Investigating the effectiveness of modified pectin extracted from *Citrus Maxima* peels on the biosorption of heavy metal ions and dyes from wastewater

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Abstract

This project investigates the use of modified pectin extracted from *Citrus maxima* peels as an adsorbent for heavy metal ions and dyes. Pectin ($C_6H_{10}O_7$) was first extracted from boiled *Citrus maxima* peels through precipitation with $FeCl_3$ and $AlCl_3$. The precipitate was then washed with HCl and ethanol before being saponified in NaOH solution at 4°C. Aqueous solutions of saponified pectin and dicarboxylic acids ($HO_2C{-}R{-}CO_2H$) were mixed and refluxed at 55-60°C. Finally, the mixture was precipitated with 95% ethanol and then dried in an oven to obtain the modified pectin. Batch experiments were carried out with modified pectin for the removal of Cu^{2+}, Fe^{3+} and methylene blue dye from water. The average maximum adsorption capacities of modified pectin for Cu^{2+}, Fe^{3+} and methylene blue dye were 0.61 mmol g^{-1}, 1.87 mmol g^{-1} and 1.12 mmol g^{-1} respectively. Lastly, the used modified pectin were regenerated and their retained adsorption capacities were measured. The results illustrates its potential application in removing heavy metal ions and methylene blue dye from wastewater.

Introduction

Over the past years, heavy metal ions has become a problematic factor in inorganic pollution of water sources. Metal ions in polluted waters such as Pb^{2+}, Hg^{2+} and Cu^{2+} ions are highly toxic and can pose a hazard to health and the environment (Anirudhan & Sreekumari, 2011). Other metal ions include iron, manganese, cadmium and barium. Synthetic dyes also contain metal ions and several thousands of them display different biological activities; they pose potential threats to health and the environment, most of which are still unknown (Forgacsa, Tibor, & Oros, 2004).

Citrus peels were identified as the most promising biosorbent due to high metal uptake in conjunction with physical stability (Schiewer & Patil, 2007). Processed pectic substances contain carboxyl groups and have good capacity of cation exchange (M. Kratchanova, A. Slavov & C. Kratchanov, 2004). Moreover, pectin can be extracted from fruit peels, which is abundant and cheap, thus having the potential to act as a cheaper alternative to current methods of heavy metal ion adsorption.

Chemical modification of natural polymers leads to derivatives with new physical, chemical, and biological properties. Cross-linking reactions can reduce pectin's hydrability (i.e. distensibility) and enhance the stability of the adsorbent (Li, Yang, Zhao & Xu, 2007). They also found that it affects the porosity and the loading capacity of pectin.

Acidic pectin polysaccharides, unlike neutral polysaccharides, have been little studied and there has been little research on using modified pectin that is crosslinked with dicarboxylic acids to improve the effectiveness of *Citrus maxima* peels at heavy metal ions and dyes adsorption. Hence, this project is carried out with the aim of investigating the feasibility and effectiveness of modified pectin extracted from *Citrus maxima* peels at removing heavy metal ions and dyes from wastewater.

1. Materials and Methods

1.1 Materials

Apparatus:

1. Reflux System
2. Centrifuge
3. Vacuum Oven
4. Shaker
5. UV-Vis spectrophotometer
6. Hot plate

Chemicals:

1. Ferric Chloride [$FeCl_3$]
2. Aluminium Chloride [$AlCl_3$]
3. Sodium Hydroxide [NaOH]
4. Hydrochloric Acid [HCl]
5. Adipic Acid [$C_6H_{10}O_4$]
6. Maleic Acid [$C_4H_4O_4$]
7. Aspartic Acid [$C_4H_7NO_4$]
8. Sulfuric Acid [H_2SO_4]
9. Ethanol [C_2H_5OH]
10. Methylene blue dye [$C_{16}H_{18}ClN_3S$]
11. Copper (II) sulfate [$CuSO_4$]

