Investigation of Effect of Concentration of Chitosan in Chitin Bioplastics and Plasticizer on adsorption of heavy metal ions

Ethan Chai Tsin Heng(4i108)

Tan Pei Feng (4i122)

Group 1 -28

Project Mentor: Ms Lena Koh

Abstract

The aim of this project is to investigate the effect of concentration and plasticizer in bioplastic on its adsorption of heavy metal ions. The chitosan was obtained via deacetylation of chitin extracted from prawn shells. The chitosan was separately plasticized to chitosan bioplastic using the plasticizers castor oil and glycerol. The concentration of chitosan in the plastics was also modified. The chitosan plastic was then placed in aqueous zinc sulfate, and the concentration of Zn^{2+} metal ions at the end of the experiment was measured using a colorimeter. The results were used to determine the relationship between the concentration of chitosan in bioplastic and the rate of heavy metal ion adsorption, and between the plasticizer used and the rate of heavy metal ion adsorption. It was concluded that an increase in the concentration of chitosan in bioplastic led to an increase in the rate of heavy metal ion adsorption. The castor oil plasticizer was found to give a greater rate of adsorption than the glycerol plasticizer.

Introduction
Rationale

According to the World Health Organization, half the World's population will be living in water stressed areas. One reason for this is the contamination of water. For example, in 2017, 29% of the world's population did not have access to a water source free from contamination. (World Health Organization, 2019). One group of deadly water contaminants is heavy metal ions. They are classified as human carcinogens (known or probable) according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer. As such, it is important to find ways to effectively remove heavy metal ions from water. Chitosan macro and nanoparticles have previously been shown to be capable of adsorption of heavy metal ions. Adsorbent had maximum efficiency at the temperature of 25 °C. At the concentration of 10 mg/L of zinc metal ions, maximum effective removal of chitosan macro and nano size particles were 90.80 and 99.10 %, respectively. (Seyedmohammadi *et al*, 2016). However, nanoparticles could have negative health implications if inhaled into lungs, and as such this contradicts the original intention of improving people's health. (Hoet *et al*, 2004) On the other hand, chitosan bioplastic is much safer to use as it is a biodegradable plastic. As such, this project has been undertaken to investigate the effect of the concentration of chitosan on the rate of adsorption of heavy metal ions, to determine the feasibility of using chitosan bioplastic for the absorption of heavy metal ions.

Literature Review

In 2017, 29% of the world's population did not have access to a water source free from contamination. (World Health Organization, 2019). Heavy metal ions, one source of contamination, are classified as human carcinogens according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer. As such, it is important to find ways to effectively remove heavy metal ions from water.

Currently, Chitin can be extracted from crab and prawn shells. In industrial processing, chitin is extracted by acid treatment to dissolve the calcium carbonate present in the cretaceous shells, followed by an alkaline solution to dissolve proteins. (Younes and Rinaudo, 2015).

Deacetylation of chitin to produce chitosan is usually achieved by hydrolysis of the acetamide groups with concentrated NaOH or KOH (40–50%) at temperatures above 100^{o}C. (Antonio *et al*, 2017).

Chitosan bioplastic has previously been synthesized using plasticizers and starch, with glycerin and acetic acid. The tensile strength of the chitosan bioplastic increased linearly with concentration of chitosan, the greatest being 60.629 for composition of starch/ chitosan at 35/65. (Mutmainna *et al*, 2019).

Modified chitosan has been used to make a chitosan-cellulose acetate-TiO_2 based membrane for adsorption of the heavy metal ion Cu^{2+}. The adsorption efficiency of the membrane was shown to be 99.7% when the initial concentration of the Cu^{2+} solution was 1.000g/L. (Yu *et al*, 2019)

Objectives and hypotheses

Objectives

Investigate the effect of concentration of chitosan on heavy metal adsorption rate.

Investigate the effect of the type of plasticizer used on heavy metal adsorption rate.

