Antibacterial activity of carboxymethyl chitosan dialdehyde starch Schiff base and its metal complex

Jinyu Ouyang (2818813124@qq.com)
Guilin University of Technology
Zhenbiao Li
Guilin University of Technology
Jincheng Miao
Guilin University of Technology
Yongtao Wang
Guilin University of Technology
Langrong Hu
Guilin University of Technology
Xiaojuan Wang
Guilin University of Technology

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Abstract

Carboxymethyl chitosan dialdehyde starch Schiff base (CMCDAS) and its metal complexes were synthesized by corn starch (St), sodium periodate, carboxymethyl chitosan and metal ions (copper, zinc, nickel, silver), and were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), thermogravimetric analyzer (TGA), energy dispersive spectroscopy (EDS) and X-ray powder diffraction (XRD). The antibacterial activities of CMCDAS against *E. coli* and *S. aureus* increased according with its increasing nitrogen content, and the best minimum inhibitory concentrations (MIC) to *E. coli* and *S. aureus* were 30 mg/mL, respectively. Furthermore, the minimum inhibitory concentrations (MIC) of the metal Complexes (copper, nickel, silver, and zinc) against *S. aureus* were 7.50 mg/mL, 30 mg/mL, 30 mg/mL, and 1.88 mg/mL, respectively; and against *E. coli* were 7.50 mg/mL, 15 mg/mL, 15 mg/mL, and 0.94 mg/mL, respectively.

Introduction

Chitosan was a kind of biodegradable, biocompatible, non-toxic polymer composed of β-(1–4) glucosamine, which always exhibited biocompatibility, anti-inflammatory, antibacterial, anti-tumor activity and anti-cancer properties[1], thereinto, antibacterial activity was the most important properties. And then, chitosan was applied in medicine, biotechnology, food and gene therapy[2] according to its action on gram-positive and gram-negative bacteria. The pyrazole substituted chitosan Schiff base derivatives chitosan[3] was synthesized by heterocyclic pyrazole, 2-acetylthiophene, 2-acetylfuran and 3-acetylpyridine, and exhibited good inhibitory effect on gram-negative bacteria, gram-positive bacteria and fungi, and was consistent with the green antibacterial materials development trend[4].

Dialdehyde starch (DAS) was synthesized by the selective oxidation starch, exhibited antiviral activity [5, 6]and direct drug attachment, so it would be a good drug carrier material[7]. The aldehyde groups gave DAS the antibacterial activity, could irreversibly destroy the bacterial cell wall and plasma membrane, and then led to the decay and death of bacterial cells[8]. Dialdehyde *β*-cyclodextrin with different oxidation degrees[9] were synthesized by *β*-cyclodextrin, sodium periodate and sodium alginate, and their antibacterial properties against *E. coli, S. aureus* and *B. subtilis* were significant.

Metal and its complexes could store oxygen and were used in disinfection, bacteriostasis and other aspects[10] through destroying the cell membrane protein. For example, Cu(II), Ag(II), Zn(II), Co(II) and their complexes showed good inhibitory effects on *E. coli*, *S. aureus*, *Salmonella* and *B. subtilis*[11, 12]. Azo Schiff base ligand 2-hydroxy-3-methoxy-5-(tolyldiazenyl) benzalde-hyde oxime[13], synthesized by 2-hydroxy-3-methoxy-5-(p-tolyldiazenyl) benzaldehyde oxime and 2-hydroxy-3-methoxy-5-(tolyldiazenyl) benzaldehyde, and its metal complexes [Ni(II), Cu(II), Zn(II)] showed best bacteriostatic effect on gram-positive and gram-negative. Thiosemicarbazide, 3-methoxy-2-hydroxybenzaldehyde[14] and their metal complexes [Co(II), Ni(II), Cu(II), Zn(II)] also showed good considerable antifungal activity on *A. flavus* and *C. albicans*.

Metal ions complexes of Schiff base ligand derived from chitosan[15] could permeate the bacterial cell membrane efficiently, and then easily prevent or inhibit the bacterial growth. In addition, the metal ions could easily combine with oxygen in organisms, and then denatured proteins or enzymes [16, 17] through effect on the synthesis of amino acids, proteins, lipoproteins and coenzymes according with the formation of stable complexes. The antibacterial activity of chitosan Schiff base metal complexes [Cu(II)[18, 19], Ag (II)[20, 21], Zn(II)[22]] against *E. coli*, *S. aureus*, *salmonella* and *B. subtilis* was significantly higher than that of free ligand, and increased with the increase of the minimum concentration[23, 24]. A novel water-soluble isoniazid grafted O-carboxymethyl chitosan Schiff base[25] was synthesized by chitosan, 1,3-diphenyl-1, 3-propanedione and mono chloroacetic acid, and then its metal complexes [Co(II), Cu(II), Zn(II)] was obtained, moreover, the results of antibacterial activity tests showed that the metal complexes exhibited better inhibitory effect on *P. aeruginosa* and *S. aureus*. A new class of organic-inorganic hybrid material[26] was synthesized by O-Carboxymethyl chitosan Schiffs base, (3 -Aminopropyl) triethoxysilane, 2-hydroxy-1-naphthaldehyde and nano-silica, and then its Cu(II) metal complexes was obtained. At the same time, the results of antibacterial activity tests showed that nano-hybrid material exhibited better inhibitory effect on gram-positive (*E. coli*) and gram-negative (*B. subtilis*) bacteria.

