tape
- Phone
- Sodium carbonate

Procedure:

1. Red oak leaves were placed on a drying rack and left to dry overnight.
2. The oak leaves were crushed, and a mortar and pestle were used to grind the leaves into smaller pieces.
3. The tannins were placed in an Erlenmeyer flask, and 500 mL of distilled water was added.
4. The solution was boiled down on a hotplate at medium heat (300^{o}C) until there was approximately 100 mL remaining.
5. At a temperature of approximately 500°C, the solution was left to evaporate on an evaporating dish and turned into a dried powder which was then scraped off.
6. Next, the starch-based biopolymer was made (see Annex I).
7. Two beakers had 1.105 g of tannins with biopolymer and one beaker had no tannins with biopolymer.
8. The tannin-embedded biopolymer and plain biopolymer were poured onto aluminum sheets and spread out. They were left to dry for three days.
9. The tannin-embedded biopolymer was peeled off the aluminum sheets and cut into 3 cm x 3 cm square pieces.
10. The masses were recorded for each biopolymer, as were the light readings using the homemade spectrometer.
11. Ten of the tannin-embedded biopolymers and one plain biopolymer were immersed into a beaker full of 100 mL of 0.1 M iron (II) sulfate solution. This step was repeated for the 0.1 M copper (II) sulfate solution and the 0.1 M zinc sulfate solution.
12. After 24 hours, each biopolymer was taken out and left to dry for a week.
13. New masses and light readings were recorded.
14. Twenty-eight Petri dishes were each prepared for five radish seeds to germinate. Four of these were controlled and received the water, four of these received the leftover iron solution, four of these received the leftover copper solution, and four of these received the leftover zinc solution. Four Petri dishes received the “before” iron solution, four Petri dishes received the “before” copper solution, and four Petri dishes received the “before” zinc solution.
15. The radish seeds were left to germinate for two days and were then counted.
16. To calculate the mass of heavy metal removed, excess sodium carbonate was reacted with the heavy metal solutions. The mixtures were filtered, and the residue was weighed when dry. The concentration of the metal was calculated using stoichiometry.

Results:

Amount of tannins isolated from 30g of oak leaves = 2.21 g

Table 1: Percent Difference in Mass of Biopolymer

Biopolymer	Percent Difference in Mass (g) Before and After Water or Metal Solution			
	Water	Iron (II)	Zinc	Copper (II)
No Tannin Added	0.23	3.17	0.72	3.56
Tannin Added	1.73	11.64*	12.18*	9.90*

*$p < 0.05$ in paired t-test comparing before and after

Table 2: Average Difference in Intensity

Biopolymer	Percent Difference in Light Intensity (Lx) Before and After Water or Metal Solution			
	Water	Iron (II)	Zinc	Copper (II)
No Tannin Added	0.10	3.51	3.51	3.51
Tannin Added	0.20	89.58*	67.71*	36.98*

