Synthesis and Properties of Chitin-Derived Hydrogels

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Abstract

This project aims to investigate the adsorption of heavy metal ions and dyes in chitin-derived hydrogels. The experiment involves the synthesis of hydrogels from chitin derived from crab shells before testing its heavy metal, and dye adsorbability. Heavy metals solutions, namely Cu^{2+}, Fe^{3+}, and Zn^{2+} ion solutions were used to determine the heavy metal adsorbability of chitin hydrogel while dye solutions, namely Methylene Blue, Direct Red 80 and Methyl Orange solutions, were used to determine the dye adsorbability of chitin hydrogel. The pH of the solutions were also changed to determine its effect on the adsorption of the Direct Red 80, and methylene blue solutions. Of the various different solutions tested, hydrogel performed better than chitin in the adsorption of methylene blue and methyl orange, and in direct red when the solution was basic at pH 12. Chitin performed better in the adsorption of the Cu^{2+} ion and direct red when neutral at pH 7. However there is negligible difference in the adsorption of Fe^{3+}, and Zn^{2+} ion solutions.

Introduction

The consumption of heavy metals through water can cause severe health conditions such as DNA damage, cell membrane damage as well as the inactivation of enzymes (Engwa, et al., 2018). For example, Copper, Zinc and Iron can be found in tap water in Dhahran, Saudi Arabia due to the corrosion of pipe materials and coatings (Alam and Sadig, 1989) while Cadmium, Cobalt, Copper and Lead can be found in groundwater sources due to the Gulf war and the burning of Kuwaiti oil wells.

According to animal tests, some dyes have been proven carcinogens and are likely to be carcinogenic to humans and therefore classified as potential human carcinogens. They are also observed causing skin sensitization, mutagenicity and other negative health effects. Dyes are also present in water streams which can lead to unexceptional effects on living life due to the activities of industries, especially the textile sector (Karishma, et al., 2017).

Hydrogels have demonstrated excellent adsorbability and adsorbance capacity of dyes (Neeraj, et al., 2018). Plenty of methods for removing heavy metal ions from wastewater have been developed, but limited progress has been made due to low efficiency, high expense and lengthy procedures. Polymeric hydrogel has been attracting attention for the effective removal of heavy metal ions from wastewater (Zeenab, et al., 2022).

Chitin is a long chain polymer of N-Acetylglucosamine found commonly in the exoskeleton or various arthropods such as crustaceans and insects. Crab shells are one of the most abundant sources of chitin. The contents of crab shells consist of 30% chitin, 16% protein, and 55% calcium carbonate (Yihun, et al., 2016). Therefore, by deproteinizing, and subsequently demineralizing the crab shells, chitin can be extracted from crab shells that can be used to create the hydrogels.

Objectives

1. To extract chitin from crab shells
2. To produce chitin-derived hydrogels
3. To adsorb heavy metal ions and dyes from water using chitin-derived hydrogels

Hypothesis

1. Chitin can be extracted from crab shells
2. Chitin hydrogel can be produced from chitin
3. Chitin hydrogel can adsorb heavy metal ions from water
4. Chitin hydrogel can adsorb dye from dye solutions
5. Changing the pH of the dye solutions will have an effect on the adsorbability of the chitin and chitin hydrogel

Materials and Methodology

Extraction of Chitin

Crab shells were retrieved and hammered into smaller pieces using a hammer, before being broken down into smaller pieces using a mortar and pestle. The crab shell pieces were then dried in the oven overnight, first at 110°C for 5 hours and then at 60°C overnight. 3 sets of 30 g crab shells were then stirred in 200 ml of 1M hydrochloric acid solution at 500 rpm overnight. Then, they were washed with deionized water until pH neutral. 28.83 g of crab shells were then submerged in 192.2 ml of 10% sodium hydroxide solution at 100°C for 5 hours and then at room temperature overnight.

