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## Synthesis and Characterization of Hydroxamic Derivative Pectin and Its Application as Sorbent for Pb(II)

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### Abstract

A hydroxamic acid derivative (PHA) obtained from commercial pectin (P) was modified with grafting of hydroxamic groups -C(O)NHOH and the sorption of Pb(II) in aqueous media was investigated. The IR band at 1634 cm<sup>-1</sup> was associated with the hydroxamic group and the degree of substitution was confirmed by elemental analysis. The thermogravimetric curves presented similar thermal events between the polymers. The derivatization on pectin structure was also confirmed with increased in the glass transition temperature of the PHA compared to the starting pectin. For Pb(II) sorption studies, PHA with degree of substitution 18% presented a sorption rate 42% higher than CP. The experimental results are described according to the Freundlich model. Computational studies reveal that the sorption of Pb(II) by PHA may be related to its ability to stabilize oxygen ligands through alpha effect. Overall, PHA was shown a potential for Pb(II) removal in wastewater better than pectin.

*Keywords:* hydroxamic derivative; decontamination; lead; molecular modeling

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### 1. Introduction

Contemporary environmental research seeks alternative sorbent materials for removing metal ions from aqueous solutions.[1], [2] Biomass, like pectin extracted from fruit residues, has emerged as a promising sorbent material and offers advantages such as abundance, availability as a by-product, low purification costs, and effectiveness in absorbing metal ions.[3], [4]

Pectin, a complex polysaccharide derived from biomass, is mainly composed of  $\alpha$ -D-galacturonic acid residues and by chemical derivatization one can modify pectin to enhance its properties for various applications, including lead recovery from the environment.[5]

Pectin interacts with divalent metal ions through its carboxyl groups, making it suitable for removing such ions, in this way modifying pectin's

ester groups can improve its metal ion sorption efficiency and selectivity.

Hydroxamic acids can be easily produced by pectins, and with their bidentate binding (N and O) properties, form stable complexes with metal ions, making them suitable for extracting potentially toxic metals (PTMs) like lead (Pb(II)) that inflicts significant environmental risks, and exposure to it can have detrimental effects on biological functions.[6] This study focused on modifying commercial pectin (CP) to obtain a hydroxamic acid derivative (PHA) and evaluating its efficiency in removing Pb(II) from aqueous solutions.[7]

### 2. Methods

#### *Materials*

The study utilized commercial pectin (CP) extracted from citrus fruits and all solvents and reagents used were of analytical grade

commercially available. The hydroxamic acid derivative (PHA) synthesis was carried out according to the procedure reported by AlKhatib et al. [8]. In this study, however, hydroxylamine was used instead of its derivatives used by the AlKhatib group. Initially, to a 500 mL commercial pectin solution (20 g L<sup>-1</sup>), pH 4.0-4.5, it was added 9.55 g (0.05 mol) *N,N'*-dicyclohexylcarbodiimide (DCCI) under stirring, to activate the carboxylic acid groups. After 2 hours, 15.46 g (0.22 mol) hydroxylamine hydrochloride was added, and the solution was stirred for another 90 min, when the pH was adjusted to pH 6.0 using NaOH, and then left to stir for 2 more hours. Finally, the pH was shifted to 9.0 and the mixture was kept under these conditions for different periods of time (24, 48, 72, 96 and 120 h). Then, the filtered polymeric material was reprecipitated with HCl (20 mL) and acetone (500 mL). PHA was separated by filtration and for the removal of dicyclohexylurea, the polymer was thoroughly washed with ethanol. The resulting mass was dissolved in 200 mL of deionized water. PHA was dialyzed in cellulose membrane for 72 h to remove any residual salts, and the final yield was about 30% after all purification procedures.

### Characterization

Various experimental techniques were used to characterize CP and PHA, like infrared (IR) spectroscopy coupled to attenuated total reflection (ATR) apparatus to confirm the presence of the hydroxamic group in PHA. The degree of esterification (*DE*) was determined using both IR spectroscopy and acid-base titration (Equation 1), and potentiometric titration was used to determine the *pK<sub>a</sub>* of CP.

$$DE(\%) = 100 \frac{ACOOR}{(ACOOR + ACOOH)} \quad (1)$$

where *DE*(%) is the degree of esterification given in percentage; ACOOR corresponds to the band height for esterified carboxylic groups, and ACOOH corresponds to the band height for non-esterified carboxylic groups.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques were used to investigate the thermal behavior of CP

and PHA. Elemental analysis has been used to estimate the degree of substitution of carboxylic acid groups by hydroxamic acids.

And finally, the sorption rate of Pb(II) by CP and PHA was evaluated at different concentrations using flame atomic absorption spectroscopy (FAAS).