*$p < 0.05$ in paired t-test comparing before and after

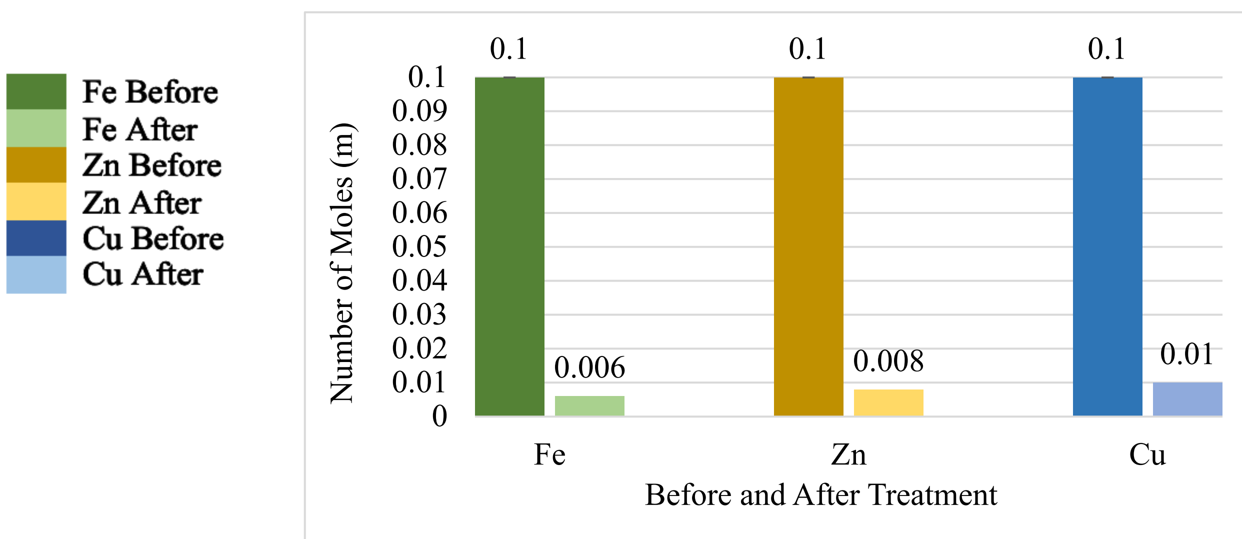

Figure 1: Average Difference in Moles Before and After the Addition of Tannin-Embedded Biopolymer.

<u>Balanced Equations for Figure 1:</u>

$ZnSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + ZnCO_3$

$FeSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + FeCO_3$

$CuSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CuCO_3$

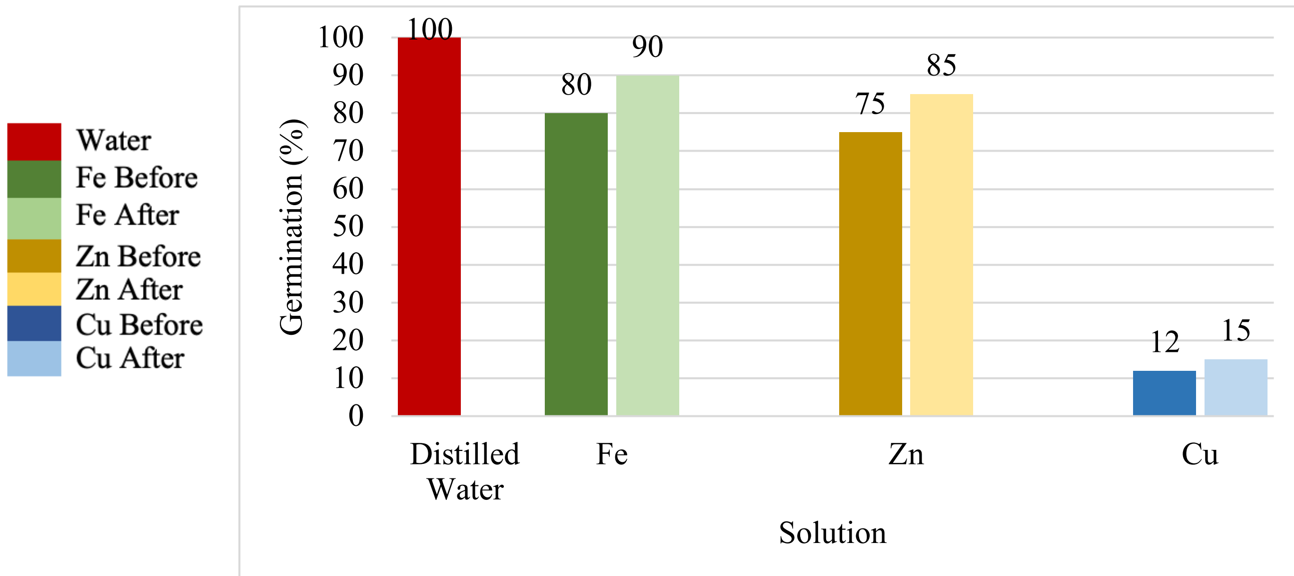

Figure 2: Radish Seed Germination Rate.