Hydrogel Synthesis

1 g of Chitin was dissolved in a solution of 15 g tetrabutylammonium fluoride (TBAF) and 85 g dimethyl sulfoxide (DMSO) and stirred over the weekend. Then, 4.93 g of succinic anhydride and 1.6 g of 4-Dimethylaminopyridine (DMAP) was added to the solution and left to stir overnight. The solution was neutralised with 10% sodium hydroxide and precipitated in 100% methanol and filtered. The resulting hydrogel was washed thoroughly with deionized water.

Direct Red 80 standard curve

5 concentrations of Direct Red 80 were prepared: 10 ppm, 8 ppm, 6 ppm, 4 ppm and 2 ppm. The absorbance value of each solution was then recorded using a UV-VIS spectrophotometer at 526 nm.

Methylene Blue standard curve

5 concentrations of methylene blue were prepared: 5 ppm, 4 ppm, 3 ppm, 2 ppm and 1 ppm. The absorbance value of each solution was then recorded using a UV-VIS spectrophotometer at 664nm.

Methyl Orange standard curve

5 concentrations of methyl orange were prepared: 10 ppm, 8 ppm, 6 ppm, 4 ppm and 2 ppm. The absorbance value of each solution was then recorded using a UV-VIS spectrophotometer at 753 nm.

FTIR

FTIR spectra of chitin and chitin-derived hydrogel were obtained using a Bruker Alpha FT-IR spectrophotometer

Iodine Number Test

A volume of 10 ml hydrochloric acid was added to 1g of our chitin or hydrogel sample. The mixture was heated on a hotplate and boiled for 30 seconds, before cooling the mixture to room temperature. 100 ml of 0.1 N iodine was then added to the mixture before being shaken vigorously for 30 seconds. The contents were then filtered. An aliquot of 25 ml of the filtrate was titrated with 0.1 N sodium thiosulfate solution using starch indicator.

Preparation of Heavy Metal Ion and Dye Solutions

50 ppm solutions of Cu^{2+}, Fe^{3+}, and Zn^{2+} was prepared by dissolving 200 mg of copper(II) sulfate ($CuSO_4$), 220 mg of iron(III) nitrate ($Fe(NO_3)_3$) and 360 mg of zinc sulfate (($ZnSO_4$)) in 1l of water in a volumetric flask.

50 ppm solutions of methylene blue, Direct Red 80, and methyl orange were prepared by dissolving 50 mg of methylene blue, 50 mg of Direct Red 80 and 50 mg of methyl orange in 1*l* of water in a volumetric flask.

Sodium hydroxide and hydrochloric acid were used to create pH 2 and pH 12 solutions of both methylene blue and Direct Red 80.

Heavy Metal Ion Adsorption Test

0.1 g of chitin and hydrogel were added into 10 ml of Cu^{2+}, Fe^{3+}, and Zn^{2+} solutions. The solutions were then put in an orbital shaker for 4 hours. The solutions were then centrifuged to separate the chitin and hydrogel from the solution before the concentration of the remaining ions was measured using a colorimeter.

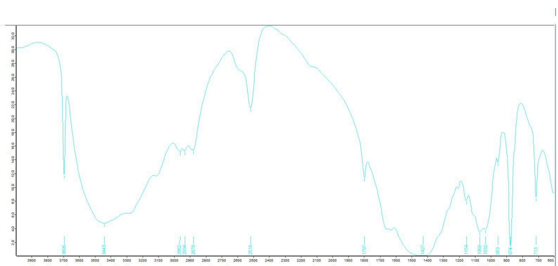
Dye Adsorption Test

0.1 g of chitin and hydrogel was added into 10 ml of methylene blue, Direct Red 80 and methyl orange solutions. The solutions were then put in an orbital shaker for 4 hours. The solutions were then centrifuged to separate the chitin and hydrogel from the solution before the concentration of the remaining dyes was measured using a UV-spectrophotometer.

