

Mechanism of mercury removal by a novel hydrazine hydrate-modified pectin

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This paper describes a novel hydrazine hydrate-modified pectin for the removal of Hg²⁺. The modified pectin was characterized by elemental analysis and FT-IR spectroscopy which indicated that hydrazine hydrate was successfully grafted on the side chains of pectin. In addition, the reaction mechanism between modified pectin and Hg²⁺ was studied by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The results revealed that the removal effect was probably due to the form of the coordination bonds between Hg²⁺ and N/O atoms. Under optimized experimental conditions, the efficiency of removal Hg²⁺ by the modified pectin reached 74.8%, which was far higher than the 30.5% obtained with unmodified pectin.

Keywords: Pectin, modification, mercury, hydrazine hydrate, mechanism

INTRODUCTION

The discharge of toxic heavy metal ions into the environment is a serious pollution problem. Major sources of water pollution with heavy metals are plating plants, mining and metal finishing manufacturing [1]. With the wastewater discharge, heavy metals enter into water, soil and atmosphere in various forms. Through the food chain they are further transferred to plants, animals, and even humans. Furthermore, heavy metals can be enriched in the body, causing serious harm. Mercury, one of the most toxic metals, has drawn much attention on account of its toxicity and impact on the public health. It is well known that Hg²⁺ has a very high tendency to bind proteins, mainly causing damage to the renal and nervous systems [2]. The main anthropogenic sources contributing to mercury contamination include wastewater discharges and atmospheric depositions from mining activities, oil and coal combustion, chlor-alkali industries, cement production, municipal waste and sewage sludge combustion, and manufacture of batteries [3-6]. Because of its high toxicity, mercury has been included in the list of priority pollutants by U.S. EPA [7]. In the early 1950s, the minamata disease broke out in Kumamoto, Japan, and after that the problem of mercury pollution has extensively aroused public attention.

Natural pectin is a vegetable polymer of L, D-

galacturonic acid partially esterified with methoxy groups. It is widely used as a coagulant additive in foods and pharmaceutical applications, as well as in some industrial productions [8, 9]. At the same time, since the first report on pectin as an efficient antidote for heavy metals poisoning, it has been found to suppress the absorption of strontium into the bone structure of rats [10]. Pectin has been widely used as a gelling agent in foodstuffs, but its application in heavy metals removal from wastewater has not been fully recognized [11,12]. Although pectin has several reactive groups, such as esterified carboxyl groups, free carboxyl groups and hydroxyl, there are still some limitations such as low removal efficiency, low resistance to acid and base, impact of the environment on the performance, and other practical issues. The performance of heavy metal ions removal by pectin can be improved through physical or chemical modification. For example, introducing functional groups with stronger combining ability can enhance the removal efficiency to heavy metals. Moreover, pectin can be extracted from fruit peels which are abundant, cheap and environmentally safe. Therefore, modified pectin has good prospects for heavy metals removal from aqueous solutions.

In this work a new approach of modified pectin preparation and its uptake capacity to heavy metal ions, especially Hg²⁺, is studied. The concentration of Hg²⁺ ions in the filtrate was determined by the dithizone-acetonitrile UV-vis method. Compared with the national standard method, the improved method was more rapid and avoided extraction.

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EXPERIMENTAL

All reagents were of chemical grade and purchased from National medicine group chemical reagent co., LTD. Pectin with high methoxy content (HMP, esterification degree of 70%) was purchased from USA. Ultrapure water was used throughout.

(1) Modified pectin (HHA-HMP) was prepared by dissolving 5 g of HMP in 300 mL of ultrapure water and stirring until it was homogeneous, followed by gradual addition of 75 mL of 80% hydrazine hydrate. Finally, the mixture was stirred and refluxed at 80 °C for 12 h and then cooled to room temperature. After reaction, the viscous gel substance was washed 4–5 times with absolute ethyl alcohol, dried in a freeze-drier for 11 h and ground to powder for use. The preparation process is shown in Scheme 1. The HHA-HMP was characterized by elemental analysis and FT-IR spectroscopy.