1.2 Extraction of pectin from *Citrus maxima* peels

To extract the pectin from *Citrus maxima* peels, 10g of washed *Citrus maxima* peels were immersed in 1L deionised water for 10 min at 100°C. The peels were extracted and dried in an oven. The peels were then stirred for 1.5 h at 70°C with a mixed solution of $FeCl_3$ and $AlCl_3$ (pH 3.5) to form a precipitate. The mixture was centrifuged to obtain the precipitate. The precipitate was then washed by mixing it with 200 ml of hydrochloric acid and ethanol. Finally, the mixture was centrifuged again and filtered to obtain the pectin.

1.3 Synthesis of modified pectin

The extracted pectin was dissolved in NaOH solution (pH 12) and stirred for 8 h at 4°C. Aqueous solutions of pectin and dicarboxylic acids (mass ratio: 10:8) along with concentrated sulfuric acid were mixed and refluxed at 55–60°C under stirring for 0.5 h. After cooling, the

mixture was precipitated with ethanol. The suspension was then centrifuged to separate the precipitate. The precipitate was washed with ethanol and dried in a vacuum oven at 60°C.

1.4 Adsorption of heavy metal ions & dyes

The adsorption experiments were performed on a platform shaker at 200 rpm using centrifuge tubes. The contact time, pH and temperature of the solutions were kept constant throughout the experiment. Individual solutions of methylene blue dye, Cu^{2+} and Fe^{3+} ions of 25ml each at 25ppm and 50ppm were prepared. 0.01g of the modified pectin were added to each sample. The mixtures were left in the shaker for 3 hours. The initial and final concentrations of the heavy metal ions were analysed using a Hach 48460-00 Colorimeter, while the initial and final concentrations of methylene blue dye were analysed using a UV-Vis spectrophotometer with reference to our calibration curve.

1.5 Regeneration of adsorbent

The used pectin was extracted by centrifuging and added into a 200ml mixture of hydrochloric acid and ethanol with stirring. The mixture was centrifuged again to obtain the regenerated pectin. The pectin was washed with deionized water on a filter paper and employed for the next cycle of adsorption in a new solution with the same concentration of metal ions and dye.

