

Optimization of Coordination Conditions of Cr(III) to Chitosan

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Abstract: Coordination conditions of Cr(III) to chitosan were optimized using multi-factor orthogonal experiment $L_{16}(4^5)$. Chitosan and Cr(III) contents of the resulting product were determined by testing the nitrogen content of the sample and using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) respectively. The results indicated that Cr(III) content of the resulting product is increased with the increase of the mol ratio of Cr(III) to structural units of chitosan, pH value of the reaction system, reaction temperature and reaction time. Main factors affecting the coordination conditions were discussed and arranged in a decreasing order according to their abilities of the effect on the coordination amount of Cr(III): concentration of PO_4^{3-} , mol ratio of Cr(III) to structural units of chitosan, reaction time, reaction temperature and pH of the reaction system. The optimal reaction conditions are: mol ratio of Cr(III) to the structural units of chitosan 1:1, pH 4.5, reaction temperature 50 °C, reaction time 8 h, and concentration of K_2HPO_4 0.10 mol/L. Chitosan and Cr(III) might form a complex with the highest chelating ratio of about 2.1:1 under optimal reaction conditions. Fourier transform infrared spectra (FT-IR) of initial chitosan and coordination product indicated that amino group as well as both primary and secondary hydroxyl groups at C-2, C-3 and C-6 positions of chitosan are chelated with Cr(III).

Key words: chitosan; chromium; coordination; optimization

1 Introduction

Renewable or natural resources polymers with reproductively, diversity, universality, environmental compatibility and functional features have won the support of many environmentalists. As the only natural alkaline polysaccharide found in the world presently, chitosan is a main derivative of chitin, which has three types of reactive functional groups, an amino group as well as both primary and secondary hydroxyl groups at the C-2, C-3, and C-6 positions, respectively ^[1]. This structural characteristic benefits chitosan in the application of uptake of metal ions ^[2], which has aroused the interest of many researchers for the application of it in the disposal of waste or industrial water.

As one of the leather producing centers, the leather making industry develops quickly in China with the expense of severe environmental contamination and ecological destruction. Waste water from tannery has been characterized by high alkalinity, strong chroma, large chemical oxygen demand (COD) value and substantive suspension, among which sodium sulfide and chromium bring most serious pollution to our environment. In addition, at the pH value of 6.4 ~ 8.5, trivalent chromium would be oxidized and converted into virulent

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hexavalent chromium, which would cause stimulation, corrosion, malformation and mutation, regardless of mouth, respiratory system or skin absorption [3]. Environmental problem has become the bottleneck in the development of leather industry, and the popularization of clean technology is the foundation of the sustainable development of leather manufacture [4,5].

As far as metal ions are concerned, it has been demonstrated that chitosan is a more excellent ligand comparing with common commercial absorbent resin [6-8]. Researches show that chitosan has strong absorption ability to hexavalent chromium, which would reach 215 mg/g~625 mg/g, depending on the modification method and detail reaction conditions [9-12].

To solve the contamination of chromium and improve the coordination of chitosan to Cr(III), and based on other researchers study result [13], the manuscript investigated the influence of n(Cr(III)):n(structural units of chitosan), reaction pH, concentration of phosphate, temperature and time on the coordination reaction of chitosan to Cr(III). The amount of chitosan in the complex was calculated by the determination of nitrogen content of the complex, whereas the chromium content in the complex was tested by ICP-AES. The structure of resulting complex was deduced by IR spectra, while TG analyzer was used to evaluate the thermal stability of the complex.

2 Experimental

2.1 Main materials and instruments

Chitosan (CTS), mass average molecular weight 290 kDa, degree of deacetylation (DD) 83%, prepared by ourselves; $\text{Cr}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ and other reagents are of reagent grade and used without further purification.