(2) The modified pectin was used for Hg²⁺ removal. 100 mL of Hg²⁺ solution (1 mmol L⁻¹) and modified pectin (0.3 g L⁻¹) were vigorously stirred at pH=4 for 30 min at room temperature. The complex of Hg-HHA-HMP is water-insoluble, so the flocculent precipitate was separated through centrifuging. The supernatant was analyzed by dithizone-acetonitrile ultraviolet spectrophotometry. The flocculent precipitate was washed 3-4 times with ultrapure water, dried in a freeze-drier for 5 h and ground to powder for use.

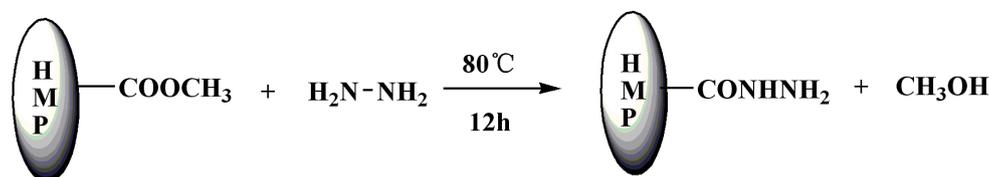
(3) The properties of dithizone are well-known, and works about using dithizone for metal analysis are largely published [13]. Unfortunately, extraction with an organic solvent is needed, preventing the choice of dithizone-based methods for on-line measurements. Other colorimetric methods for the determination of Hg²⁺ were proposed [14-17], but all of them require complex and time-consuming sample pretreatment. The

method described in this work was rapid and without extraction, using dithizone dissolved in acetonitrile. This method can directly determine the content of Hg²⁺ in the aqueous phase. Dithizone-acetonitrile spectrophotometric determination of low concentrations of Hg²⁺ is based on the formation of an orange-red complex between dithizone and Hg²⁺ under acidic conditions in a homogeneous medium, the absorption of which is measured at 480 nm. Various concentrations of Hg²⁺ (0-8.33 μmol L⁻¹) were mixed with dithizone (1 mmol L⁻¹) in acetonitrile solution (pH=2). The absorption values were measured at 480 nm and 600 nm by UV-vis spectrometry.

RESULTS AND DISCUSSION

The elemental analysis (E.A.) results of HMP and HHA-HMP are shown in Table 1. Compared with HMP, the nitrogen content of HHA-HMP increased after modification, indicating that the –CONHNH₂ groups were grafted to the pectin.

IR analysis is used to identify some characteristic functional groups, and the spectra of HMP and HHA-HMP are shown in Fig. 1 (a, b). In the HMP spectrum, the broad and intense absorption peak at 3423 cm⁻¹ corresponds to O-H stretching vibration. The peak at 2922 cm⁻¹ can be attributed to the C-H stretching vibration of methyl, methylene and methoxy groups. The peaks at 1721 cm⁻¹ and 1622 cm⁻¹ in the HMP spectrum are usually representative of ester carbonyl (C=O) groups and carboxylate ions (COO⁻) stretching bands, respectively [18]. The bands in the range of 1300-1000 cm⁻¹ can be assigned to the C-O stretching vibration of carboxylic acids and alcohols [19]. The IR spectrum of HHA-HMP



Scheme 1. Preparation process of HHA-HMP.

Table 1. Results of E. A. of the sample (wt %)

Sample	C (%)	H (%)	O (%)	N (%)
HMP	38.12	6.05	55.44	0.39
HHA-HMP	35.90	6.25	53.31	4.54

shows various distinctive absorption peaks: the broad bands in the region 3326 cm^{-1} can be attributed to the stretching of -OH groups of HHA-HMP and overlapping stretching bands of -NH. In addition, a sharp peak appeared at 1601 cm^{-1} , corresponding to the C=O stretching vibration of the amide group (-CONH₂) [20]. It indicates that the ester carbonyl (C=O) groups switch to amide group (C=O). Besides, the peaks at 1468 cm^{-1} and 1360 cm^{-1} can be attributed to N-H bending vibration and C-N stretching vibration, respectively. Thus, these results confirm that HHA-HMP was successfully obtained.