### Molecular Modeling

Molecular modeling was used to study the interactions of CP and PHA with Pb(II) in an aqueous environment, using molecular mechanics and ab initio (HF/3-21G up to 6-31G(d) basis set) theory levels to optimize the geometries of the oligosaccharide structures. The force fields used were OPLS\_2005 [9] for carbohydrates and ions and SPC-E to the explicit waters. The canonical equilibration was processed using Martina-Tobias-Klein isotropic barostat at 1 atm and Nose-Hoover thermostat.[10]

### Sorption Studies

Experimental isotherms of Pb(II) adsorption by PHA at 25 °C were obtained at different concentrations to understand the sorption behavior, and the sorption capacity (*SC<sub>exp</sub>*) was determined by measuring the residual Pb(II) concentration in the supernatant after reaching saturation.

Langmuir, Freundlich, and SIPS [11] isotherm models were tested to analyze the experimental data.

## 3. Results and Discussions

### Characterization

The derivatization of the pectin structure was confirmed through an elemental analysis, and the percentage of nitrogen in the PHA samples was used to determine its degree of substitution. The degree of substitution in the PHA samples was found to be 18%. Elemental analyses of hydroxamic derivatives obtained at different synthesis times (24, 48, 72, 96, and 120 h) were performed, and the corresponding percentages of nitrogen were 18%, 19%, 10%, 12%, and 8%. A similar increase in the degree of substitution (from

2.68% to 10.43%) was observed by Rha [12], when the reaction time was increased from 4 h to 48 h. Nevertheless, we observed that after 48 h of exposure to hydroxylamine, the percentage of nitrogen decreased, probably due to hydrolysis under high pH conditions (approximately 9.0), and that was confirmed by IR spectra, as evidenced by the new absorption band at  $1634\text{ cm}^{-1}$ , which was associated with hydroxamic acid [12]. The *DE* value for CP, which was determined through infrared spectroscopy and calculated using equation 1, was 49.9%, whereas the value for titration was  $51.5\% \pm 0.18$  ( $n = 3$ ). The purpose of the titration was to provide reliability in determining *DE*. The infrared technique presented considerable advantages over titration, such as practicality and throughput.

Through potentiometric titration, the  $pK_a$  value of CP was found to be 4.4. The  $pK_a$  of pectin is directly related to its *DE*; that is, the lower the  $pK_a$  value, the lower the *DE* value, due to the higher number of carboxylic acid groups. Based on these results, pectins may have a  $pK_a$  value between 3.5 and 4.5.

TGA and DSC analyses showed that PHA has lower thermal stability than CP, possibly due to increased hydrogen bonding in its structure and the increase in  $T_g$  of PHA compared to CP further supported the successful modification of the pectin structure.

### *Pb(II) Sorption*

PHA exhibited superior sorption capacity for Pb(II) compared to CP, effectively removing almost all Pb(II) present in the solution at all tested concentrations, what was supported by the statistical analysis. The sorption rate of CP decreased with increasing Pb(II) concentration, suggesting a limited number of available sorption sites.

### *Molecular Modeling*

Molecular dynamics simulations revealed, by root-mean-square deviation (RMSD) and radius of gyration ( $R_g$ ) analysis that the PHA-Pb(II) system was more compact than the pectin-Pb(II) system. The distances between the charged centers in both

carboxylate-Pb(II) and hydroxamate-Pb(II) systems were similar, indicating comparable ionic forces.

The simulations suggested that PHA's higher efficiency in removing Pb(II) was not solely due to ionic interactions but also because of its ability to stabilize a higher number of Pb(II) ions per volume, where we could point the "alpha effect" [14] as main hypothesis, where nitrogen's ability to stabilize oxygen during interactions, could enhance Pb(II) removal capacity. For PHA, the first case was observed and reported by McCready and Reevein 1955 [15], when they created a selective test to analyze pectin in plants.

### *Sorption Isotherms*

The SCexp values obtained from the sorption experiments indicated that PHA reached saturation in both shaken and unshaken conditions. Langmuir, Freundlich, and SIPS isotherm models were evaluated for their ability to describe the experimental results. While all models showed acceptable fits based on the  $\chi^2$  test, the Freundlich model was found to be the most suitable for describing the Pb(II) adsorption by PHA, which has suggested an electrostatic attraction between PHA and Pb(II), contributing to the efficient removal of Pb(II) ions from the solution.

## **4. Conclusions:**

The study successfully synthesized and characterized PHA, demonstrating its potential as a sorbent material for Pb(II) removal. PHA showed superior sorption capacity for Pb(II) in comparison to CP, highlighting the significance of chemical derivatization in enhancing metal ion removal efficiency. The molecular modeling studies provided insights into the mechanism of PHA-Pb(II) interactions, emphasizing the role of nitrogen in stabilizing Pb(II) ions and contributing to the overall sorption process. Freundlich's model effectively described the adsorption of Pb(II) by PHA, corroborating the computational evidence of electrostatic interactions between the sorbent and the metal ions. The study concluded that PHA holds great promise as an environmentally friendly and efficient material for Pb(II) removal,

particularly in aquatic decontamination applications.

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