BÜCHI automatic nitrogen determination system with a digest system (BÜCHI K-437) and a distillation unit (BÜCHI 339), BÜCHI, Switzerland; Fourier transform infrared spectroscopy (FT-IR), Perkin Elmer (Spectrum one); Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), Perkin Elmer (Optima 2100 dv); Thermogravimetric Analyzer, NETZSCH (TG 209 F1).

2.2 Preparation of chitosan-Cr(III) complex

In order to optimize the reaction conditions of CTS to chromium, orthogonal test was adopted. Main controllable variables, viz. Cr(III) : chitosan structural units (mol/mol) (A), reaction pH (B), reaction temperature (C), reaction time (D), and concentration of K_2HPO_4 (E) were selected. Reference to the experimental design theory, the orthogonal array $L_{16}(4^5)$ was chosen to arrange the aforementioned coordination reaction conditions.

The experiment was carried out according to Table 1. In a flask with heating equipment, 0.5 g (weight accurately to 1 mg) CTS and 40 mL 0.5% (v/v) acetic acid was added. After thoroughly dissolution of CTS (agitation for 1 h), K_2HPO_4 with certain concentration was added. 0.5 h later, certain amount of $\text{Cr}_2(\text{SO}_4)_3$ solution was dropped, and the pH value of the reaction system was adjusted using 10% HCl/NaOH. The reaction was ended by the addition of 200 mL ethanol/acetone (v/v = 1:1). The resulting product was obtained by thoroughly washing, centrifugation, and drying in a vacuum oven at 50 °C for 48 h and conditioning in a silica gel desiccator for two weeks prior to following determination.

Table 1 The variables and their levels of the coordination of chitosan with Cr(III)

Variables investigated	Levels of each variable			
	1	2	3	4
A: Reactants ratio ¹⁾	0.25	0.5	1.0	2.0
B: pH value	3.5	4.0	4.5	5.0
C: Temperature/ °C	30	40	50	60
D: time/h	8.0	6.0	4.0	2.0
E: K ₂ HPO ₄ /mol·L ⁻¹	0	0.025	0.05	0.1

1) n(Cr(III)):n(structural units of chitosan)

2.3 Determination of chitosan content

Nitrogen contents of samples were analyzed by a BÜCHI fully automatic nitrogen determination system. In the digestion tube containing 0.15 g (weight accurately to 0.001 g) sample, 0.3 g (weight accurately to 0.05 g) CuSO₄·5H₂O, 3 g (weight accurately to 0.05 g) and 10 mL concentrated sulfuric acid (98%, w/w) were added. After digestion at 370 °C for 2.5 h in the digestion instrument, the nitrogen content of resulting transparent green or blue liquor was determined in digestion system.

The CTS content of the sample was calculated based on this test:

$$W(\text{CTS})=100\times W(\text{N})/7.12$$

Where: $W(\text{CTS})$ is the weight percentage of CTS in final product, 7.12 is the weight percentage of N in initial CTS, and $W(\text{N})$ is the weight percentage of N in final product.

2.4 Determination of Cr(III) content

Cr content of the sample was tested by ICP spectrum after the digestion of it by aforementioned method and the filtration of it. Cr₂(SO₄)₃ solution with the Cr(III) content of 52 mg/L was used as calibration solution. Since CTS has reducibility, and Cr₂(SO₄)₃ solution was used to simulate the coordination ability of CTS to Cr(III) in practical tanning sewage, it is reasonable to suppose no conversion of Cr(III) to Cr(VI) under the reaction condition. So, Cr content of the sample determined by ICP spectrum would be regarded as Cr(III) content of it.

2.5 IR spectrum

FT-IR spectrum of the sample was detected under dry air using KBr pellets.

2.6 TG analysis

The thermogravimetric stability of the sample was studied in Al₂O₃ pot with nitrogen atmosphere (20 mL/min) at the heating rate of 10 °C/min (35~850 °C).