Dithizone-acetonitrile UV-vis spectrophotometry is an improved method based on the national standard method. The ultraviolet absorption spectra

are presented in Fig. 2a. The new absorption peak of the dithizone-Hg²⁺ chelate was measured at 480 nm. The calibration curve (absorption ratio ($A_{480\text{ nm}}/A_{600\text{ nm}}$) versus concentration) covered a linear range from 0.83 to 8.33 $\mu\text{mol L}^{-1}$ (Fig. 2b). The experiments were carried out at room temperature with 30 min reaction (HHA-HMP=0.3 g L^{-1} , [Hg²⁺]=1 mmol L^{-1} , pH=4), and the removal efficiency of HHA-HMP toward Hg²⁺ was 74.8% (the binding capacity of modified pectin is 2.49 mmol g^{-1}). It was far higher than the 30.5% removal efficiency of HMP (1.02 mmol g^{-1}). The higher removal efficiency was mainly due to the participation of N atoms, which enhanced the coordinating effect between Hg²⁺ and HHA-HMP.

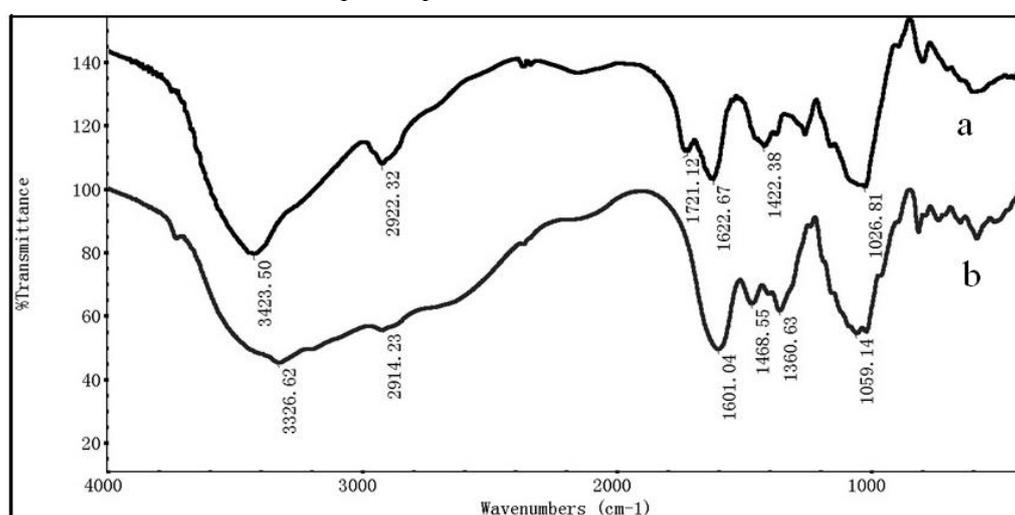


Fig. 1. IR spectra of HMP (a) and HHA-HMP (b).