Figure 3: Plain Biopolymer Before Going onto the Hotplate.

Figure 4: Biopolymer with Tannins Before Drying.

Figure 5: Homemade Spectrometer to Measure the Lux (light reading) of Each of the Biopolymers.

Discussion:

Tannins are derivatives of gallic acid and, as shown in *Figure 6*, consist of oxygen, hydrogen, and a tannin benzene ring (Lee, 2014). Tannins can react with iron to form a ferric tannate precipitate (Logan, 2019). Heavy metals bond to the hydroxyl groups attached to the benzene ring of the tannins. In this case, the heavy metal ions, which are positively charged, are attracted to the negatively charged oxygen ions. In the process, the hydrogen in the hydroxyl groups is removed, producing ferric tannate, cupric tannate, or zinc tannate.

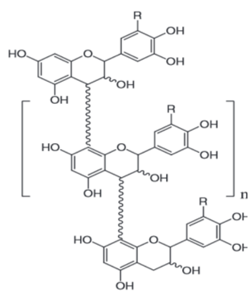

Figure 6: Structure of Tannins (Barbehenn, 2011).

The hypothesis that tannin-embedded biopolymers will clean heavy metals out of contaminated water was supported by the evidence obtained from this laboratory research trial. The first method used was weighing the biopolymers. The biopolymers were weighed before and after being submerged in each solution. After submersion, the biopolymers without tannins had approximately the same mass as before submersion. However, the biopolymers with tannins showed an increase in mass. The tannins in the tannin-embedded biopolymer attached to the heavy metal, which caused the Fe, Cu, and Zn molecules to cling to the biopolymer. This resulted in an increase in mass. When viewing the tables, it is evident that the biopolymers with the tannins changed in mass. The zinc and iron, in particular, had drastic percentage differences. It would be expected that the biopolymers with no tannins should not have had a change in mass; however, the mass decreased slightly. This may be due to some degradation of the biopolymers in the solutions.

The second method used to determine if heavy metals were captured by the tannin-embedded biopolymer was by using a homemade spectrometer. The amount of light that travelled through the biopolymer was measured using a lux meter on a smart phone. An application called Google Science Journal was downloaded onto a phone. Light was transmitted through the biopolymer in a dark box, and the lux was measured. The measurements were compared to the readings of light without a biopolymer filter. The biopolymers were all tested before and after being submerged in the heavy metal solutions, and the biopolymers without tannins showed to have very little differences in light readings. The biopolymers with tannins, however, significantly decreased in light readings. This showed that more heavy metal molecules bonded to the biopolymers because of the tannins, which made it more opaque. Therefore, the light readings were much lower.

The third method used to determine if heavy metals were captured by the tannin-embedded biopolymer was using a bioassay testing radish seedling germination. The percent germination of radish seedlings in before and after solutions of each heavy metal were compared. The before solutions were heavy metal solutions. The after solutions were the heavy metal solutions after the tannin-embedded biopolymers had been submerged for three days, then taken out. During this time period, it was expected that the heavy metals were bonding with the tannins and were attaching onto the biopolymers. When using the before solutions to test seed germination, a few seeds germinated in each Petri dish. However, when using the after solutions, more seeds germinated than the before solutions. This meant that the heavy metal molecules attached to the tannin-embedded biopolymers causing the water to become cleaner and allowing proper germinating conditions for the radish seeds. Some types of metals are important to help plants grow and develop. However, in large amounts, the same metals can be toxic and affect the rate of growth of the plants.

The fourth method used was calculating the amount of heavy metal removed. Excess sodium carbonate was reacted with the heavy metal solutions after the tannin-embedded biopolymer was submerged in it. The mixtures were filtered, and the residue was weighed when dry. The concentration of the metal was calculated using stoichiometry. The concentration of the heavy metal before and after having the biopolymer in the solutions were compared. It was found that the amount of heavy metal in the beaker decreased significantly, indicating that the biopolymer with tannins successfully removed the heavy metals from the beaker.