0.1 g of chitin and hydrogel was added into 10 ml of methylene blue, Direct Red 80 solutions at pH 2 and pH 12. The solutions were then put in an orbital shaker for 4 hours. The solutions were then centrifuged to separate the chitin and hydrogel from the solution before the concentration of the remaining dyes was measured using a UV-spectrophotometer.

Results and Discussion

Chitin and Hydrogel FTIR Spectrophotometer Graph



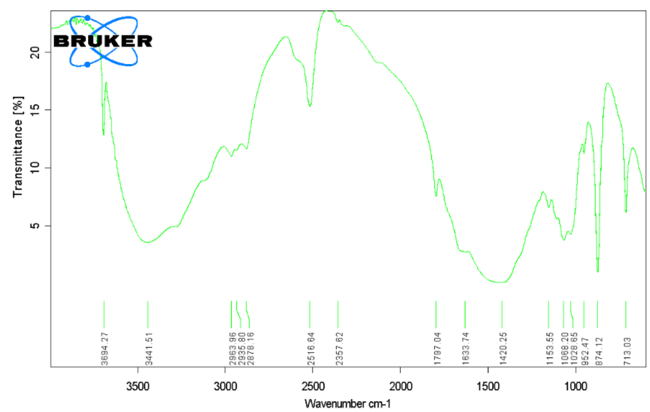


Figure 1: Graph of FTIR Spectrophotometer reading on our derived Chitin

Figure 2: Graph of FTIR Spectrophotometer reading on our derived Hydrogel

In the both FTIR spectrums (Figures 1 and 2), the broad band at 3443 cm^{-1} is attributed to the presence of the -NH2 and -OH groups' stretching vibrations and intermolecular hydrogel bonding. A single broad band suggests that the chitin obtained from the crab shells was β-chitin (Focher, et al., 1991). The absorption band at 1658 cm^{-1} can be attributed to the stretching of C=O group hydrogen that are bonded to the N–H. The absorption band at 1631 cm^{-1} can be attributed to a specific hydrogen bond of C=O with the hydroxyl-methyl group of the next chitin residue of the same chain (Dahmane, et al., 2014).

Iodine Number

The adsorption capacity of chitin and hydrogel were calculated using the following formula:

$$Adsorption\ Capacity\ (mg/g) = \frac{A - (DF \times BS)}{M}$$

S = volume (ml) of sodium thiosulfate used; M is the mass (g) of the sample = 1

A = N2 × 12693, where N2 is the normality of iodine solution = 0.1 N; B = N1 × 126.93, where N1 is the normality of the Sodium Thiosulfate solution = 0.1 N, DF = dilution factor

For Chitin, 22.43 ml of Sodium Thiosulfate was used. Therefore, substituting the numbers in the formula listed above, gives us an Adsorption Capacity of 984.6 mg/g. For Hydrogel, 21.73 ml of Sodium Thiosulfate was used. Therefore, substituting the numbers in the formula listed above, gives us an Adsorption Capacity of 993.5 mg/g.

Meteku (2014) had data compiled from Cuhadaroglu and Uygun (2008) showed that the relationship between Adsorption Capacity and Surface Area could be plotted on a graph of y = 0.94x - 120.3. Therefore, the surface area can be calculated using the formula:

$$S = \frac{94(A + 120.3)}{100}$$

S = Surface Area

A = Adsorption Capacity

For chitin, the surface area calculates to 1175 m^2/g. For hydrogel, the surface area calculates to 1185 m^2/g.