3 Results and discussion

3.1 Optimization of orthogonal experiment

Table 2 is the result of orthogonal experiment. It demonstrated that Cr(III) content of the complex was raised with the increase of the K₂HPO₄ concentration, n(Cr₂(SO₄)₃):n(structural units of chitosan), reaction pH and reaction time. Different from the complexation of chitosan to Cu(II) [14], the coordination of chitosan to

Cr(III) was greatly influenced by the reaction time. This may be explained by the chemical dynamic inertia of Cr(III). As far as the influence of pH to the reaction is concerned, at low pH value (pH = 3.5), -NH_2 group in CTS would react with H_3O^+ and form $\text{NH}_3^+\cdot\text{H}_2\text{O}$, which would hamper the coordination reaction by losing the lone pair electrons and forming a homogeneous charge with Cr(III). When pH value of the reaction system is higher than 4.7, Cr(III) is prone to hydrolyze and deposit, which would restrain the separation and reaction of it to CTS. This would explain the optimal reaction pH (4.5) gained in the experiment. In the experimental range, increasing the reaction temperature would favor the complexation reaction, but when the reaction temperature is higher than $50\text{ }^\circ\text{C}$, it has little influence on the coordination of Cr(III) to CTS. On the one hand, heightening the system temperature would increase the collision probability of the reactants and facilitate the complexation reaction. On the other hand, as an exothermic reaction, elevating the reaction temperature inhibits the formation of the product. When the temperature is higher than $50\text{ }^\circ\text{C}$, it has little impact on the reaction. In summary, the best coordination reaction condition is $n(\text{Cr(III)}):n(\text{structural units of chitosan}) = 2:1$ (namely, $n(\text{Cr}_2(\text{SO}_4)_3):n(\text{structural units of chitosan}) = 1:1$), pH = 4.5, K_2HPO_4 0.10 mol/L, temperature $50\text{ }^\circ\text{C}$, and time 8 h. Fixing the reaction condition as run 14, product with highest $n(\text{Cr(III)}):n(\text{structural units of chitosan})$ would be obtained as 2.08.

R values in Table 2 indicated that factors affecting the coordination reaction would be arranged in a decreasing order according to their abilities of the effect on it: concentration of K_2HPO_4 (C), reactants ratio (A), reaction time (E), reaction temperature (D) and pH (B). This indicated that in the experimental range, concentration of K_2HPO_4 and reactants ratio have great influence on the Cr(III) amount in the resulting product, while the pH value of the reaction system has little effect on it.

3.2 FT-IR spectra analysis

Fig. 1 is the FT-IR spectra of the resulting products of CTS and K_2HPO_4 in different time interval. It illuminated that the IR spectra changed more or less along with the elapsing of the reaction time since the addition of K_2HPO_4 at chitosan's acetic acid solution: $\nu_{\text{O-H}}$ and $\nu_{\text{N-H}}$ band of CTS at 3434 cm^{-1} transfer to 3560 cm^{-1} and 3280 cm^{-1} , indicating the interaction of -OH and -NH to K_2HPO_4 ; $\nu_{\text{C=O}}$ at 1655 cm^{-1} shifts to 1665 cm^{-1} and the peak is broadened; the deformation vibration of methyl and methylene groups at 1420 cm^{-1} is weakened; and the absorption at 1075 cm^{-1} and 1031 cm^{-1} is slipped and broadened obviously. All of these indicated the inter-reaction of primary and secondary -OH with K_2HPO_4 . Along with the addition of K_2HPO_4 , the charge density around -NH_2 and -OH in the main chain of CTS might be increased, and might exhibit higher attraction to metal ions that shorts of electrons, which in turn enhance the coordination reaction. Besides, 0.5 h later, the change of the FT-IR spectra of the resulting products of CTS and K_2HPO_4 is neglectable, so, $\text{Cr}_2(\text{SO}_4)_3$ solution was added 0.5 h after the addition of K_2HPO_4 in this experiment.

