

2022 S.T. Yau High School Science Award (Asia)

Research Report

The Team

Registration Number: Chem-082

Name of team member: LAU Kit Fai

School: King's College

Country: China

Name of team member: WONG Tsz Ho

School: King's College

Country: China

Name of team member: NG Chak Yau

School: King's College

Country: China

Name of supervising teacher: LUI Bob

Job Title: Teacher

School: King's College

Country: China

Natural Product-based Polymer for Metal Ion Refining

A Research Report Sample for 2021 S.T. Yau High School Science Award (Asia)

Date

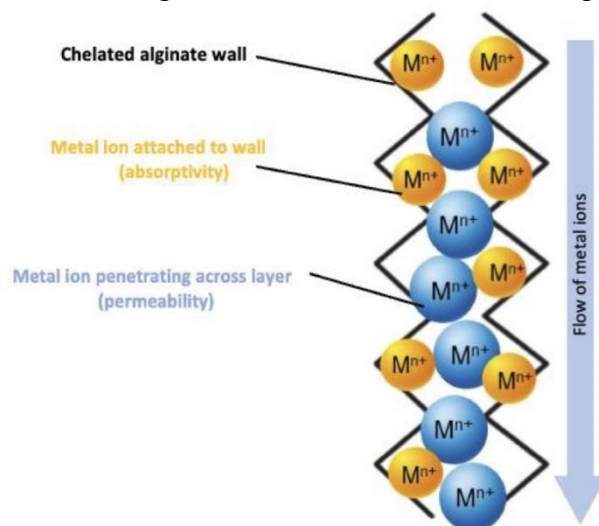
27 August 2022

Abstract

To maintain eco-friendly and chemical conservation, we explored the possibilities of a polymer-based metal ion separation with chelation of alginate, a biodegradable polysaccharide. In our experiment, calcium alginate (CaAlg), aluminum alginate (AlAlg), calcium-aluminium alginate mixture (CaAlAlg) in a fixed ratio (3:2) and chitosan/alginate mixture in ratios were the chelated subjects for forming differentially permeable membranes to separate Cd^{2+} and Pb^{2+} .

Ion channels in the alginate chains acted as ‘gateway’ to aid metal ion penetration, while charge density of heavy metal and chelating metal ions was the ‘ticket’ through the ion channels. Hence, manipulation of certain cationic permeability and absorption of heavy metal ions was achieved by altering the charge density.

Our results indicated that Pb^{2+} and Cd^{2+} generally showed high affinity towards alginate permeability and absorptivity respectively. We concluded that CaAlAlg of 0.6 M $\text{Ca}^{2+}/\text{Al}^{3+}$ mixture and 0.80% alginate had the most significant effect in metal ion separation, with the highest Pb^{2+} permeability (31.32%) and Cd^{2+} absorptivity (40.16%) among the alginate category, exhibiting an outstanding selectivity ratio (permeability of $\text{Pb}^{2+} : \text{Cd}^{2+}$) of 19.5 :1. Chitosan/Alginate mixture was also found to delay the breakdown of alginate chain thanks to chitosan’s poor biodegradability.



Flow of metal ion in a chelated ion channel

Keywords: alginate, chitosan, permeability, absorptivity, chelation, ion channels, differential permeability

Acknowledgement

We would like to extend our sincere gratitude to the following people:

- Chemistry teacher
- Lab assistant
- Lab technician

We are also thankful for the enormous support and resources provided by the school. Without their generous contributions, it would be impossible for our team to continue our research thus far.

Commitments on Academic Honesty and Integrity

We hereby declare that we

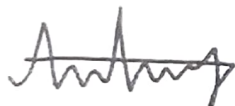
1. are fully committed to the principle of honesty, integrity and fair play throughout the competition.
2. actually perform the research work ourselves and thus truly understand the content of the work.
3. observe the common standard of academic integrity adopted by most journals and degree theses.
4. have declared all the assistance and contribution we have received from any personnel, agency, institution, etc. for the research work.
5. undertake to avoid getting in touch with assessment panel members in a way that may lead to direct or indirect conflict of interest.
6. undertake to avoid any interaction with assessment panel members that would undermine the neutrality of the panel member and fairness of the assessment process.
7. observe the safety regulations of the laboratory(ies) where the we conduct the experiment(s), if applicable.
8. observe all rules and regulations of the competition.
9. agree that the decision of YHSA(Asia) is final in all matters related to the competition.

We understand and agree that failure to honour the above commitments may lead to disqualification from the competition and/or removal of reward, if applicable; that any unethical deeds, if found, will be disclosed to the school principal of team member(s) and relevant parties if deemed necessary; and that the decision of YHSA(Asia) is final and no appeal will be accepted.

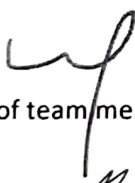
(Signatures of full team below)

X 

Name of team member: LAU Kit Fai

X 

Name of team member: WONG Tsz Ho

X 

Name of team member: NG Chak Yau

X 

Name of supervising teacher: LUI Bob


<p>Noted and endorsed by</p> <div style="text-align: center; margin: 20px 0;">  </div> <p>(signature)</p> <p>Name of school principal: Ms WONG Chau-ling</p>
--

Table of Contents

Abstract	i
Acknowledgement	ii
Commitments on Academic Honesty and Integrity	iii
1. Introduction	1
2. Literature Review	2
3. Our Approach & Methodology	4
4. Data Analysis	14
5. Applications	26
6. Conclusion	27
7. References	28

Introduction

Alginates are salts comprised of metal ions and alginic acid. They exist naturally in the form of polysaccharides derived from brown seaweeds. Alginic acid is a polymer consisted of L-glucuronic acid (G-blocks) and D-Mannuronic acid (M-blocks) linearly connected to each other via 1,4-glycosidic linkages.

Alginate has been extensively employed for medical applications and food preservations. Also, thanks to its excellent biodegradability, it is believed that alginate can play a major role in environmental protection, as in our project for separating metal ions.

The composition of alginate used is as follows:

Constituent components	Composition
G-blocks	16%
M-blocks	38%
Alternate units	46%

Note: 1. G/M ratio = 8:19

2. The information about the composition of alginate was obtained from Sales Team of Philip Harris

We proposed that only G-blocks among the three constituents contribute to metal ion diffusion through the alginate membrane. For example, CaAlg is chosen as the alginate membrane since the G-blocks show the best chelation effect towards Ca^{2+} , followed by gelation. Hence, the Ca-chelated alginate can either retain metal ions or let them penetrate, sorting two types of toxic ions into two groups.

Besides, a mechanical set-up is integrated to control the operation of metal ion separation human-free with improved efficiency and accuracy.

Literature Review

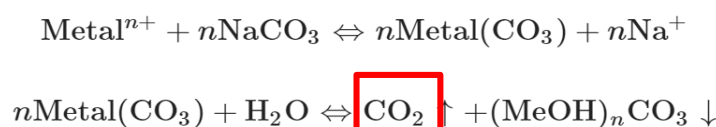
1. Precipitation with hydroxide / carbonate / sulphate

Most metal ions can react with hydroxide, sulphate or carbonate to form precipitates. The metal ions in solid form are extracted through sedimentation and become sludge finally.

Downside:

Many metal ions react with hydroxide to form an amphoteric hydroxide (e.g. $\text{Pb}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$). The difference in their solubility at a different pH complicates the metal ion separation as one type of metal hydroxide precipitating out at a certain pH may cause other metal hydroxides to solubilize back to the solution, due to both the acidic and basic natures.

Na_2CO_3 and CaCO_3 are often used to precipitate metal ions but carbon dioxide is often released as a byproduct.



Also, all the above form sludge with high concentrations of heavy metal ions and impurities. The production of sludge is a problem after problem.



Sludge as waste product after metal ion precipitations

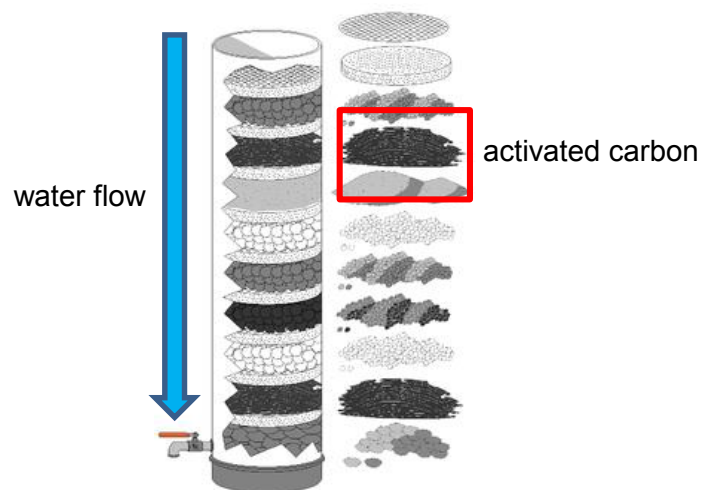
2. Activated carbon

AC is full of incredibly tiny pores and possess a large surface area. It was found that 3 g of activated carbon has the surface area of a football field. The large surface area holds metal ions by trapping them inside during sewage treatment.