Direct Red 80, Methylene Blue and Methyl Orange Standard Curve

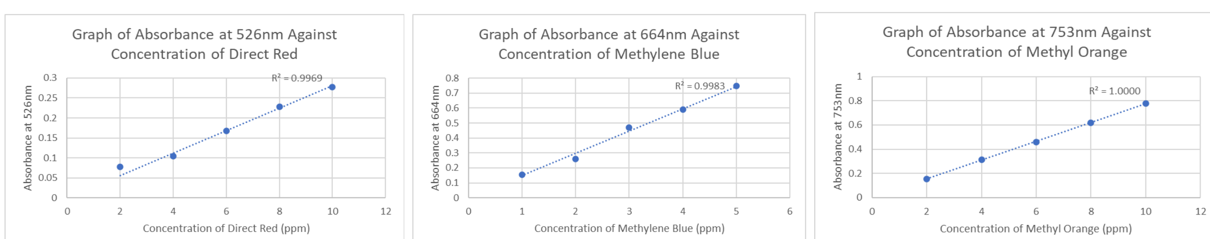


Figure 3: Standard curves of Direct Red, Methylene Blue and Methyl Orange

Heavy Metal Ion Adsorption Test

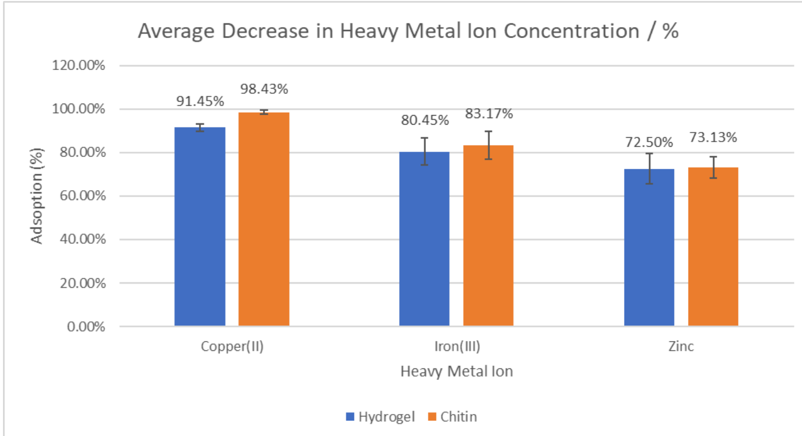


Figure 4: Graph of percentage adsorption of heavy metal ion after 4 hours

From Figure 4, the use of hydrogel showed a negligible difference when compared to the use of chitin when used to adsorb iron(III) and zinc ions. However chitin showed better adsorbency compared to hydrogel when used to adsorb copper(II) ions.

From the results obtained from the heavy metal ion adsorption test, it can be concluded that chitin is better in adsorbing copper(II) ions.

Chitin performed better than chitin hydrogel possibly due to the differences in surface area to volume ratio of chitin to the chitin hydrogel. It is also found that Cu^{2+} ions are readily adsorbed by chitin as compared to other heavy metal ions (Anastopoulos, et al., 2017) which may contribute to the difference in Cu^{2+} adsorption, and why the other heavy metals showed little difference.

Dye Adsorption Test

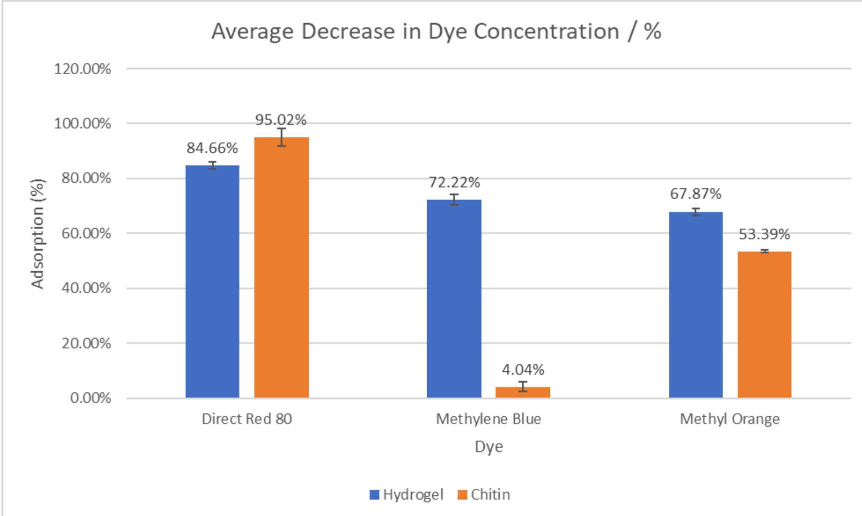


Figure 5: Graph of percentage decrease in dye concentration after 4 hours

From Figure 5, the use of hydrogel showed a better performance in dye adsorbency compared to the use of chitin when used to adsorb methylene blue and methyl orange. However chitin showed better adsorbency compared to hydrogel when used to adsorb Direct Red 80 dyes.