Table 2 Experimental arrangement and test results ¹⁾

Run	Reagent Ratio ²⁾	pH	K ₂ HPO ₄ / mol·L ⁻¹	T/°C	t/h	W(CTS) /%	W(Cr) %	Complex Ratio ²⁾
1	0.25	3.5	0	30	8.0	78.93	3.27	0.1281
2	0.25	4.0	0.025	40	6.0	59.52	9.29	0.4827
3	0.25	4.5	0.05	50	4.0	63.25	11.70	0.5721
4	0.25	5.0	0.1	60	2.0	59.69	16.09	0.8336
5	0.5	3.5	0.1	40	4.0	55.48	15.32	0.8540
6	0.5	4.0	0.05	30	2.0	58.96	8.31	0.4359
7	0.5	4.5	0.025	60	8.0	55.09	15.67	0.8796
8	0.5	5.0	0	50	6.0	71.06	5.49	0.2389
9	1.0	3.5	0.025	50	2.0	53.97	9.18	0.5260
10	1.0	4.0	0	60	4.0	61.32	2.53	0.1276
11	1.0	4.5	0.1	30	6.0	35.20	17.15	1.5067
12	1.0	5.0	0.05	40	8.0	43.15	19.22	1.3776
13	2.0	3.5	0.05	60	6.0	30.77	16.05	1.6130
14	2.0	4.0	0.1	50	8.0	26.93	18.11	2.0793
15	2.0	4.5	0	40	2.0	57.07	5.74	0.3111
16	2.0	5.0	0.025	30	4.0	38.56	10.30	0.8260
K ₁	0.504	0.780	0.201	0.724	1.116			
K ₂	0.602	0.781	0.679	0.756	0.960			
K ₃	0.884	0.817	1.000	0.854	0.595			
K ₄	1.207	0.819	1.318	0.863	0.527			
R	0.703	0.039	1.117	0.139	0.589			

1) the outcome is the mean value of three tested results.

2) n(Cr(III)):n(structural units of chitosan).

In Fig. 2 a and b are the FT-IR spectra of CTS and chitosan-Cr(III) respectively. The result showed that the $\nu_{\text{O-H}}$ and $\nu_{\text{N-H}}$ band of chitosan at 3434 cm^{-1} shift to 3274 cm^{-1} after the coordination with Cr(III), which indicates the interaction of -OH and -NH with Cr(III). The deformation vibration of N-H bond at 1598 cm^{-1} moves to the lower wave number of 1548 cm^{-1} , which might be explained by the coordination of Cr(III) with atom N and the decrease of the energy needed for the deformation vibration of N-H by moving of electron cloud from N atom of amino to Cr(III). Deformation vibration of O-H 1260 cm^{-1} was weakened and nearly disappeared after the reaction, and the peaks at 1076 cm^{-1} and 1031 cm^{-1} of C-O shifted to 1063 cm^{-1}

and 1028 cm^{-1} and strengthened, indicating the participation of the primary and secondary $-\text{OH}$ in the complexation reaction. $\nu_{\text{C=O}}$ at 1655 cm^{-1} shifts to 1651 cm^{-1} and the peak is broadened, suggesting the change of the chemical environment of it. All of those changes are similar to that of CTS that complexes with $\text{Cu}(\text{II})$ [14], indicating the similarity of the complexation pattern of chitosan-Cr(III) with chitosan-Cu(II).

In conclusion, $-\text{NH}_2$ and $-\text{OH}$ groups of CTS are taken part in the reaction, and the chemical environment of $-\text{NHCOCH}_3$ has changed.