Downside:

AC has a short service life. When AC can no longer accommodate metal ions, it reaches the maximum capacity. The cost of constantly replacing AC is high and it is not economical to apply such method to a large-scale sewage treatment.

Also, toxic metal compounds absorbed by activated carbon are broken down for bioregeneration using bacteria. Toxic substances are desorbed in the process.



Sewage treatment with activated carbon

Our approach & methodology

A. Choices of set-up

1. Sink sieve

To separate heavy metal ions into two distinct groups through ion diffusion, we proposed the use of sink sieve as the intermedium coated with a differentially permeable alginate membrane.

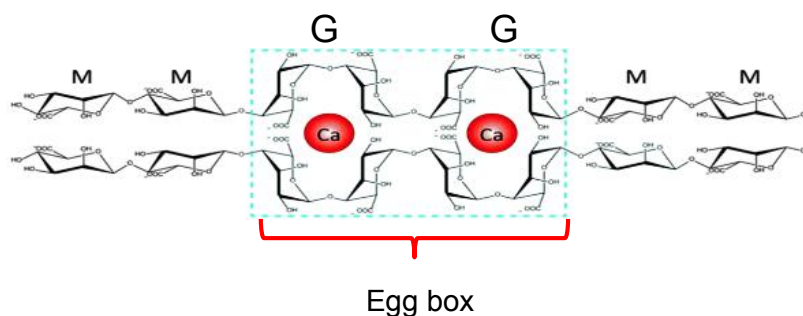
First, the sink sieve provides sufficient mechanical strength for the adhesion of alginate membrane. Alginate is a form of hydrogel with a soft and gelatinous texture. By adhering itself to the mesh, the layer would not deform or tear apart because of the fixed attachment to the mesh. At the same time, metal ions can diffuse through the pores beneath the sieve through a steady alginate layer throughout the whole experiment.

Besides, the surface of a sink sieve is coated with stainless steel. This feature appeals to us since it can be used for long-hour metal ion diffusion without showing signs of rusting or wearing out when immersed in water. Also, the heavy metal ions to be separated would not easily 'eat away' the metallic surface of the sieve, preventing a quality degradation. A consistent provision of good-quality performance is guaranteed.

2. Metal-ion Chelation of Alginate

Alginate is a natural and biocompatible polymer known for cosmetic and medical applications. To push the application of alginate further, we were interested in investigating its ability to selectively separate metal ions. The hydroxyl groups and negatively-charged carboxylate ions of alginate actively participate in the chelation process of NaAlg. The original loosely-bonded Na^+ are displaced with divalent ions or other multivalent ions (Ca^{2+} and Al^{3+}) of higher charge density. The central metal ions then form stronger dative covalent bonds with the alginate cage. Afterwards, polymers crosslink one another and expand into an infinite network through gelation, leading to an increase in the viscosity of the chelated alginate gel. The membrane is then tested for its feasibility of separating metal ions.

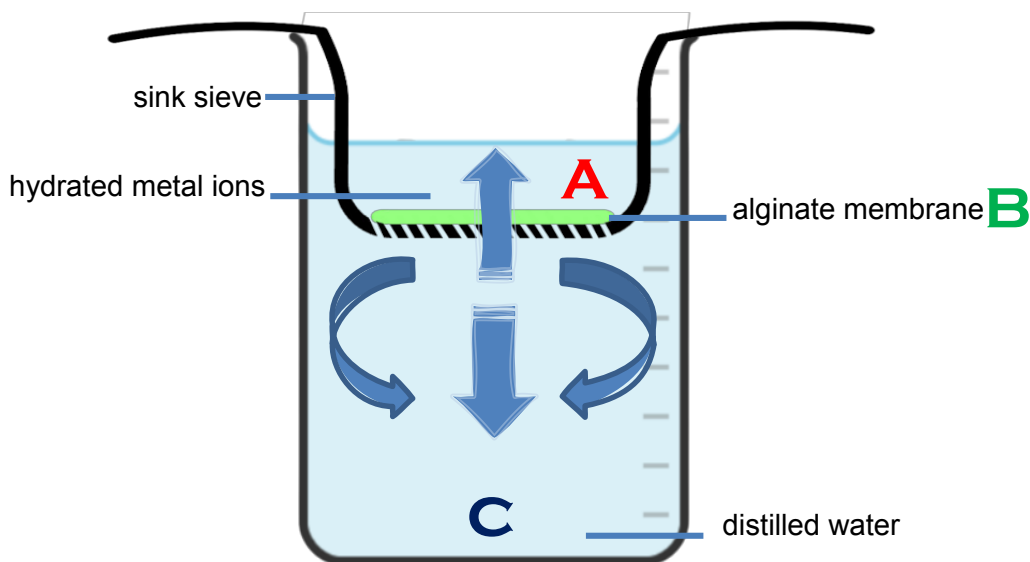
Also, L-glucuronic acid (G-blocks) and D-Mannuronic acid (M-blocks) make up the composition of alginate and exist in different ratios, depending on the species of brown seaweeds. G-block are the main determining factor for the formation of chelated ‘egg box’, metal-ion chelation in a chain of alginate polymers. The ion channels between the alginate walls are the pathway for metal ion diffusion.



The configuration of a chelated alginate polymer chain resembles an egg box

3. Heavy metal ion diffusion

Due to a higher metal ion concentration above the sieve, metal ions were free to diffuse across the alginate layer down the concentration gradient, which resulted in their distinctive absorptivity and permeability.



Equations for calculating absorptivity and permeability are as follows:

shows the direction of net movement of metal ion diffusion

A sample of a typical set-up

$$\text{Absorptivity} = \frac{\text{mass}_{\text{total}} - \text{mass}_A - \text{mass}_C}{\text{mass}_{\text{total}}} \times 100\%$$

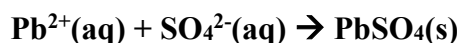
$$\text{Permeability} = \frac{\text{mass}_C}{\text{mass}_{\text{total}}} \times 100\%$$

B. Gravimetric analysis

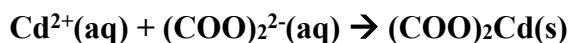
1. Precipitation & filtration

To quantify absorptivity and permeability achieved by metal ions, we chose to solidify the following metal ions in aqueous medium via precipitation, followed by filtration.

Precipitation with Pb^{2+} ,

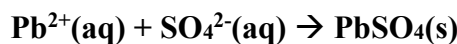


Precipitation with Cd^{2+} ,

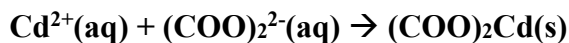


For mixed ions (Pb^{2+} & Cd^{2+}),

a) Precipitation with Pb^{2+}



b) Precipitation with Cd^{2+}



Filter the precipitates with weighed filter paper and wash the paper thoroughly with distilled water. The aim of continuous washing was to ensure that all the excess chemicals (not intended for measurement) and impurities already dissolved through the paper before heating.

2. Heating in oven

Heat all the filter paper in an oven at 120°C for 1.5 h to remove all the water contained in the paper. This could avoid an overestimation of data as water was weighted as well.

Note: Drying the filter paper at 120°C was the most preferable as a higher temperature would dehydrate the cellulose in filter paper

3. Weight measurement

Since filter paper and metal ion precipitates absorbed water from the atmosphere at the instance they were taken out of the oven. It was best to measure their weights as quickly as possible to prevent any overestimation of reading.

Experiments— lead (Pb)

A) Formation of a calcium alginate layer on sieve

Chemicals required	Apparatus
Sodium alginate solution (0.40%, 0.60%, 0.80%, 1.0%)	1 mL syringe
Calcium nitrate solution (0.20 M, 0.40 M, 0.60 M, 0.80 M, 1.0 M)	Sprayers
Tap water	Measuring cylinder
	Dry sink sieve
	Petri dish

Procedures:

1. Spread 0.5 mL NaAlg(aq) evenly on the inner metallic net of sink sieve with syringe
2. Spray $\text{Ca}(\text{NO}_3)_2(\text{aq})$ to the inner metallic net for five times
3. Let the sieve rest for 1 min
4. Spray $\text{Ca}(\text{NO}_3)_2(\text{aq})$ to the underside of the metallic net for five times
5. Let the sieve rest for 1 min
6. Fill up the sieve with 44 mL tap water using a measuring cylinder to check waterproofing

Note: 0.1 mL / spray

Remarks: Proceed to Part B if the sieve shows positive result towards waterproofing



Figure 1a: Spraying $\text{Ca}(\text{NO}_3)_2(\text{aq})$ to a sieve



Figure 1b: Checking waterproofing of an alginate-coated sieve

B) Testing the absorptivity and permeability of Pb^{2+} with CaAlg

Chemicals required	Apparatus
0.05 M lead(II) nitrate solution	Measuring cylinder
1 M sodium sulphate solution	Sink sieve coated with CaAlg
Distilled water	2 beakers
	2 funnels
	2 conical flasks
	Weighed filter paper
	Glass rod

Procedures:

1. Fill a beaker with 88 mL distilled water
2. Pour 44 mL $\text{Pb}(\text{NO}_3)_2(\text{aq})$ into the sieve slowly
3. Set the sieve still on top of the water-filled beaker labelled as 'Down'
4. Allow the set-up to stand for 2 h
5. After 2 h, lift the sieve and pour the remaining solution above it into another beaker labelled as 'Up'
6. Add 4 mL $\text{Na}_2\text{SO}_4(\text{aq})$ into both beakers, followed by slow stirring
7. Filter the content in both beakers with weighed filter paper using the conical flasks
8. Wash both pieces of filter paper with distilled water for several times
9. Heat all the filter paper at 120°C in an oven for 1.5 h
10. Perform gravimetric analysis
11. Repeat Parts A and B with different concentrations of NaAlg and $\text{Ca}(\text{NO}_3)_2(\text{aq})$



Figure 2a: Counting down for Pb^{2+} diffusion



Figure 2b: Washing filter paper w/ lead precipitate

Experiments— cadmium (Cd)

C) Formation of a calcium alginate layer on sink sieve

Refer to the chemicals & apparatus listed in Part A

Follow the procedures in Part A

D) Testing the absorptivity and permeability of Cd^{2+} with CaAlg

Chemicals required	Apparatus
0.05 M cadmium(II) nitrate solution	Measuring cylinder
1 M potassium oxalate solution	Sink sieve coated with CaAlg
Boiled distilled water	2 beakers
	2 funnels
	2 conical flasks
	Weighed filter paper
	Glass rod

Note: 0.05 M $\text{Cd}(\text{NO}_3)_2(\text{aq})$ was prepared by mixing 44 mL boiled distilled water with $\text{Cd}(\text{NO}_3)_2(\text{s})$ to avoid precipitation of $\text{CdCO}_3(\text{s})$

Procedures:

1. Fill a beaker with 88 mL distilled water
2. Pour 44 mL $\text{Cd}(\text{NO}_3)_2(\text{aq})$ into the sieve slowly
3. Set the sieve still on top of the water-filled beaker labelled as 'Down'
4. Cover the set up with a watch glass and leave it still for 2 h
5. After 2 h, lift the sieve and pour the remaining solution above it into another beaker labelled as 'Up'
6. Add 8 mL $(\text{COOK})_2(\text{aq})$ into both beakers, followed by slow stirring
7. Filter the content in both beakers with weighed filter paper using the conical flasks
8. Wash both pieces of filter paper with distilled water for several times
9. Heat all the filter paper at 120°C in an oven for 1.5 h
10. Perform gravimetric analysis
11. Repeat Parts C and D with different concentrations of NaAlg and $\text{Cd}(\text{NO}_3)_2(\text{aq})$

Formation of aluminium alginate layer on sink sieve

Chemicals required	Apparatus
Sodium alginate solution (0.40%, 0.60%, 0.80%, 1.0%)	1 mL syringe
Aluminium nitrate solution (0.20 M, 0.40 M, 0.60 M, 0.80 M, 1.0 M)	Sprayers
Tap water	Measuring cylinder
	Dry sink sieve

Procedures:

1. Spread 0.5 mL NaAlg(aq) evenly on the inner metallic net of sink sieve with syringe
2. Spray $\text{Al}(\text{NO}_3)_3(\text{aq})$ to the inner metallic net for five times
3. Let the sieve rest for 1 min
4. Spray $\text{Al}(\text{NO}_3)_3(\text{aq})$ to the underside of the metallic net for five times
5. Let the sieve rest for 1 min
6. Fill up the sieve with 44 mL tap water using a measuring cylinder to check waterproofing

Note: 0.1 mL / spray

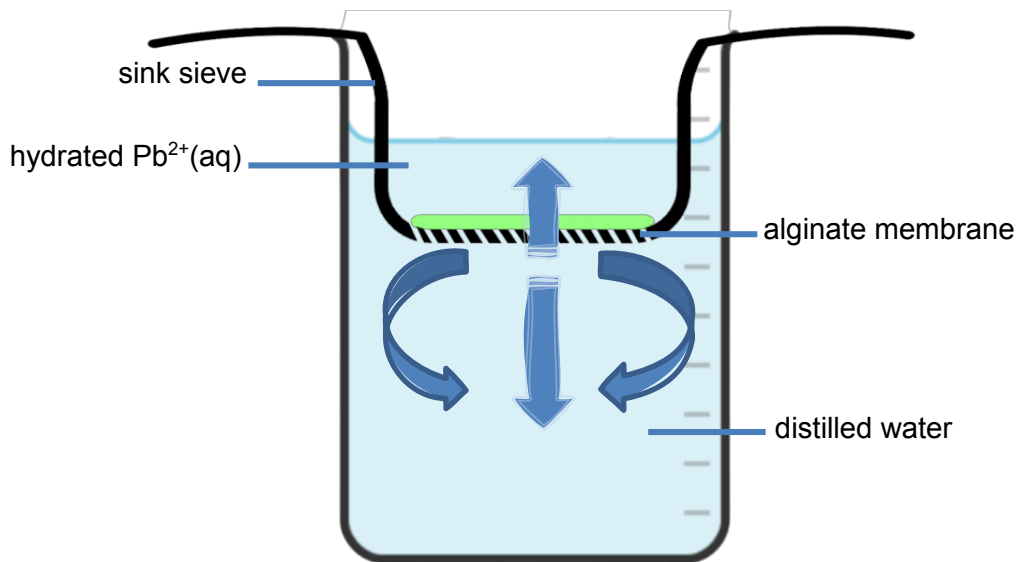
E) Testing the absorptivity and permeability of mixed metal ions (Pb^{2+} & Cd^{2+}) with CaAlg / CaAlAlg

Chemicals required	Apparatus
0.05 M lead(II) nitrate solution	Measuring cylinder
0.05 M cadmium(II) nitrate solution	Sink sieve coated with CaAlg / CaAlAlg
0.5 M potassium sulphate solution	4 beakers
1 M potassium oxalate	4 funnels
Distilled water	4 conical flasks
	Filter paper

Procedures:

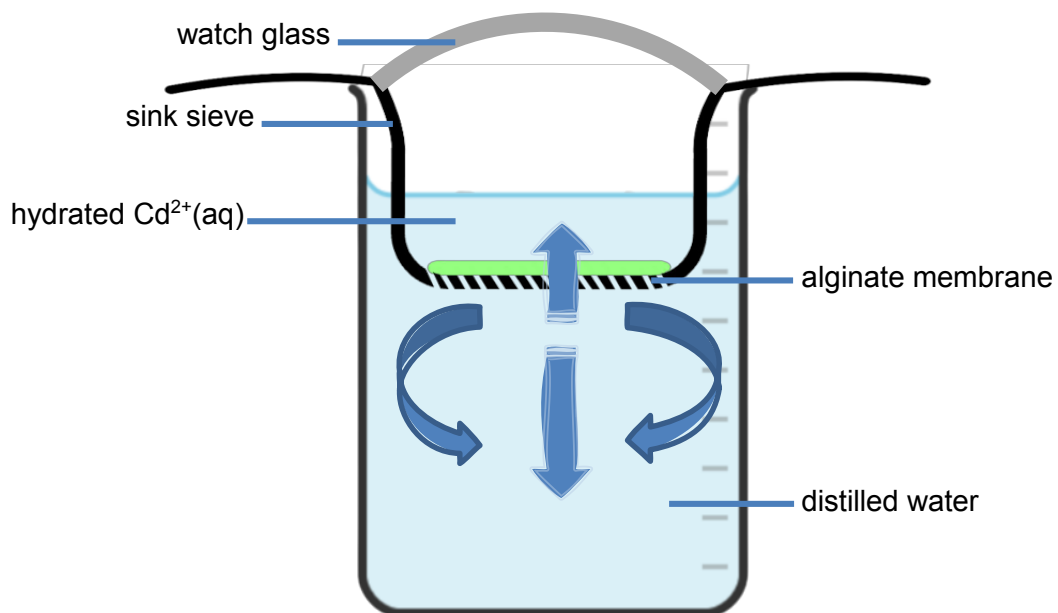
1. Fill a beaker with 88 mL distilled water
2. Pour a mixture of 22 mL 0.05 M $\text{Pb}(\text{NO}_3)_2(\text{aq})$ & 22 mL 0.05 M $\text{Cd}(\text{NO}_3)_2(\text{aq})$ into the sieve slowly
3. Set the sieve still on top of the water-filled beaker labelled as 'Down L' and cover it up with a watch glass
4. Allow the set-up to stand for 2 h
5. After 2 h, lift the sieve and pour the remaining solution above it into another beaker labelled as 'Up L'
6. Add 16 mL $\text{K}_2\text{SO}_4(\text{aq})$ into both beakers, followed by slow stirring
7. Filter the content in both beakers with weighed filter paper using the conical flasks
8. Wash the filter paper with distilled water for several times
9. Transfer the filter paper to a rack and add 8 mL $(\text{COOK})_2(\text{aq})$ to the bottom of both conical flasks labelled as 'Up C' and 'Down C' with stirring
10. Filter the solution in both flasks with new filter paper, followed by washing with distilled water
11. Heat the four filter paper at 120°C in an oven for 1.5 h
12. Perform gravimetric analysis