As part of an ongoing experiment, procedures have been taken to remove the heavy metal from the biopolymer. Results showed that sodium bicarbonate precipitated some of the iron off of the biopolymer. If the heavy metals could be removed from the biopolymers, the biopolymers could either be reused, or left to degrade into the earth. In the future, the sodium bicarbonate could be tested on the zinc and copper biopolymers. It could then be observed to see if the results were similar to the iron.

These results are important because they demonstrate that heavy metals can be removed by using organic, cost-effective, and eco-friendly materials. It is important to solve the issue of heavy-metal contaminated water because it impacts upon northern Ontario, Canada, and many parts of our world, especially with the economic importance and corresponding proliferation of mining. Tannin-embedded biopolymers may not only be effectively used within our local community (northern Ontario), but also in developing and developed countries. This line of research proposes an environmentally friendly method to rid our water systems of heavy metals. Also, heavy metal poisoning could be eradicated from developing countries that rely upon unfiltered water for human consumption. So, in developing countries, the impact could be exponentially more significant.

Environment Canada, a national government agency, could use the important results of this study locally and nationally. Since the tannin-embedded biopolymers were useful in extracting the heavy metals from contaminated water, Environment Canada could take this knowledge and incorporate it into mining projects, perhaps even making it mandatory. For example, this product could be used in the possible future mining project, "The Ring of Fire," located in northern Ontario. With this new knowledge, they could filter natural bodies of water and extract the heavy metals. This would save the surrounding animals from ingesting the water and dying from heavy metal poisoning, and the aquatic plants could be protected as well.

While substantial research has been conducted through using tannin as an absorbent (Bacelo et al., 2016; Pei et al., 2017; Sanchez-Martin, Beltan-Heredia, & Gibello-Perez 2011; Sengil & Mahmut 2009; Xinghau et al., 2017), fewer environmental studies have close similarities with the present research project. In terms of similar research, one project that took a parallel approach to this current project was: "Removing heavy metals from polluted surface water with a tannin-based flocculant agent" (Betràn Heredia, J., and J. Sánchez Martin, 2009). In this experiment, tannins, retrieved from Acacia mearnsii trees, were used to remove heavy metals from contaminated water. However, the testing was not done with just plain tannins. The tannins were slightly chemically modified so that they had a higher flocculant power. This product was called Tanfloc. In the experiment, contaminated surface water was tested. This water contained copper (II), nickel (II), and zinc. Similar to this project, two of the heavy metals (Zn and Cu) used in the experiment were identical. The main goals of both projects were the same: to reduce the concentrations of the heavy metals and ultimately remove them.

After conducting the experiment, Heredia and Martín's research team found that Tanfloc was effective at heavy metal removal for surface water treatment. The concentration of copper reduced to a greater extent when compared to zinc. This was different from the present project because zinc had a slightly higher reduction in concentration than copper. Perhaps this could have been because Heredia and Martín had slightly modified the tannins, whereas in the present research project the tannins were left natural. In addition, Heredia and Martín had only tested the concentration of the heavy metals before and after. In the present research project, there were three additional tests conducted in order to see if the heavy metal was removed or not including the change in mass, change in clarity, and the effects on radish seedling germination.

It was worthy to note that Heredia and Martín had only used the modified tannins alone in the contaminated water, which was not the case in the present research study. The Tanfloc had reacted with the heavy metals and then formed a precipitate as expected. However, the method used to remove this precipitate from the water was not mentioned. That is why the present research project used the biopolymers to hold the tannins in place. This made it easier to clean the water, as the precipitate did not remain in the beaker.