From the results obtained from the dye adsorption test, it can be concluded that hydrogel is better in adsorbing methylene blue and methyl orange. Chitin on the other hand showed better performance than hydrogel when adsorbing Direct Red 80 dyes.

Dye Adsorption Test at different pH

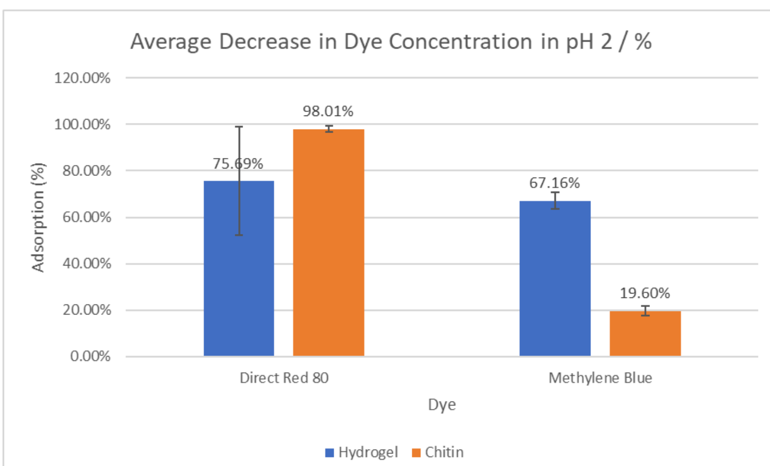


Figure 6: Graph of percentage decrease in dye concentration in pH 2 after 4 hours

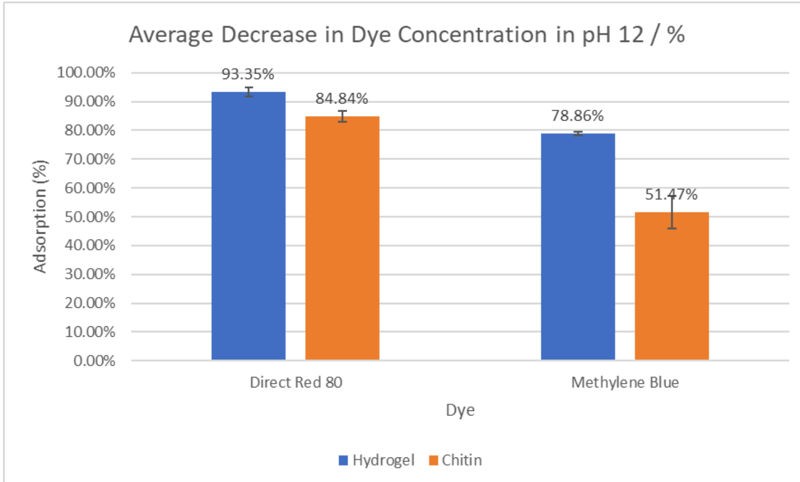


Figure 7: Graph of percentage decrease in dye concentration in pH 12 after 4 hours

From Figure 6, the use of hydrogel showed a better performance in adsorbing compared to the use of chitin when used to adsorb methylene blue and methyl orange. However chitin showed better adsorbency compared to hydrogel when used to adsorb Direct Red 80 dyes.

From Figure 7, the use of hydrogel showed a better performance in dye adsorbency in pH 12 compared to the use of chitin when used to adsorb methylene blue and Direct Red 80.

From the results obtained from the dye adsorption test, it can be concluded that hydrogel is better in adsorbing methylene blue and methyl orange. Chitin on the other hand showed better performance than hydrogel when adsorbing Direct Red 80 dyes.