For Pb²⁺



➡ shows the pathway of net movement of metal ion diffusion

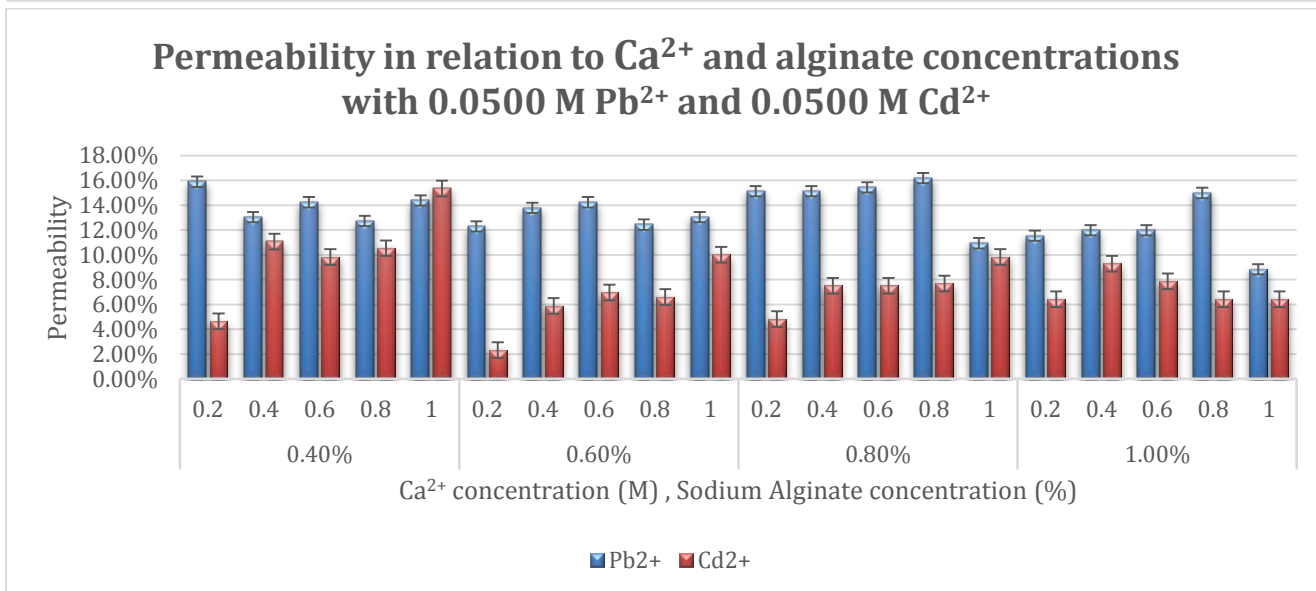
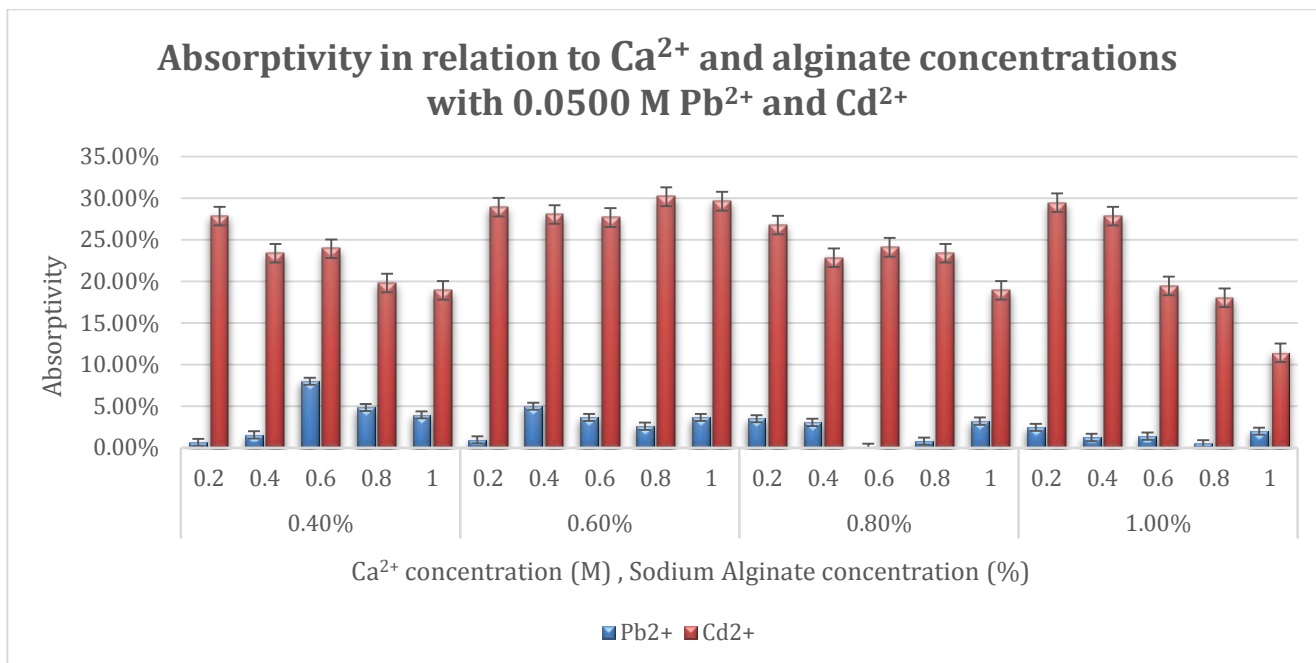
For Cd²⁺



➡ shows the pathway of net movement of metal ion diffusion

Data Analysis

Calcium Alginate Layer



Discussion

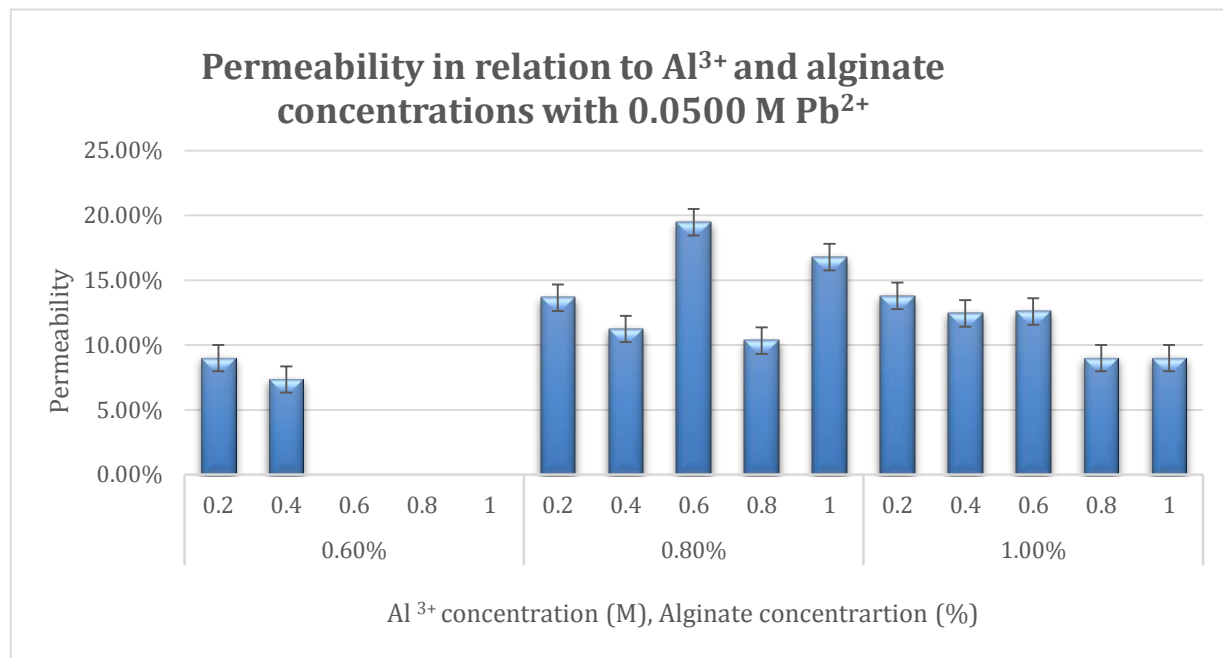
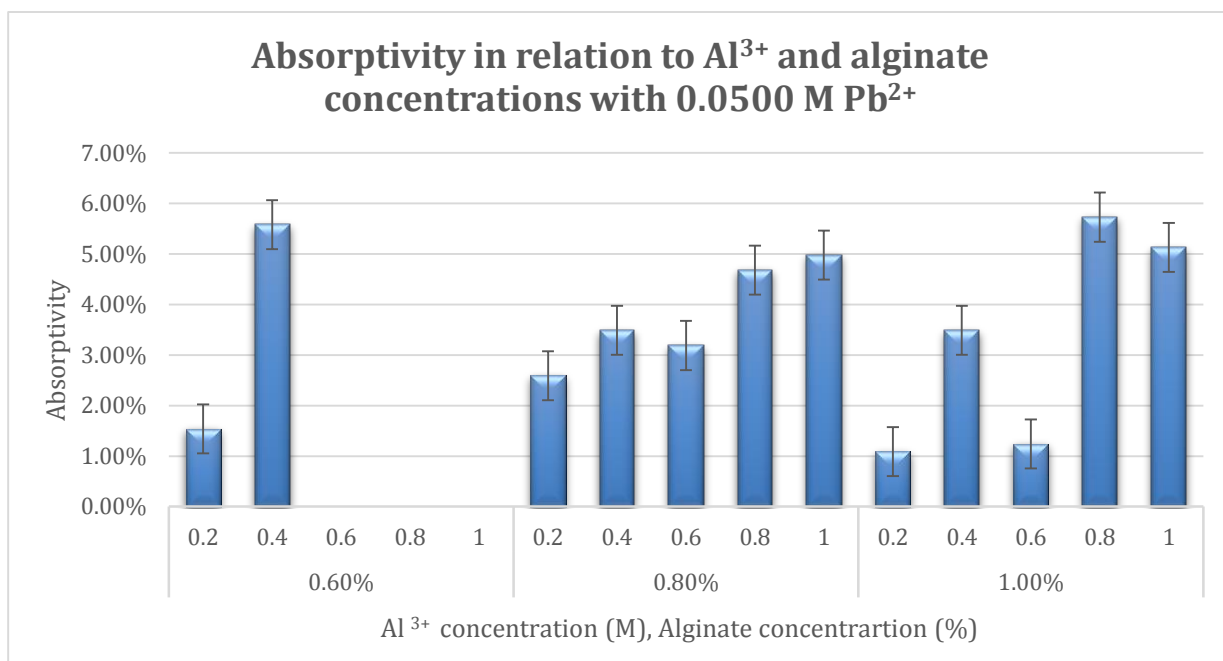
It was found that the permeability of Pb^{2+} was higher than that of Cd^{2+} in all concentrations of Ca^{2+} and alginate.