2. Results and Discussion

2.1 Characterisation of products

2.1.1 FTIR Analysis of unmodified and modified pectin

Figure 1.1 - FTIR spectrum of Pectin maleate

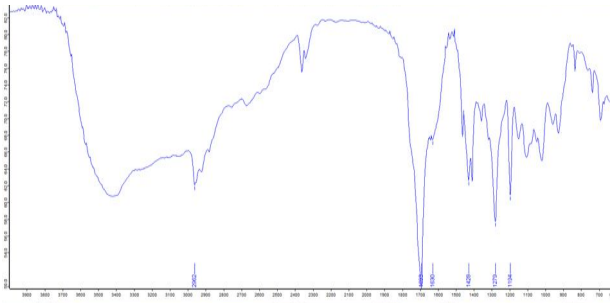

Figure 1.2 - FTIR spectrum of Pectin adipate

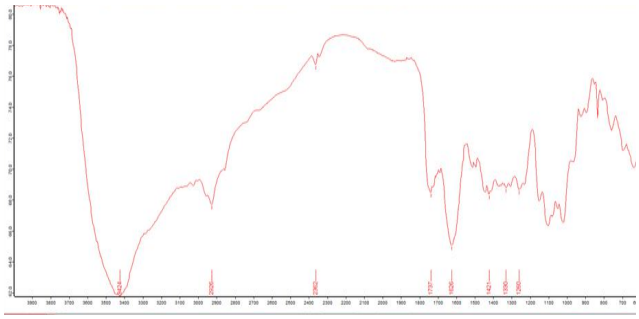

Figure 1.3 - FTIR Spectrum of Pectin aspartate

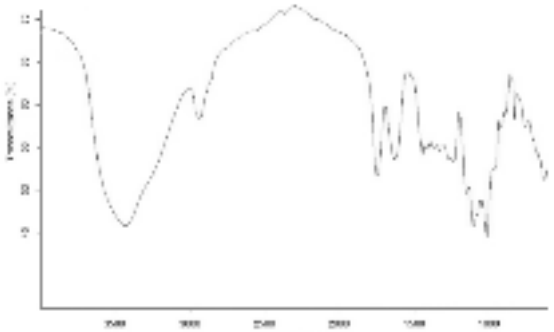

Figure 1.4 - FTIR Spectrum of unmodified pectin

FTIR was used to characterize extracted pectin and modified pectin (Fig. 1.1–1.4). The peaks at 2925 cm^{-1} and 2962 cm^{-1} indicate C–H stretching vibrations and those between 950 cm^{-1} and 1200 cm^{-1} correspond to the resonance adsorption of the pyranoid ring in the pectin molecule (Fig 1.1-1.3), indicating that the structure of pectin was preserved (Li, Yang, Zhao & Xu, 2007). The peaks at 1700 cm^{-1} indicate C=O stretching vibrations. The peaks near 1442cm^{-1} and 1637cm^{-1} correspond to the symmetric and antisymmetric vibration of ionic carboxyl groups respectively. The intensity of the peak at 1693 cm^{-1} in Fig 1.2 as compared to Fig 1.4 is much higher which signals the increase in the number of C=O bonds (D. F. Swineharf, 1962), confirming the high degree of interaction between adipic acid and pectin.