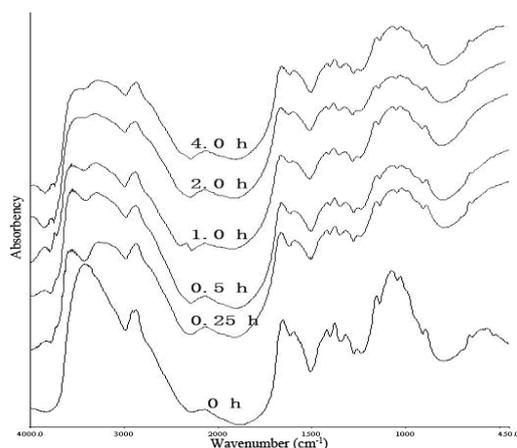


Fig. 1 IR spectra of resultants of CTS and K_2HPO_4

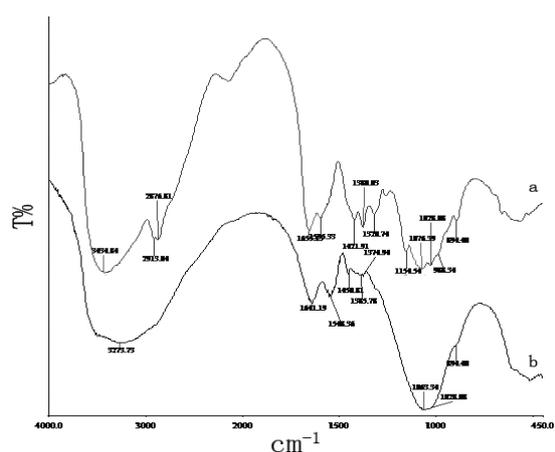


Fig. 2 IR spectra of CTS (a) and CTS-Cr(III) (b, sample 14)

3.3 TG analyses

Fig. 3 exhibits the TG profiles of pyrolysis

for chitosan and chitosan-Cr(III) at predetermined heating rate. CTS shows two weight-losing events centered at about 104.1°C and 297.8°C , while Chitosan-Cr(III) contains three separated weight-losing steps that centered at $115 \sim 125^\circ\text{C}$, $210 \sim 220^\circ\text{C}$ and $260 \sim 285^\circ\text{C}$. The first thermal event for CTS and CTS-Cr(III) is related to the evaporation of water present in the samples. Thanks to the hydrophilic

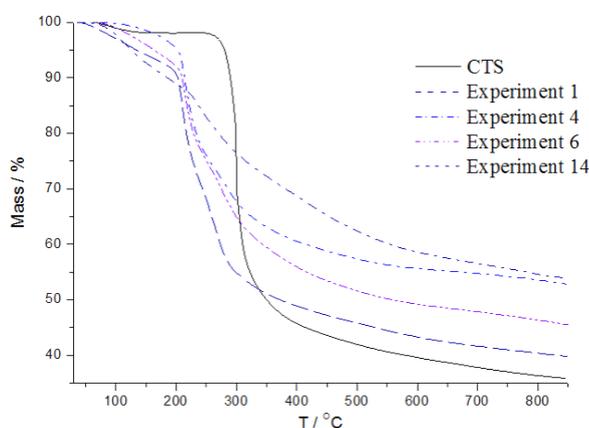


Fig. 3 TG profiles of CTS and CTS-Cr(III)

chromium atom, chitosan-Cr(III) shows better water combination capability, and the water content increases from 3.5% to 7% ~ 14% after the coordination reaction. After complexation, the microstructure of chitosan-Cr(III) might be different from that of chitosan. The structural units of CTS that complexed with Cr(III) might form one phase, while the others might form another one. So the complex presents two degradation steps while CTS has only one. The decreasing of the degradation temperatures of CTS after the complexation with Cr(III) suggests the reduction of

the thermal stability of the complex. This phenomenon could be explained by the demolish of inter- and intra-molecular hydrogen bond of CTS due to the interaction of active groups of CTS with Cr(III), which lowered the structural regularity and its thermal stability. Similarly, when the temperature is higher than 450 °C, the mass of both CTS and chitosan-Cr(III) is decreasing tardily. This could be explained by the cyclization of the remaining parts of samples [15]. When the temperature reached 700 °C, CTS and the complex start dehydrogenation, and the resulting substances with graphite structure (i.e. carbonization) are found [15]. Comparing with CTS, the residual weight percentages of complexes number 1, 6, 4, and 14 increased stepwise, which is consistent with the results of ICP analyses, and demonstrates that the Cr(III) contents in those samples increase gradually.