Hypothesis

The greater the concentration of chitosan, the higher the rate of heavy metal adsorption.

Castor Oil as a plasticizer will lead to higher rates of heavy metal adsorption.

Methods and Materials

Demineralization

Demineralization was carried out by adding 1 M HCl shrimp shells at a solid to solvent ratio of 1:15(g/ml). The reaction proceeded at room temperature under agitation at 250 rpm for 0.5h. Afterwards, the demineralized shells were filtered and washed with distilled water until neutral pH.

Deproteinization

Deproteinization was performed by adding 1 M NaOH to the dried demineralized shells at a solid/liquid ratio of 1:10 (g/mL). Reaction was carried out under agitation at 80^{o}C for 3 h. The solid was filtered and washed with distilled water until it achieved neutral pH. The chitin residue collected was bleached with 0.13% hypochlorite solution with a solid to solvent ratio of 1:10 (g/ml) for 1h at room temperature. After bleaching, it was washed and filtered as above and dried at 60^{o}C for 1h.

Chitosan Production

Deacetylation of chitin was achieved by reacting chitin with 5% NaOH at a solid/liquid ratio of 1:20 (g/mL) for 120min at 120^{o}C on a hot plate.

Bioplastic synthesis (modification of concentration of chitosan)

With total masses of 2.00 g, samples of different ratios of starch /chitosan by mass of, 60/40, 50/50 and 40/60 were prepared. The chitosan and starch were both dissolved in 5% acetic acid with magnetic stirring. Both solutions were mixed in a beaker. 15% castor oil was added as plasticizer. After the samples began to form a gel, the sample was poured over a mold and dried over a hot plate at 75^{o}C until all solvents were evaporated and a thin plastic film was obtained.

Bioplastic synthesis (modification of plasticizer)

1.00g of chitosan and 1.00g of starch were separately dissolved in 5% acetic acid with magnetic stirring. Both solutions were dissolved in a beaker. 15% castor oil and glycerin were added as plasticizers to the resulting solution. After the samples began to form a gel, the sample was poured over a mold and dried over a hot plate at 75°C until all solvents were evaporated and a thin plastic film was obtained.

Test for adsorption of heavy metal ions

Plastic of the same mass and shape but of varying ratios of chitosan to starch were immersed in 0.22g/L aqueous hydrated zinc sulfate. To ensure similar mass and shape of chitosan bioplastic, the plastic was grinded into small particles and then sieved to ensure a particle size of less than 2.0 mm. To measure the concentration of heavy metal ions at the end, a colorimeter was used. A colorimeter measures the intensity of light shining through a coloured solution compared to the intensity of light passing into the solution. A detector measures the transmittance (T) (% of light passing through) of the solution. This is mathematically converted to absorbance (A = #log10T). The absorbance is directly proportional to the concentration (Beer#Lambert law).

Variables

Independent	Dependent	Controlled
• **Plasticizer (castor oil / glycerin)** • **Ratio of chitosan to starch**	• **Rate of adsorption of heavy metal ions (Zn^{2+})**	• **Temperature of solution.** • **pH of solution** • **Concentration and type of heavy metal ions in solution at the start.** • **Mass of adsorbents**

Results and Discussion

Table 1.1: Table showing the effect of the mass of chitosan and type of plasticizer used in bioplastic (grinded) on the concentration of zinc ions left in solution after 6 hours.