We reasoned that Cd^{2+} had a higher affinity towards alginate ions, compared to Pb^{2+} . Since the cationic size of Cd^{2+} was smaller (ionic radii: 95 pm), compared to Pb^{2+} (ionic radii: 119 pm), the charge density of Cd^{2+} were higher than that of Pb^{2+} .

For Cd^{2+} , the absorptivity decreased along with the concentrations of Ca^{2+} and alginate. We suggested that when there were abundant Ca^{2+} and alginate polymers, more ion channels would be formed for ion exchange. For the case of Pb^{2+} , it had both peak and trough of absorptivity for every concentration of alginate with various Ca^{2+} concentrations. It was believed that when the concentration of Ca^{2+} was low, Pb^{2+} would chelate NaAlg by replacing sodium with lead. When there was a moderate amount of Ca^{2+} (0.60 M), enough ion channels would be formed to allow Pb^{2+} to diffuse freely through the alginate layer. But when there was an overly high concentration of Ca^{2+} (1.00 M), the ion channels would be excessively chelated to form zipping dimers, which meant that the most ion channels were disrupted by the overloading amount of Ca^{2+} . The channels were no longer functional and Pb^{2+} were hindered to diffuse any further, resulting in a higher absorptivity.

Based on our observation, the permeability of Pb^{2+} and Cd^{2+} usually had a peak at an optimum level of Ca^{2+} density for each concentration of NaAlg. It was found that Pb^{2+} generally had a higher permeability than Cd^{2+} . It was also suggested that permeability of Pb^{2+} was at a higher Ca^{2+} concentration than Cd^{2+} for almost all alginate concentrations. We deduced that a wider ion channel was required if Pb^{2+} had to fit through the membrane via diffusion. Therefore, when Ca^{2+} existed in low concentrations, the ion channels formed by chelated-alginate polymers were only loosely packed. And for 1.0 M Ca^{2+} and 1.0% alginate concentration, alginate polymers were too closely packed, Cd^{2+} were forced to press against one another and were easily repelled due to the same positive charge. Therefore, Cd^{2+} became more easily trapped in ion channels when the alginate concentration increased, showing a negative relationship between alginate concentration and permeability for Cd^{2+} .

Aluminium Alginate Layer



Based on the results, Pb²⁺ reached an absorptivity peak of 5.73% and a permeability peak of 19.48% towards an AlAlg of 0.80 M Al³⁺ and 1.0% alginate & 0.60 M and 0.80% alginate respectively. For absorptivity, a general rising trend was observed from 0.2 M to 1.0 M Al³⁺ at 0.80% alginate. Oppositely, for permeability, a general declining trend was indicated from 0.2 M to 1.0 M Al³⁺ at 1.0% alginate.

A stable and regular trend was not seen for both absorptivity and permeability with AlAlg. But in general, permeability of Pb²⁺ towards AlAlg surpassed absorptivity. We proposed that the non-uniform formation of AlAlg was the cause of such irregular absorptivity and permeability.

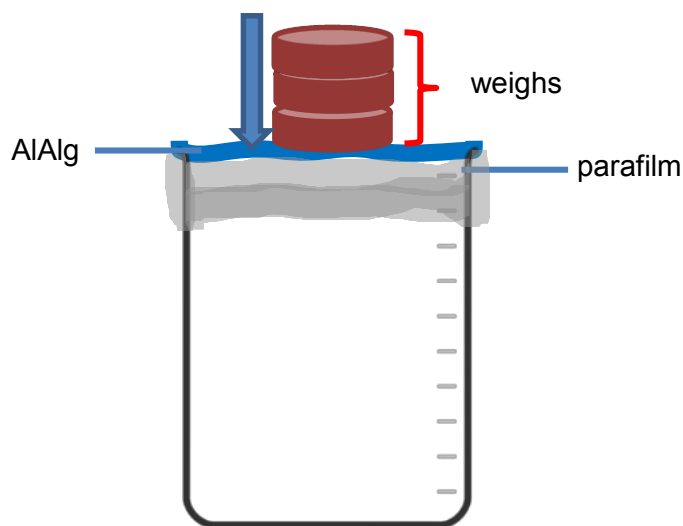
Strength Test

A test was conducted to investigate the mechanical strength of AlAlg.

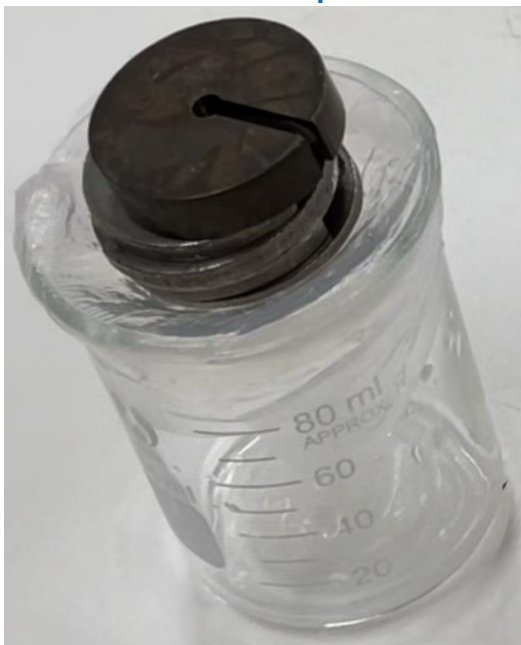
Procedures:

1. Spray excess $\text{Al}(\text{NO}_3)_3(\text{aq})$ to the surface of $\text{NaAlg}(\text{aq})$ evenly spread on a petri dish
2. Wait for 1 min to let AlAlg coagulate
3. Carefully detach the AlAlg from the petri dish with a spatula
4. Slowly cover the opening of an empty beaker with the layer and seal the side of beaker and AlAlg with parafilm tape*
5. Stack up the weighs one by one (begin with the lightest) on top of the layer until it breaks
6. Measure the weight of all the masses fallen and calculate the pressure needed to puncture the layer

**The use of parafilm tape prevents the layer from sliding inwards the beaker once placed on top*



Before collapse



A clear hole was shown



After collapse



Mass of total fallen weighs = **165 g**

We also measured the diameter of a weigh using dial caliper

Diameter of each weigh = 25.4 mm

$$\begin{aligned}
 \text{Pressure} &= \frac{\text{Force}}{\text{Surface area}} \\
 &= \frac{0.165 \times 9.81}{0.0127^2 \pi} \\
 &= \underline{\underline{3194.4 \text{ Nm}^{-2} \text{ (corr. to 1 d.p.)}}}
 \end{aligned}$$

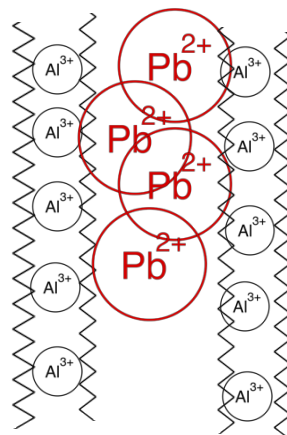


Discussion

After testing with all types of alginates, it was found that AlAlg held the highest mechanical strength, giving the layer a hard but brittle nature. It was proposed that the major reason was the hard but brittle nature of AlAlg. This induced a higher difficulty for the AlAlg layer to enlarge through gelation, forming a porous alginate membrane of unequal thickness. The pores then allowed Pb^{2+} to permeate at irregular patterns. For example, after many trials, we still could not successfully produce AlAlg of 0.60 M, 0.80 M and 1.0 M Al^{3+} with 0.60% alginate, which all failed to show waterproofing ability.