2.1.2 SEM Analysis of modified pectin

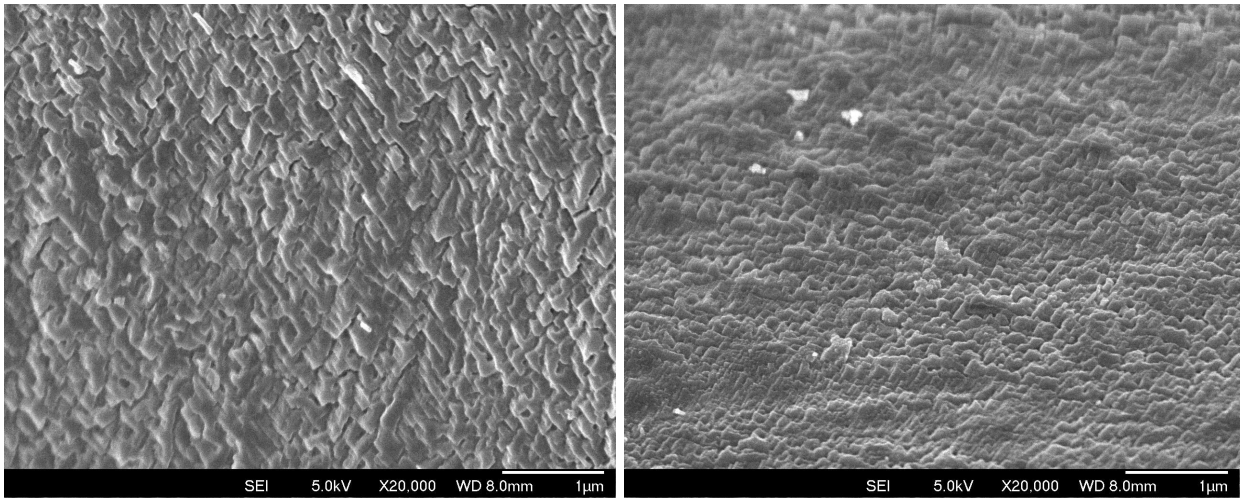

Figure 2.1 SEM image of Pectin aspartate

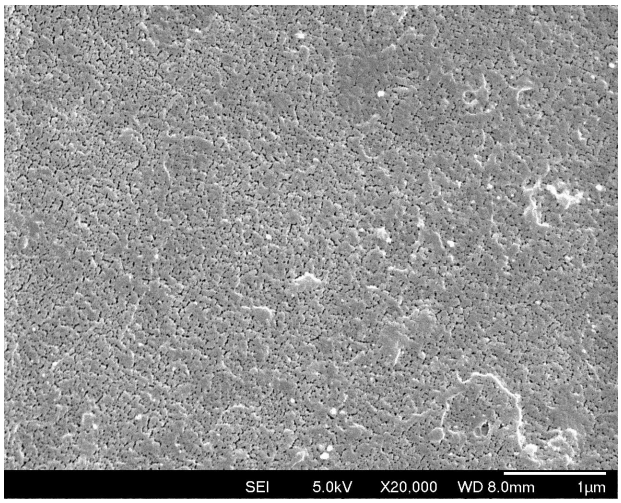

Figure 2.2 SEM image of Pectin maleate

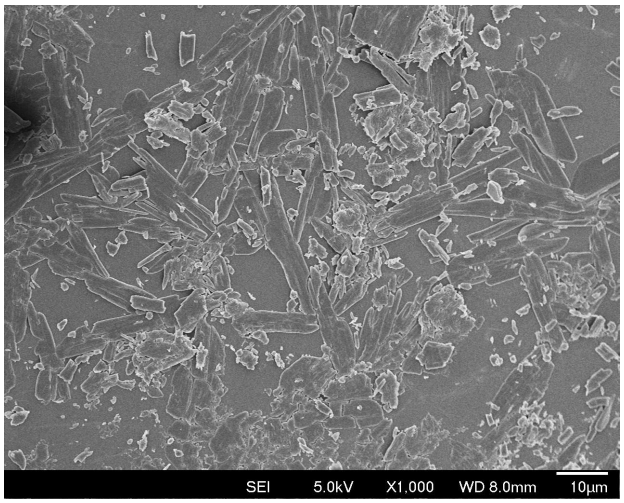

Figure 2.3 SEM image of Pectin adipate

To analyse the physical properties of the produced pectin compounds, the respective samples were dried and their SEM images were taken at different resolutions. SEM was used to analyse the surfaces of modified pectin (Fig 2.1-2.3). Pectin aspartate is characterized by a high surface area (Fig 2.1), thereby enhancing its adsorption properties (Cao, Xie, Lv, Bao 2006). Pectin maleate is also characterized by its highly porous surface, increasing its effectiveness of heavy metal ions adsorption (Lo, Wang, Tsai, Lin, 2012).

2.2 Adsorption Test

Pollutant	Adsorbent	Adsorption Capacity (mmol/g)
Cu^{2+}	Commercial pectin	0.12
	Pectin maleate	0.72
	Pectin adipate	0.61
	Pectin aspartate	0.49
Fe^{3+}	Commercial pectin	0.53
	Pectin maleate	1.86
	Pectin adipate	1.97
	Pectin aspartate	1.78
MBD	Commercial pectin	0.56
	Pectin maleate	1.26
	Pectin adipate	1.13
	Pectin aspartate	1.17

Figure 3 - Adsorption capacities of modified pectin

Adsorption tests were conducted on aqueous solutions of Cu^{2+}, Fe^{3+} and methylene blue dye (MBD) with Pectin maleate, Pectin adipate and Pectin aspartate respectively. Mann Whitney U Tests were conducted on data (Fig 3). The null hypothesis is "There is no significant difference in adsorption capacity between unmodified pectin and modified pectin."

Sample Comparison	Pollutant	p-value	Conclusion
0.01g Citrus Pectin vs Pectin-Dicarboxylic Acid	Cu^{2+}	0 (< 0.01)	*Null Hypothesis rejected*
0.01g Citrus Pectin vs Pectin-Dicarboxylic Acid	Fe^{3+}	0 (<0 .01)	*Null Hypothesis rejected*
0.01g Citrus Pectin vs Pectin-Dicarboxylic Acid	MBD	0 (<0 .01)	*Null Hypothesis rejected*

The null hypothesis was rejected for all tests. Modified pectin displayed a significantly higher adsorption capacity than unmodified pectin in adsorbing dyes and heavy metal ions, Cu^{2+}

and Fe^{3+}.