Mass of	Plasticizer	Average	Standard	Standard Error

Chitosan in Bioplastic/g		concentration of Zn^{2+} ions/(mg/L)	Deviation	
0.0	NA	3.30	0.000	0.000
0.8	Castor Oil	2.73	0.0164	0.00735
1.0	Castor Oil	2.16	0.0278	0.0124
1.0	Glycerol	2.64	0.0286	0.00128
1.2	Castor Oil	1.56	0.0158	0.00707

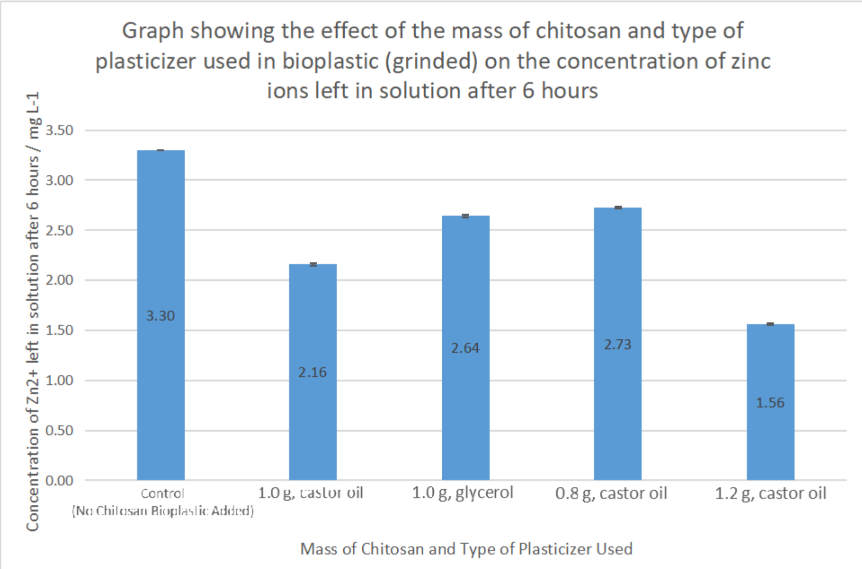
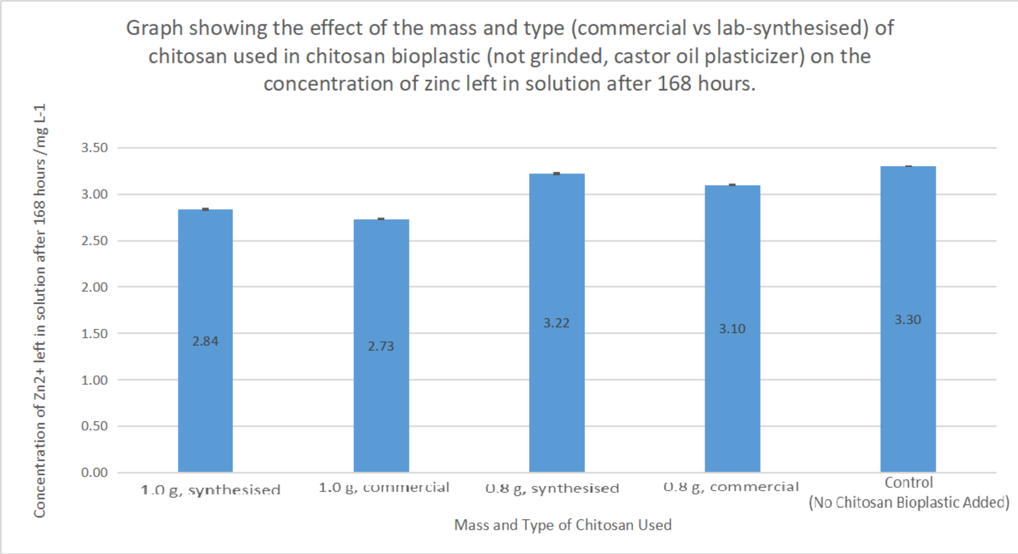


Table 1.2: Table showing the effect of the mass and type (commercial vs lab-synthesised) of chitosan used in chitosan bioplastic (not grinded, castor oil plasticizer) on the concentration of zinc ions left in solution after 168 hours.