Apart from that, Al^{3+} carried a positive charge of 3. We reasoned that the high charge density of Al^{3+} ($\rho = 364 \text{ C mm}^{-3}$) created a more powerful attraction towards G-blocks of alginate solution and binded to them much more strongly than Ca^{2+} ($\rho = 52 \text{ C mm}^{-3}$), which was only doubly charged. The diameter of the aluminium-chelated ion channel was longer, lengthening the gap between the walls of a channel, despite a possible increase in the abundance of ion channels for ion diffusion. This therefore accounted for the relatively high permeability of Pb^{2+} .

An illustration showing the penetration of Pb^{2+} under the repulsive effect of AlAlg



Cationic radii of $\text{Pb}^{2+} = 119 \text{ pm}$

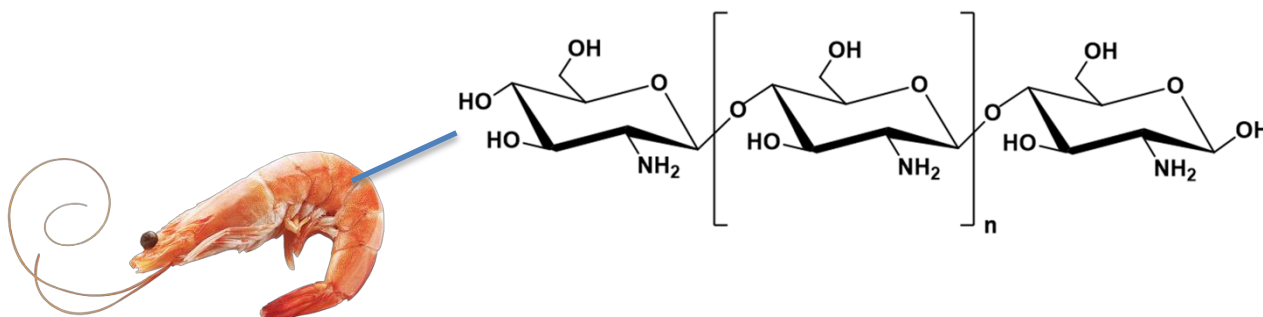
Cationic radii of $\text{Al}^{3+} = 53.5 \text{ pm}$

In terms of absorptivity, the sets of AlAlg made of 1% alginate absorbed Pb^{2+} more than other combinations. It was proposed that the alginate with high aluminium concentration increased the overall charge of chelated-alginate layer since the influx of Al^{3+} overly binded to alginate polymers. During diffusion, Pb^{2+} ($\rho = 32 \text{ C mm}^{-3}$), having a much smaller charge density than Al^{3+} ($\rho = 364 \text{ C mm}^{-3}$), tended to be repelled by Al^{3+} as they both carried a positive charge. The repulsive force hence kept Pb^{2+} from reaching the other end of the ion channel, retaining them in the midst of Al-chelated alginate polymers. It was believed that the repulsion between Al^{3+} and Pb^{2+} gave rise to higher absorptivity of AlAlg at a higher alginate concentration.

Extension --- Chitosan As A Potential Capping Agent

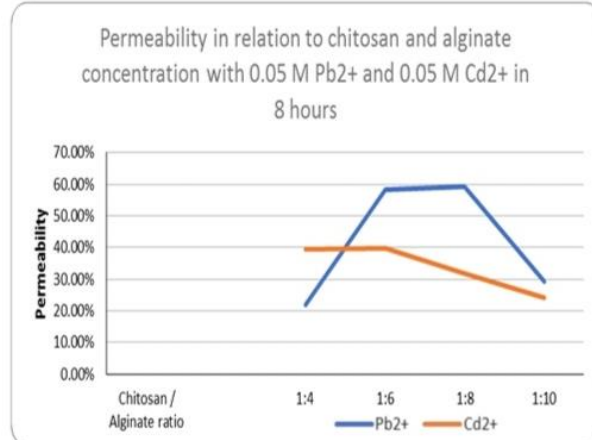
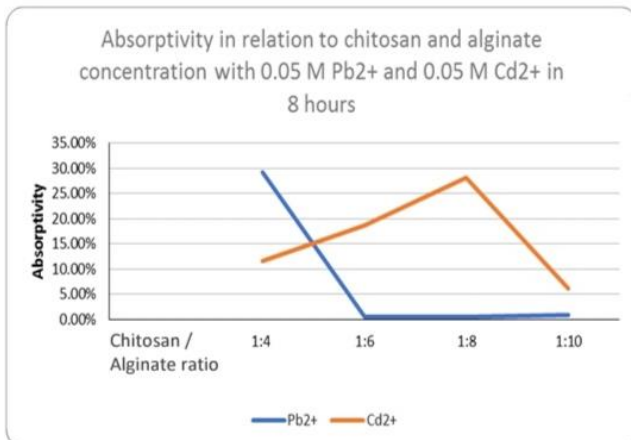
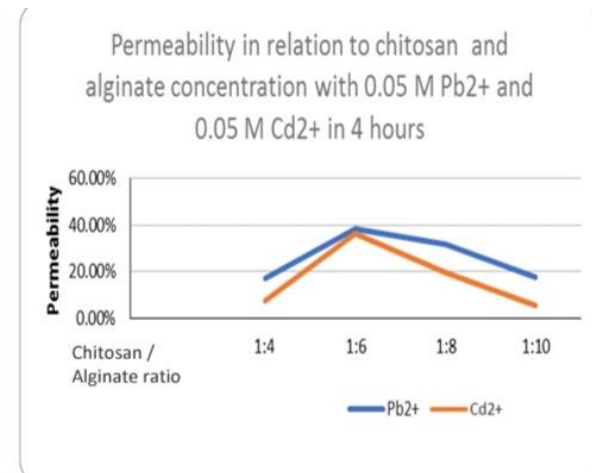
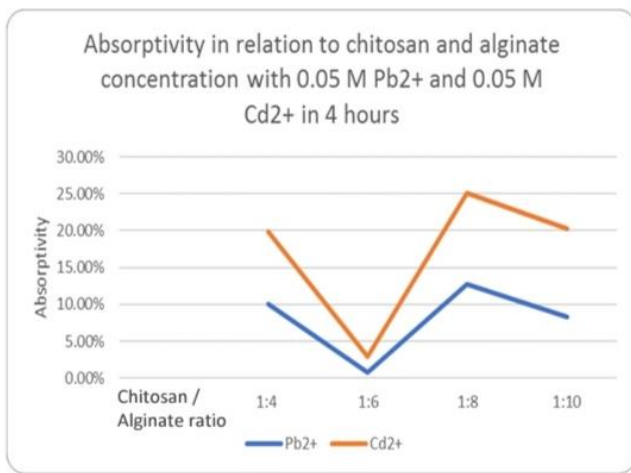
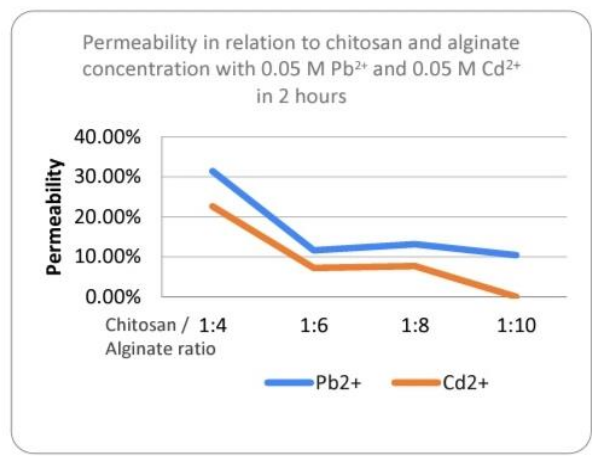
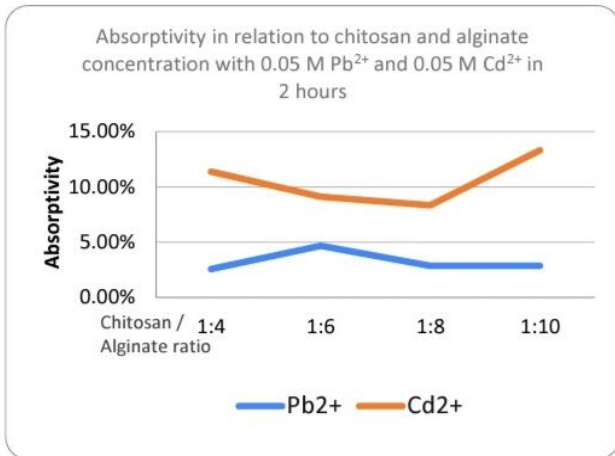
Chitosan

Chitosan is a natural biopolymer commonly found in the outer shells of sea crustaceans such as shrimps and crabs. It exists in the form of linearly connected polymer chains, which exhibited low water solubility. In the experiment, chitosan was dissolved with a small amount of acetic acid with mild heat.



While alginate mainly relies on hydroxyl groups (-OH) and carboxylate ions (RCOO^-) chelating with metal ions, chitosan possesses a functional group that is absent in alginate ---- amine group (-NH₂). It was worth exploring whether amine groups could be a useful capping agent to provide more binding sites for metal ion chelation. Also, chitosan is not as biodegradable as alginate is in nature, which implies that mixing chitosan could theoretically delay the hydrolysis of the alginate itself. Hence, the chelated membrane could sustain longer and allow more penetration or absorption of metal ions. However, chitosan could not be applied alone to form a differentially membrane because its pure form was too glutinous and could not be spread around evenly on the sink sieve. To increase its adaptability to form an intact hydrogel, alginate was added in various proportions to determine how their relationships contributed to a more effective metal ion separation. The experiments were also repeated in different durations.