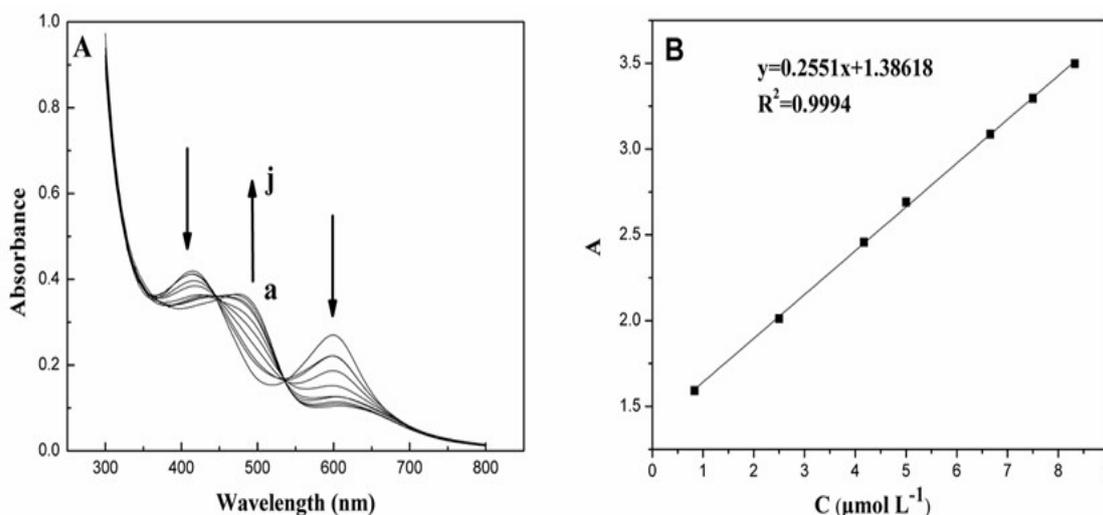


Fig. 2. (A) Absorption change of dithizone (1 mmol L^{-1}) upon addition of different Hg²⁺ concentrations (a-j): 0, 0.17, 0.50, 0.83, 2.50, 4.17, 5.00, 6.67, 7.50, 8.33 $\mu\text{mol L}^{-1}$ in acetonitrile solution (pH=2); (B) Calibration curve (absorption ratio ($A_{480\text{ nm}}/A_{600\text{ nm}}$) vs Hg²⁺ concentration (0.83-8.33 $\mu\text{mol L}^{-1}$).

Variation of the metal uptake with pH is shown in Fig. 3. The binding capacity of HHA-HMP does not increase at pH above 4-5, which is due to fact that the formation of the species $Hg(OH)_2$ achieves 100% at pH about 5 [21]. It follows from this result that the most favorable pH providing the best uptake effectiveness, is pH 4 where Hg^{2+} is present mostly in cationic form.

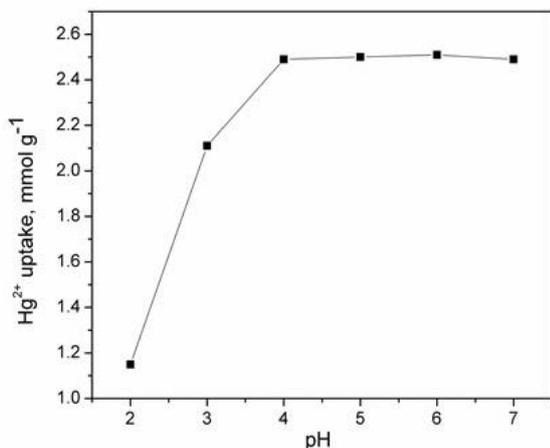


Fig. 3. Effect of pH on the uptake of Hg^{2+} by HHA-HMP (100 mL, 0.3 g L⁻¹ HHA-HMP; 100 mL, 1 mmol L⁻¹ Hg^{2+} ; 25°C; 30 min).

The XRD patterns are shown in Fig. 4.

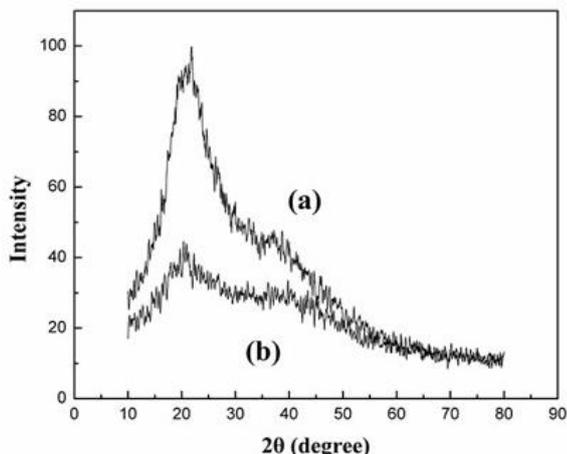


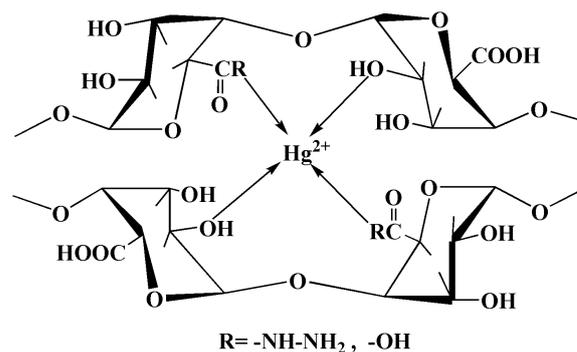
Fig. 4. XRD diffraction pattern of HHA-HMP (a) and HHA-HMP- Hg^{2+} (b).