Mass of Chitosan in Bioplastic/g	Commercial vs lab-synthesised	Average concentration of Zn^{2+} ions/(mg/L)	Standard Deviation	Standard Error
0.8	Lab-synthesised	3.22	0.0268	0.0120
1.0	Lab-synthesised	2.84	0.0130	0.00583
0.8	Commercial	3.10	0.00707	0.00316
1.0	Commercial	2.73	0.0114	0.00510
0.0	NA	3.30	0.000	0.000



Kruskal-Wallis Test

p-value of Commercial VS Lab-synthesised Types of Chitosan Used in Chitosan Bioplastic Synthesis Concentration of Zinc Ions left in Heavy Metal Adsorption Test	
1.0 g	0.8 g
Commercial VS Lab-synthesised Chitosan	Commercial VS Lab-synthesised Chitosan
Commercial Chitosan leads to more zinc ions adsorbed, $p<0.05$	Commercial Chitosan leads to more zinc ions adsorbed, $p<0.05$

p-value of Castor Oil VS Glycerol Types of Plasticizer Used in Chitosan Bioplastic Synthesis Concentration of Zinc Ions left in Heavy Metal Adsorption Test
Castor Oil VS Glycerol Plasticizer
Castor Oil leads to more zinc ions adsorbed, $p<0.05$

p-value of 0.8 g VS 1.0 g VS 1.2 g Masses of Chitosan Used in Chitosan Bioplastic Synthesis Concentration of Zinc Ions left in Heavy Metal Adsorption Test
0.8 g VS 1.0 g VS 1.2 g
1.2 g of chitosan leads to the most zinc ions adsorbed,followed by 1.0 g then 0.8 g $p<0.05$

For our data analysis, we carried out a Kruskal-Wallis Test. Blue is used to represent significant p-values, while red is used to represent insignificant ones.

Since the p-values of commercial vs lab-synthesised chitosan used in chitosan bioplastic synthesis are statistically significant for both 1.0 g and 0.8 g of chitosan used in chitosan bioplastic synthesis, our lab-synthesised chitosan was not as effective in heavy metal ion adsorption as commercial chitosan. A possible reason for this is that the purity of the lab-synthesised chitosan is too low. An additional step to concentrate the lab-synthesised chitosan can be performed in a future study.

Since the p-value of castor oil vs glycerol plasticizer used in chitosan bioplastic synthesis is statistically significant, castor oil can aid in heavy metal adsorption better than glycerol. However, it is unclear whether the plasticizer aids in heavy metal adsorption directly, or aid in heavy metal adsorption only by complementing chitosan. More specific data can and should be taken in future studies, by having a control plastic with no chitosan added. Furthermore, while castor oil plasticizer used in chitosan bioplastic synthesis leads to better heavy metal ion adsorption, it is unclear what effects the type of plasticizer have on the physical properties of the plastic. An additional step investigating the effect of the type of plasticizer on the flexibility and tensile strength of chitosan bioplastic synthesised can be performed in a future study.

Since the p-value of 0.8 g vs 1.0 g vs 1.2 g is statistically significant, the chitosan is most likely the primary heavy metal adsorbent in the chitosan bioplastic, and starch and other constituents play relatively minor roles in terms of heavy metal adsorbent. However, while higher concentrations of chitosan used in synthesis of chitosan bioplastic lead to better heavy metal adsorption, it also leads to a more rigid and brittle plastic structure. If a more flexible plastic membrane is required, for example for water filtration in NEWater production, a lower concentration of chitosan can be considered. More specific data can and should be taken on the effect of concentration of chitosan used in bioplastic synthesis on the flexibility and tensile strength of the bioplastic.

Conclusion and Recommendations for future work

In conclusion, using the heavy metal ion Zn^{2+}, an increase in the concentration of chitosan in chitosan bioplastic has been shown with great certainty to lead to an increase in the rate of heavy metal ion adsorption. Chitosan can thus be concluded to be the primary adsorbent in the chitosan bioplastic. Castor Oil plasticizer also yielded chitosan bioplastics with higher rate of heavy metal ion adsorption.