3.4 Chemical structure of CTS-Cr(III)

The outer electronic structure of Cr³⁺ is 3d³4s⁰4p⁰. Two 3d empty orbitals, one 4s empty orbital and three 4p empty orbitals would process d²sp³ heterozygosity, and form 6 tracks with same energy. So Cr(III) would form complex of octagonal configuration with nucleophilic substance (Viz. CTS in this experiment). Under optimal experimental condition, the mol ratio of Cr(III) to structural units of CTS would be 2.08:1.

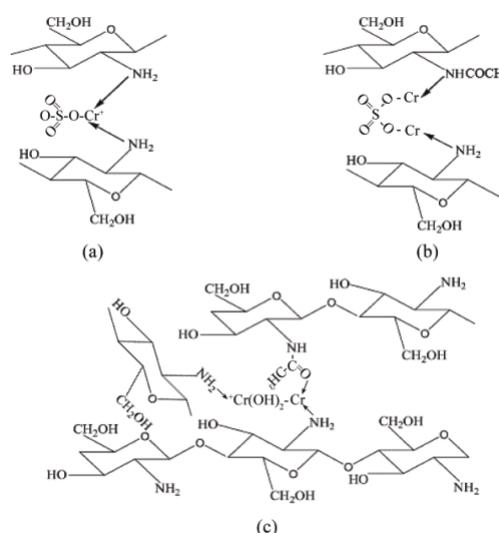


Fig. 4 The possible structure of CTS-Cr(III)

Considering the insolubility of resulting complex in common acids, which would be explained the reticulate structure of the product; and in view of the analytical result of FT-IR, the sketch structure of resulting complex would be deduced as Fig. 4.

Fig. 4 indicated that Cr(III) would chelate with two -NH₂ of two CTS main chains (Fig. 4(a)), or with sulfate ion and -NH₂ or might also -NHCOCH₃ (Fig. 4(b)). According to the insolubility of the product in acidic solution, the mode of complexation with multi-chelating points and multi-nuclear might widely exist in the resultant (Fig. 4(c)).

4 Conclusions

According to the nitrogen content and ICP analyses of the complex, factors affecting the complexation reaction would be arranged in a decreasing order according to their abilities of the effect on it: concentration of K₂HPO₄, reactants ratio, reaction time, reaction temperature and pH value.

In the experimental range, Cr(III) content of the complex is enhanced with the increase of the K₂HPO₄ concentration, n(Cr₂(SO₄)₃):n(structural units of chitosan),

reaction pH and reaction time. The best coordination reaction condition is $n(\text{Cr(III)}):n(\text{structural units of chitosan}) = 2:1$ (namely, $n(\text{Cr}_2(\text{SO}_4)_3):n(\text{structural units of chitosan}) = 1:1$), $\text{pH} = 4.5$, K_2HPO_4 0.10 mol/L, temperature 50°C , and time 8 h.

FT-IR analysis indicated that after the addition of K_2HPO_4 , the electronic density of $-\text{NH}_2$ and $-\text{OH}$ might be increased, and might show higher affinity to metal ions and in turn facilitate the coordination reaction. According to the FT-IR spectra of chitosan-Cr(III), O-H and N-H groups in chitosan might involve in the coordination with Cr(III).

TG profiles of pyrolysis for chitosan and chitosan-Cr(III) demonstrated the better water combining ability of the latter, with the water content increases from 3.5% to 7% ~ 14%. The complex presents two degradation steps, with main weight-losing temperature centered at $210 \sim 220^\circ\text{C}$ and $260 \sim 285^\circ\text{C}$. The demolish of inter- and intra-molecular hydrogen bond of chitosan due to the interaction of active groups of chitosan with Cr(III) also lower the structural regularity and its thermal stability.

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