Note: 0.6 M $\text{Ca}^{2+}/\text{Al}^{3+}$ (3:2) served as the control chelating agent for chitosan/alginate below



Discussion

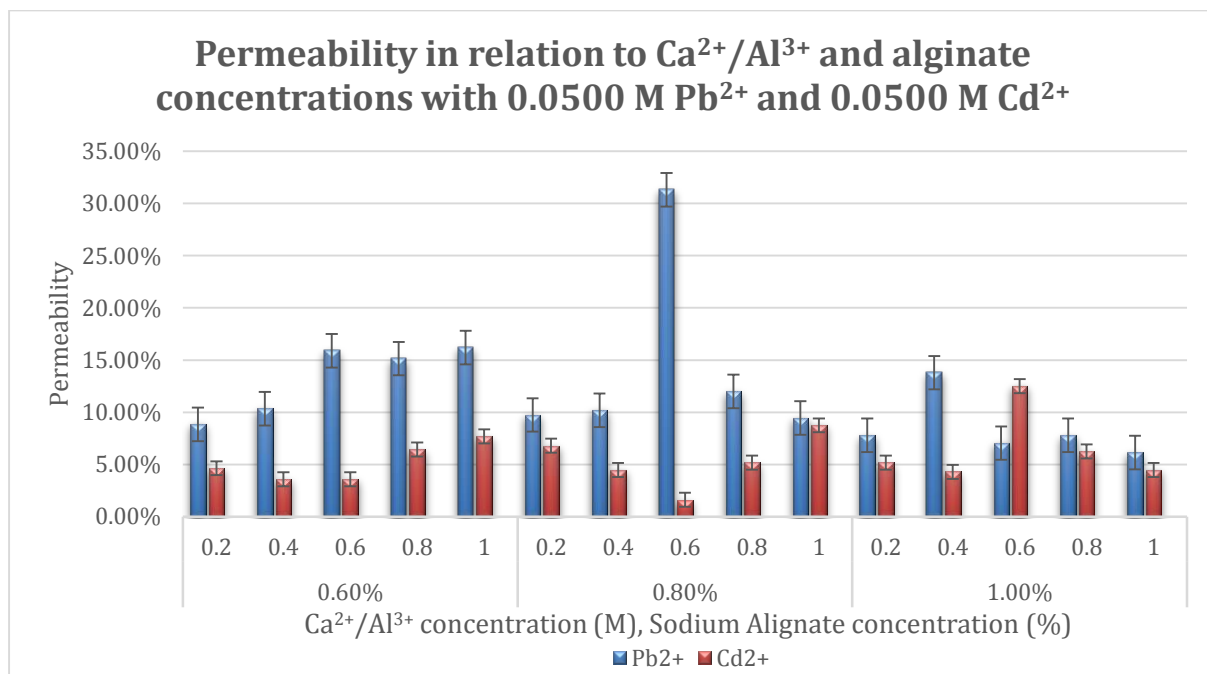
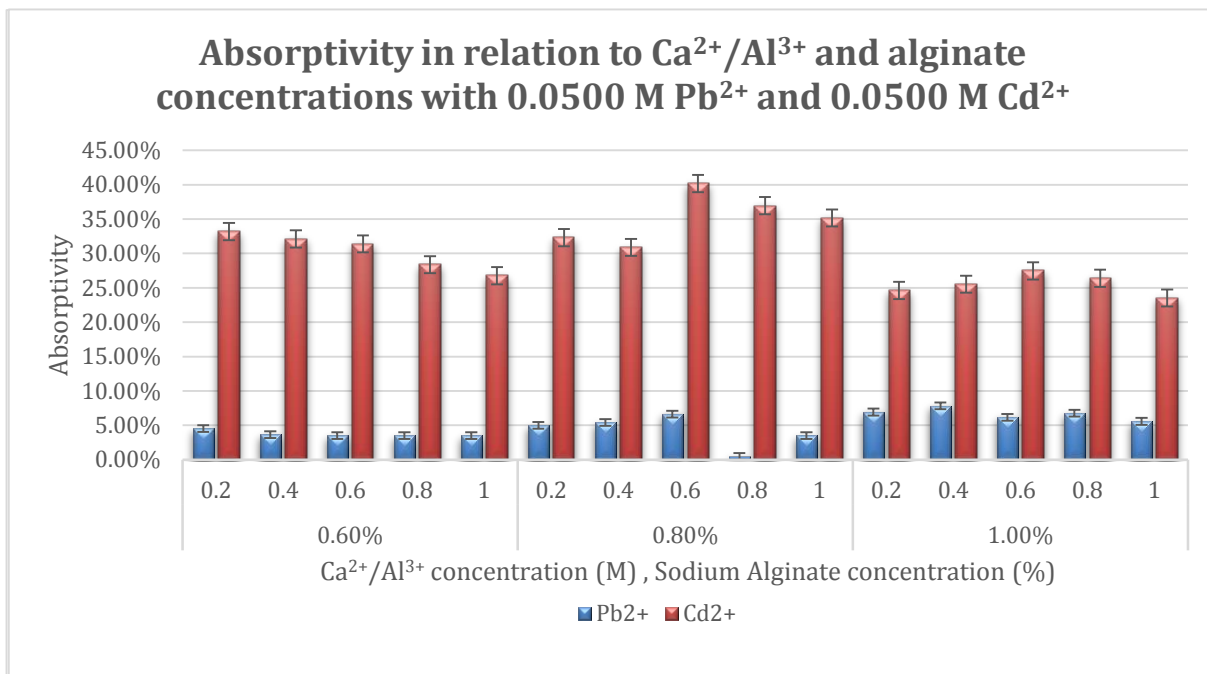
The *highest* Pb^{2+} permeability (59.36%) and Cd^{2+} absorptivity (28.08%) were recorded with 1:6 chitosan/alginate in 8 hours. The corresponding selectivity ratio (Pb^{2+} permeability: Cd^{2+} permeability) was 1.87:1.

For Pb^{2+} permeability, a general rising trend was displayed along with increasing hours of diffusion. It was believed that the non-biodegradable nature of chitosan helped extend the service life of alginate and maximized its potential to permeate more Pb^{2+} .

In terms of Cd^{2+} absorptivity, a mutual correlation between concentrations of chitosan and absorption of Cd^{2+} was not observed, which meant heavy metal absorption mainly depended on the attractive force of the carboxylate ions and hydroxyl groups, but not amine groups.

Therefore, we concluded that chitosan could at most serve as a capping agent which delayed the hydrolysis process and allowed more Pb^{2+} permeation but had no significant effect in contributing to extra absorption of metal ions.

Calcium-Aluminium Alginate Layer



Note: $Ca^{2+}: Al^{3+} = 3: 2$

Discussion

Based on our results, it was observed that Cd^{2+} were highly absorptive, compared with Pb^{2+} in all cases with different Ca^{2+} and alginate concentrations, proving its high tendency of being absorbed as part of the alginate membrane. The highest peak of permeability by Cd^{2+} recorded was 40.16% with 0.60 M $\text{Ca}^{2+}/\text{Al}^{3+}$ and 0.80% alginate, which was more than five times the highest absorptivity achieved by Pb^{2+} .

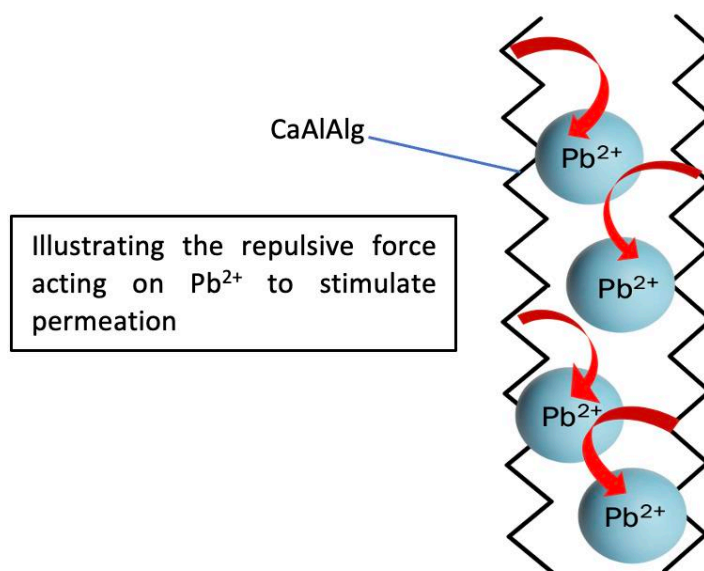
On the other hand, more than 90% of the cases, Pb^{2+} displayed a much higher permeability than Cd^{2+} , with the highest permeability of 31.32% at 0.60 M $\text{Ca}^{2+}/\text{Al}^{3+}$ and 0.80% alginate, which was the same set indicating the highest absorptivity of Pb^{2+} .