As illustrated in Fig. 4a, the peak of HHA-HMP is remarkably sharp and the peak intensity near $2\theta=20^\circ$ indicates that HHA-HMP has a crystalline area, which is primarily ascribed to intramolecular hydrogen bonding. However, the XRD pattern of HHA-HMP- Hg^{2+} (Fig. 4b) shows that the

crystallization peak significantly decreases at around 20° which is due to the decreased intramolecular hydrogen bonding and the increased steric hindrance between the molecules. The XRD results showed that coordination bonds are formed between HHA-HMP and Hg^{2+} .

XPS provides identification of the sites involved in the accumulation of metals, as well as the species on the biopolymer [22]. The surface element electron binding energy data of HHA-HMP and HHA-HMP- Hg^{2+} are displayed in Table 2. The electron binding energies of C atoms before and after complexation are unchanged, indicating that the C atoms of the chemical environment on the HHA-HMP ligand surface are not different. However, the electron binding energies of N, O and Hg have changed. The changes show an apparent decrease in the binding energy of Hg4f and correspondingly an increase in the electron binding energy of N1s and O1s [23]. The results suggest that the removal of Hg^{2+} can be considered as a result of the complexation between Hg^{2+} and N/O atoms. The N and O atoms have a tendency of losing electrons and the Hg atoms have a tendency of getting electrons or sharing electron pairs, so it may be considered that the N and O atoms provide lone electron pairs to the empty orbits of the Hg atoms.

According to this, the reaction mechanism of HHA-HMP and Hg^{2+} involves the formation of coordination bonds of Hg^{2+} with N and O. The possible reaction mechanism of HHA-HMP with Hg^{2+} is shown in Scheme 2.



Scheme 2. Possible mechanism of the reaction of HHA-HMP with Hg^{2+} .

Table 2. Comparison of the electron binding energies of HHA-HMP and HHA-HMP- Hg^{2+} (ev)

Samples	C(1s)	N(1s)	O(1s)	Hg(4f)
HHA-HMP	284.88	398.77	531.06	
Hg^{2+}				101.56
HHA-HMP- Hg^{2+}	284.88	399.28	531.29	99.88

CONCLUSION

This study presents a novel hydrazine hydrate-modified pectin. On the basis of this study, a possible schematic mechanism for mercury uptake by HHA-HMP was proposed. Removal of Hg^{2+} by HHA-HMP from aqueous solutions is due to the complexation between Hg^{2+} and N/O atoms on the polymer matrix. So, the modified pectin has good prospects for the removal of heavy metals from aqueous solutions.

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МЕХАНИЗЪМ ЗА ОТСТРАНЯВАНЕ НА ЖИВАК ЧРЕЗ ЕДИН НОВ МОДИФИЦИРАН С ХИДРАЗИН ХИДРАТ- ПЕКТИН

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(Резюме)

В тази работа се описва нов пектин, модифициран с хидразин-хидрат, изследван за отстраняването на Hg^{2+} . Модифицираният пектин е охарактеризиран чрез елементен анализ и FT-IR спектроскопия, която показва, че хидразин-хидратът успешно се присажда към страничната верига на пектина. Освен това механизмът на реакцията между модифицирания пектин и Hg^{2+} е изследван чрез рентгеноструктурен анализ и рентгенова фотоелектронна спектроскопия (XPS). Резултатите показват, отстраняването на живачни йони се дължи на координационни връзки между Hg^{2+} и азотните и кислородните атоми. Ефективността на отстраняване на живака с модифициран пектин достига 74.8% при оптимизирани условия, което много над известните 30.5%, получени при природния пектин.