2.3 Reusability Test

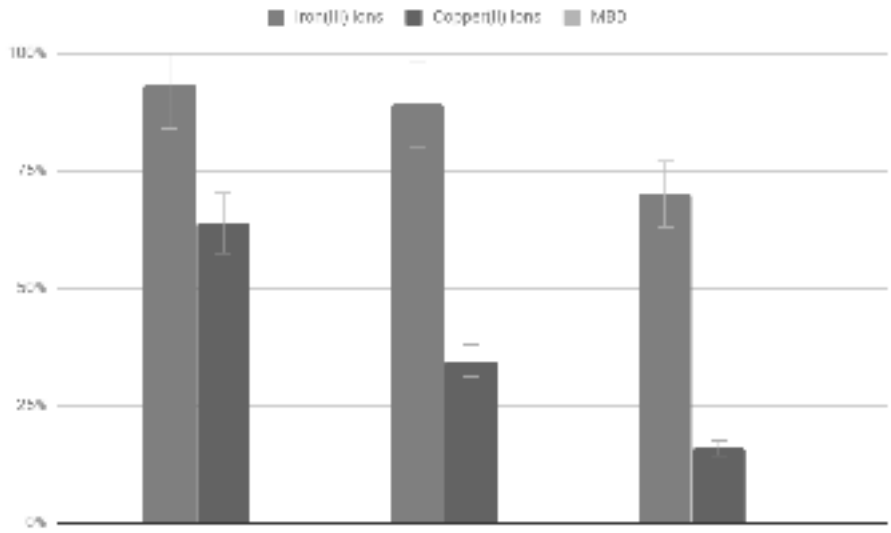

Figure 4 - Reusability of modified pectin

Reusability of modified pectin for different pollutants was investigated through 3 cycles of regeneration and adsorption testing. For regeneration, the used pectin was added into a 200ml mixture of hydrochloric acid and ethanol with stirring. It is then centrifuged and employed for the next cycle of adsorption in a new solution with the same concentration of metal ions and dye. In Fig 4, the average adsorption capacities of the modified pectin for the heavy metal ions decreased after every stage of regeneration. The adsorption capacity of the modified pectin samples for methylene blue dye decreased exponentially after the first adsorption test. This is likely due to the fact that the acidification process used to remove metal ions do not remove the methylene blue dye on the modified pectin.

3. Conclusion

Modified pectin from *Citrus maxima* peels was synthesised through reflux and stirring of pectin and dicarboxylic acids. The results of the adsorption tests conducted on Cu^{2+}, Fe^{3+} and methylene blue dye solutions showed that modified pectin demonstrates a significantly higher adsorption capacity than unmodified pectin. This was due to the higher presence of carboxyl

functional groups in modified pectin, leading to more effective ion exchange which is utilised in the adsorption of heavy metal ions and the larger surface area of modified pectin that came into play during the adsorption of methylene blue and heavy metal ions. The reusability tests showed that modified pectin used for the adsorption of heavy metal ions can be regenerated by carrying out acidification of spent pectin samples using hydrochloric acid. However, regeneration of modified pectin used for the adsorption of methylene blue was proven to be ineffective as methylene blue molecules could not be effectively removed from the surface of the modified pectin through the process of washing or acidification.

4. Future Works

Reacting pectin with polycarboxylic acids has not been investigated. The reaction between polycarboxylic acids and pectin may have an impact on the adsorption capacity of the novel adsorbent due to the greater presence of carboxylic acid functional groups. Further testing could be done to optimise the ratio of pectin to dicarboxylic acids during the binding process to allow for optimum adsorption capacities of modified pectin, while ensuring that the stability of the biosorbent is retained and the structure of pectin is preserved.

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