The grinded chitosan bioplastic had a much greater rate of heavy metal ion adsorption than the non-grinded chitosan bioplastic, with the grinded bioplastic resulting in the zinc sulfate solution having lower concentrations of Zn^{2+} after a shorter time span of 6 hours than the non-grinded bioplastic after a much longer time span of 168 hours. This can be attributed to the increase in surface area of the grinded chitosan bioplastic.

FTIR Spectroscopy

Unfortunately, FTIR spectroscopy could not be conducted on the chitosan synthesised from prawn shells due to time constraints. In the future, FTIR spectroscopy can be conducted on the chitosan to determine the functional groups in the chitosan that allow for its adsorption of heavy metal ions.

Determination of Degree of Deacetylation

In addition, titration could not be performed on the chitosan synthesises from prawn shells due to time constraints as well. As such, the degree of deacetylation could not be determined, and the quality of the synthesised chitosan could not be determined. In the future, titration can be conducted on the lab-synthesized chitosan to determine the degree of deacetylation and hence the quality of chitosan produced, to determine the effectiveness of the method used for synthesis chitosan from prawn shells.

Test for Mechanical Properties of Bioplastic

Furthermore, quantifiable tests could not be conducted on the physical properties of the plastic synthesised, for example flexibility and tensile strength. Such tests could be done in the future.

Test for Adsorption of Heavy Metal Ions

More readings of the final concentration of zinc sulfate solution could be taken, with more different masses of chitosan in chitosan bioplastic. This way, the results would be more accurate, and a better correlation between mass of chitosan in chitosan bioplastic and rate of adsorption of heavy metal ions can be established.

Due to a lack of time, the heavy metal ion adsorption test conducted on the grinded chitosan bioplastics was only over a period of 6 hours, resulting in the poor adsorption results and a lack of sufficient results to determine the rate of adsorption. Ideally, more readings of the concentration of Zn^{2+} ions could be taken at regular intervals over a period of time to determine the change in the rate of adsorption over time.

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Appendix 1
Methods for Future work.

Determination of Degree of Deacetylation.
To determine the degree of deacetylation, 0.3g-0.5g of Chitosan could be dissolved in 30 mL 0.1 M HCl at 20 ± 5 °C with stirring in a 250 mL flask and then two drops of methyl orange indicator should be added. 0.1 M NaOH is used to titrate the solution. At the final point of titration, the color changes from pink to orange yellow. The method was augmented to include the use of a pH meter to make the final titration point determination more precise. To calculate water content, 0.5 g chitosan was heated at 105 °C until a constant weight was reached. The percent of free NH2 groups in chitosan was calculated as follows:

$NH2\% = [(C1V1 - C2V2) \times 0.016] / [G\ (100 - W)] \times 100$

$Free\ NH2\% = NH2\%/9.94\% \times 100\%$

Chitosan theoretic NH2 content % = (16/161) × 100% = 9.94% C1: Concentration of HCl (M); C2: Concentration of NaOH (M); V1: the volume of HCl added (mL); V2: the volume of NaOH added by titration (mL); G: Sample weight (g); W: sample water content (%); 0.016: equal to NH2 content (g) in 1 mL of 1 M HCl.

Tests for Mechanical Properties of Bioplastic.
A universal testing machine can be used to test tensile strength. To measure flexibility, Young's modulus of plastic can be determined. A sample of plastic with known length and cross-sectional area is stretched with a known force, using a weight of known mass to stretch. The change in length is noted. Young's modulus is calculated using the formula $E=(FL)/(A\Delta L)$, where E is young's modulus, F is the force applied on the object, L is the original length of the object. A is the cross-sectional area of the object and ΔLis the change in length of the object. The lower the young's modulus, the more flexible the object. In the future, such quantitative tests could be conducted to determine the plastic's practicality and usefulness.