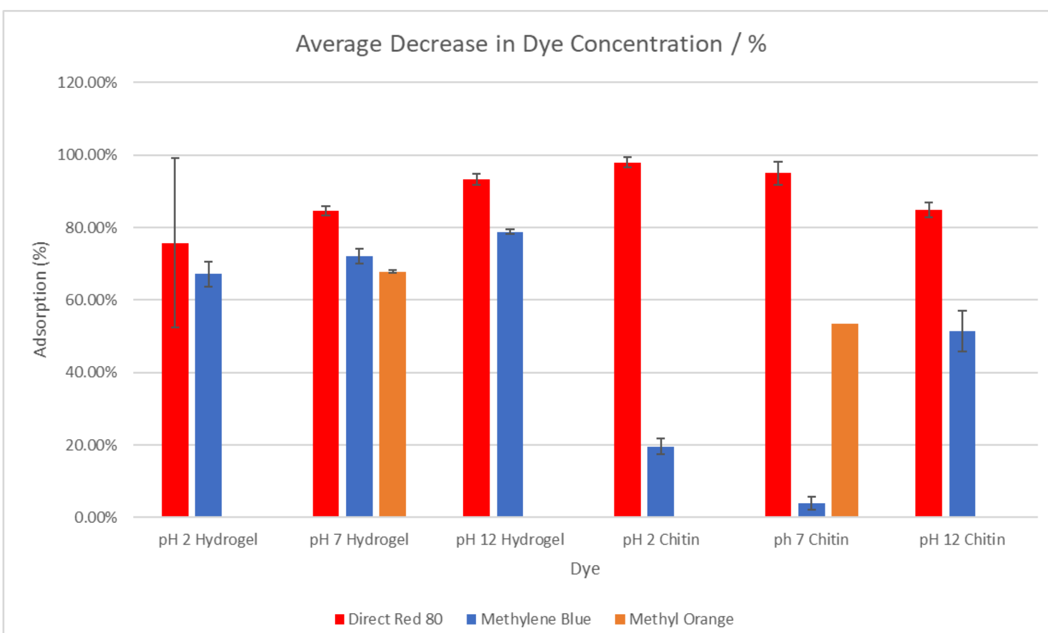


Fig. 8

From Figure 8, it is observed that Hydrogel's adsorption of dyes improves when the solution becomes more basic. For chitin. Its adsorption of direct red improves when its solution becomes more acidic. The adsorption of methylene blue on the other hand, shows that chitin adsorbs methylene blue the worst when in a neutral solution, while improving as the solution becomes more acidic or basic. It is however observed that it performs better in a basic solution of pH 12.

Conclusion

It was observed that chitin did better than chitin hydrogel when placed in an orbital shaker for 4 hours and overnight in adsorbing all three different solutions of heavy metal ions. It is not known exactly why this is the case; however, it is hypothesised that the ability of the chitin hydrogel to adsorb is vastly outperformed by the larger surface-to-volume ratio of the powdered chitin, hence it is unable to adsorb as much heavy metal ions as chitin. To further the findings of this research, hydrogel and chitin's adsorption of other heavy metal ions should be considered as well. Both hydrogel and chitin can also be tested in the speed in which heavy metal ions and dyes can be adsorbed. Temperature is another variable that should be taken into consideration in future experimentations, to find its effects on the adsorption of heavy metal ions and dyes.

Limitations

In calculating the surface area of the hydrogel and chitin, it was noticed that the adsorption capacity exceeded the range of adsorption capacities recorded in the experiment. Therefore, it is possible that the graph drawn is deviated from the actual relationship between adsorption capacity and surface area.

Application

Due to the ability of chitin and hydrogel both to adsorb different heavy metal ions and dyes effectively, it is possible to use a mixture of both to adsorb dyes and heavy metal ions from wastewater (e.g within taps to clean the water). It may also be possible to use chitin and hydrogel to depollute water in ponds and other smaller water bodies.

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