The exceptionally high absorptivity of Cd^{2+} , proven by earlier investigations, was due to their high affinity towards the alginate membrane, regardless of the alginate concentrations. For the set of 0.60 M $\text{Ca}^{2+}/\text{Al}^{3+}$ and 0.80% alginate, nearly all Cd^{2+} (40.16%) were absorbed by the membrane and just a tiny fraction (1.61%) penetrated along with Pb^{2+} . However, when compared with previous absorptivity of Cd^{2+} towards CaAlg at 0.8% alginate and all concentrations of Ca^{2+} , not even one of the absorptivity reached as high as the CaAlAlg set under the same alginate concentration (0.8%). We deduced that it was the involvement of Al^{3+} that led to the increment in absorptivity. It was believed that the high charge density of Al^{3+} ($\rho = 364 \text{ C mm}^{-3}$) aided the process of Cd^{2+} absorption with Ca^{2+} ($\rho = 52 \text{ C mm}^{-3}$). The overall charge density increased, narrowing the passages of ion channels. As discussed before, Al^{3+} was known to provide mechanical strength, which contributed to a stronger alginate layer and CaAlg tended to be chelated to form zipping dimers (functionless ion channels) at a high Ca^{2+} concentration (1%). We theorized that the mechanical strength provided by the Al^{3+} prevented the CaAl -chelated ion channels from being destroyed so easily like in Ca -chelated channels alone.

The additional strength given to CaAlAlg improved the tolerance of Ca^{2+} and thus delayed the occurrence of zipping dimers. The maximum capacity of Cd^{2+} increased, which explained the high absorptivity with CaAlAlg .

For permeability, Pb^{2+} reached the peak at 31.32% with the same concentrations of alginate and $\text{Ca}^{2+}/\text{Al}^{3+}$ as the highest absorptivity of Cd^{2+} . We proposed that the ion channel at that point was just enough for almost all Pb^{2+} to pass through, while maintaining high absorptivity of Cd^{2+} . The permeability of Pb^{2+} plummeted for the next two concentration of $\text{Ca}^{2+}/\text{Al}^{3+}$ mixture (e.g. 0.80 M & 1.0 M). Therefore, we regarded 0.8 M $\text{Ca}^{2+}/\text{Al}^{3+}$ mixture as the turning point of permeability of Pb^{2+} . It was believed that after 0.60 M $\text{Ca}^{2+}/\text{Al}^{3+}$ and 0.80% alginate was the threshold of aggregation of dimers. The absorptivity of Cd^{2+} of all concentrations of $\text{Ca}^{2+}/\text{Al}^{3+}$ under 1.0% alginate remained consistent, which proved that the zipper dimer had absorbed the maximum amount of Cd^{2+} and Pb^{2+} also reached the lowest permeability.

Since Pb^{2+} and Cd^{2+} both reached the highest permeability and absorptivity respectively at 0.60 M $\text{Ca}^{2+}/\text{Al}^{3+}$ and 0.80% alginate, it was found that this particular alginate served as the most effective heavy metal ion separator. Hence, such alginate fulfilled the requirements of a differentially permeable membrane two types of metal ions were selectively sorted into two separate groups.

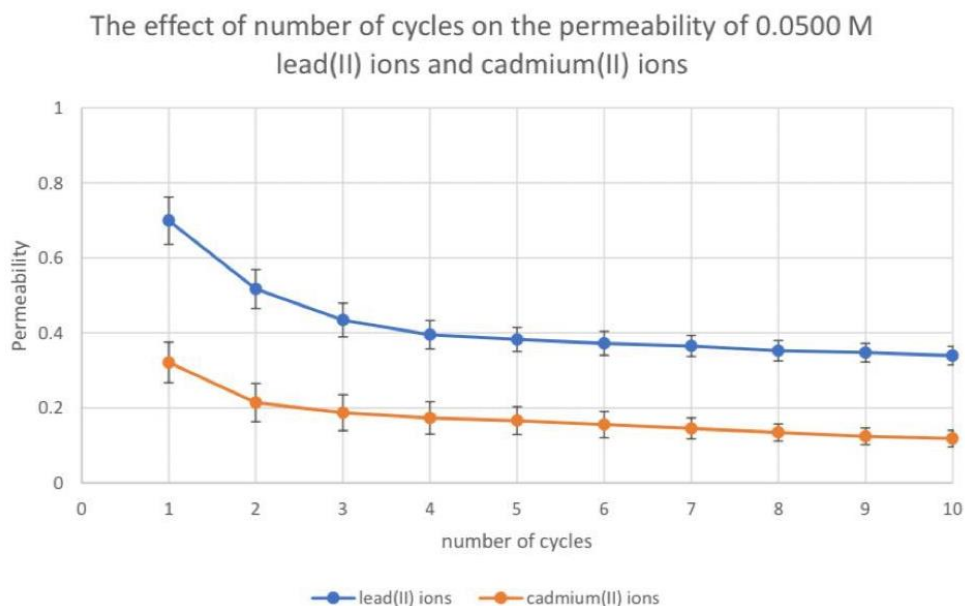


Applications

Our investigative model for selective separation of metal ions could be applied to general water treatment, particularly for those in battery-making industries, where heavy metal ions (e.g. Pb^{2+} & Cd^{2+}) discharged into water frequently.

Furthermore, the capability of alginate to separate distinctive metal ions into different solutions boosts the effectiveness to recycle the used metal ions. Through recycling, used metal ions can be re-used to manufacture batteries again, achieving chemical conservation.

The alginate membrane synthesized in our project was also tested with its sustainability. The following graph exhibits the reusability of an alginate membrane by showing the number of cycles of metal ion separations an identical alginate membrane can process without acid leaching.



The alginate membrane still exhibits high efficiency in separating metal ions with a less than 5% decline in permeability each time. The decent reusability allowed the alginate membrane to be reused up to 10 cycles, maximizing its potential in separating metal ions.

Also, the biodegradability of alginate gives it an eco-friendly nature and no side products such as toxins are released into the environments during its service. Its function as a differentially permeable membrane requires no energy but time, making it an eco-friendly and energy-conserving option to separate metal ions.

Conclusion

From our experiments, we observed that the absorptivity and permeability were dependent upon the concentrations & types of chelating metal ions and alginate. It was also found that the charge density of chelating metal ions influenced the mechanical strength of alginate hydrogel (e.g AlAlg).

In general, a negative relationship between permeability and absorptivity of heavy metal ions was observed. In other words, absorptivity of heavy metal ions declined with the increasing amount of chelating metal ions, and vice versa. Also, we theorized that the permeability of heavy metal ions was supposedly at the extremes (highest vs. lowest) when chelating metal ion concentrations were at the peak or bottom.

Based on our data, Cd^{2+} displayed a high likelihood to be absorbed by both CaAlg and CaAlAlg. Compared to CaAlg, AlAlg held the highest mechanical strength, higher absorptivity and lower permeability towards Pb^{2+} . As for CaAlAlg ($\text{Ca}^{2+}:\text{Al}^{3+} = 3:2$), its permeability (31.32%) and absorptivity (40.16%) achieved were both the highest towards Pb^{2+} and Cd^{2+} respectively, which made its performance in metal ion separation far exceed all the other alginates with a selectivity ratio of **19.5 :1**.

For chitosan/alginate, the most significant Pb^{2+} permeability (59.36%) and Cd^{2+} absorptivity (28.08%) were attained with 1:6 $\text{Ca}^{2+}/\text{Al}^{3+}$ chelated chitosan/alginate in 8 hours of diffusion time. The corresponding selectivity ratio was 1.87:1.

Therefore, we reached a conclusion that the most efficient differentially permeable membrane for separating metal ions would be **a mixed alginate layer comprised of 0.60 M $\text{Ca}^{2+}/\text{Al}^{3+}$ and 0.80% alginate**.

References

1. njp clean water
Removal of heavy metal ions from wastewater: a comprehensive and critical review
<https://www.nature.com/articles/s41545-021-00127-0>
2. International Journal of Current Advanced Research
ISSN: O: 2319-6475, ISSN: P: 2319-6505, Impact Factor: 6.614
GROWTH AND CHARACTERIZATION OF CADMIUM OXALATE CRYSTAL USING SILICA GEL
<http://journalijcar.org/sites/default/files/issue-files/6693-RW-2018.pdf>
3. Effective ionic radii in pm of elements in function of ionic charge and spin
https://en.wikipedia.org/wiki/Ionic_radius
4. Charge Densities of *Selected Ions*. APPENDIX 2. A-13
<https://bcs.whfreeman.com/WebPub/Chemistry/raynercanham6e/Appendices/Rayner-Canham%205e%20Appendix%202%20-%20Charge%20Densities%20of%20Selected%20Ions.pdf>
5. Journal of Nanomaterials / 2016 / Article
One-Step Green Synthesis of Metallic Nanoparticles Using Sodium Alginate

<https://www.hindawi.com/journals/jnm/2016/9790345/>
6. Concentration and M/G ratio influence the physiochemical and mechanical properties of alginate constructs for tissue engineering
<https://journals.sagepub.com/doi/pdf/10.1177/228080000600400203>
7. Mechanisms of oligoguluronate modulating the calcium-induced gelation of alginate
<https://www.sciencedirect.com/science/article/abs/pii/S0032386115301464>