Conclusion:

The main goal of this laboratory experiment was to determine if tannins in biopolymers would remove the metal from a heavy metal solution. The heavy metals tested were iron (II) sulphate, copper (II) sulphate, and zinc sulphate. After the laboratory testing was completed, the research team discovered that tannins were successful at removing heavy metals.

In the first test, the tannin-embedded biopolymers did increase in mass after being in the heavy metal solutions. The metals attaching to the tannins caused this increase in mass. In the second test, the tannin-embedded biopolymers had a decrease in light reading after being in the metal solutions. Since the metals attached to the tannins, the biopolymers became more opaque and less light was able to travel through them. In the third test, there was a difference in germination rate using the solutions. The solution after the tannin-embedded biopolymers had been resting in and cleaning, provided water with less heavy metals for the radish seeds to germinate. In the fourth test, it was found that there was a lower concentration of the heavy metals after the biopolymers were submerged in the solution than before the biopolymers had filtered the solutions.

The first methodological advancement would be to take an incredibly large sheet of tannin-embedded biopolymer, place it on the surface of the pond using a net, leave it in for a certain amount of time, then remove it. It is possible for tannin powder to be used without the biopolymer; however, the tannins would react with the heavy metals and form a precipitate which would settle. This would be very difficult to scoop out, so the biopolymer would assist the tannins in remaining stationary.

A second method would be to form small spheres made out of the tannin embedded biopolymer and place them in the contaminated pond. This would increase surface area and potentially be more effective. If this method was used in a natural pond, it could serve to save the lives of aquatic plants and animals.

The final method that could be used strictly for lakes or ponds would be to make large tannin-embedded biopolymer disks and attach them together with rope, ensuring that there is space between each disk for the water to flow through (see Annex II). Using a floatation device, these disks could float in the water and attract the heavy metals. This would provide clean drinking water for people and a better environment for the aquatic life.

Finally, if there is a way to extract the heavy metals from the biopolymer after being in a heavy metal solution, those heavy metals could be reused. For instance, there is currently a zinc shortage that could benefit from this method. The clean biopolymer could then either degrade naturally or be reused.

In terms of future research plans, this experimental project could be applied to real-world problems as noted within the "The Ring of Fire" located in northern Ontario. Mining and smelting are very common and booming practices in northern Ontario; and because of this, heavy metals could accumulate in bodies of water or in tailings ponds, potentially making their way into drinking water. As suggested, this exploratory research could be used as a preventative environmental protection strategy for this upcoming 2024 technological-ecological event.

As Canada is a recognized leader in mining and technology, it is important that technology is used as a tool to protect, and not harm the environment. Striking a balance between development and progress, together with caring for the environment, is crucial. This research project is exemplary in embodying responsible leadership with technological advancement in the environment. After all, this research project demonstrates nature (natural tannin) being used to heal nature (water system).

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Annexes:

Annex I. Method used to make the tannin-embedded biopolymer

Specific Materials for the Formation of Tannin-Embedded Biopolymer

- Balance
- Glycerol
- Potato starch
- 5% acetic acid
- Hot plate with stirrer
- Magnetic stirrer
- 1000 mL beaker

Specific Procedure for the Formation of Tannin-Embedded Biopolymer

1. 100 mL of water were obtained. It was put into a 1000 mL beaker.
2. 5 mL of glycerol were measured and added to the beaker.
3. 5 mL of 5% acetic acid was measured out and added to the beaker.
4. 9.5 g of starch was weighed and added to the beaker.
5. Tannin powder obtained from the evaporating dish was added.
6. The beaker was put on the hot plate. The magnetic stirrer was added.
7. The heat was turned to high on the hot plate and heated until the mixture was thick, and the magnetic stirrer could no longer turn.
8. Biopolymer was poured onto aluminum sheets.
9. The biopolymer was spread out evenly.
10. The biopolymer was left to dry out for three days.
11. Once dried, the biopolymer was peeled off of the aluminum foil.
12. The biopolymer was into 3 cm by 3 cm squares.

Annex II. Model of heavy metal extractor for lakes and ponds (TEB)