Carboxymethyl chitosan dialdehyde starch Schiff base was synthesized by crosslinking reaction between dialdehyde starch and carboxymethyl chitosan, and then was coordinated by metal ions (Cu[II], Zn[II], Ni[II], Ag[I]). All products were characterized by XRD, SEM, EDS, TGA and FT-IR. The antibacterial activity of carboxymethyl chitosan dialdehyde starch Schiff base and its metal complexes against *E. coli* and *S. aureus* was tested, and the results showed that (1) carboxymethyl chitosan dialdehyde starch Schiff base and its metal complexes represented obvious antibacterial activity; (2) the antibacterial activity of the metal complexes was higher than that of carboxymethyl chitosan dialdehyde starch Schiff base.

Materials And Methods

Materials and Instruments

Corn starch (Food Grade) with M_w $1\times10^5\sim1\times10^6$ was purchased from Longkou Wugu Food Co., Ltd. (China), carboxymethyl chitosan (GDMCC) from Shanghai Yien Chemical Technology Co., LTD. (China), sodium periodate (AR, S817518-100 g) from Shanghai Macklin Biochemical Co., Ltd. (China), *E. coli* (GDMCC 1.176) and *S. aureus* (GDMCC 1.1220) from Guangdong Institute of Microbiology (China), silver nitrate (AR) from Sinopagic Chemical Reagent Co., LTD. (China), copper nitrate (AR) from Kelon Chemical Reagent Factory of Chengdu (China), and all other chemicals were of analytical reagents grades and purchased from Xilong Science Co., Ltd..

Fourier transform infrared spectrometer (FT-IR, Nexus 470, Nicolet, USA), X-ray powder diffractometer (XRD, Pert Powder, PANalytical B.V., Netherlands), field emission scanning electron microscope (SEM, Hitachi 5V5000, Hitachi Hi-Tech Co., Ltd.), nitrogen analyzer (KDN-08C(04C), Shanghai Huarui Instrument Co., Ltd.), and thermal gravimetric analyzer (TGA, SDT Q600) were used to characterize CMCDAS. Vertical pressure steam sterilization pot (LDZX-50KBS, Shanghai Shenan Medical Device Factory) and microplate reader (lMark, Bio-Red Laboratories, Inc) were used to determine the antibacterial activity.

Synthesis of dialdehyde starch (DAS)

Dialdehyde starch (DAS) was synthesized by the selective oxidation of corn starch solution with a certain amount of sodium periodate in a stirred three-neck flask at pH = 3.5 at 25 ºC for 6 h [27], and then the content of aldehydes in DAS were determined by alkali loss method.

Synthesis of carboxymethyl chitosan dialdehyde starch Schiff base

Carboxymethyl chitosan dialdehyde starch Schiff base was synthesized through dialdehyde starch and carboxymethyl chitosan in the isopropanol/water mixture (4:1) at 50 ºC for 12 h, and then the sample was washed with distilled water and methanol successively, filtered, and dried at 50 ºC for 2 h in a vacuum drying oven. The nitrogen content of chitosan-dialdehyde starch Schiff base was measured by Kjeldahlmethod[28] and calculated by the following equation:

$$\mathrm{N\%} = \frac{(V - V_0) \times N_0 \times 0.014 \times 100}{W}$$

Where, V was the volume of sulfuric acid standard solution used for sample determination, (mL); V_0 was the volume of sulfuric acid standard solution used for blank determination (mL); N_0 is the equivalent concentration of H_2SO_4; W was the sample weight (g).

Synthesis of carboxymethyl chitosan dialdehyde starch Schiff base metal complexes

Carboxymethyl chitosan dialdehyde starch Schiff alkali metal complex was prepared by reaction of carboxymethyl chitosan dialdehyde starch with 0.05 mol/L metal salt solution (copper sulfate, silver nitrate, nickel nitrate and zinc nitrate) in a beaker at 25℃ for 6 h [27], and then filtered and dried at 50 ºC for 2 h in a vacuum drying oven. The adsorption capacity of copper[II], nickel[II] and zinc[II] was determined by EDTA titration, and silver[I] was titrated by potentiometric titration with potassium bromide. The adsorption capacity was calculated by the following equation:

$$\mathrm{Q} = \frac{\left(C_i - C_t\right) V_1}{m}$$

Where, Q was the adsorption capacity (mmoL/g); C_i was the initial ion concentration (mmol/L); C_t was the residual ion concentration (mmol/L); V_1 was the liquid volume (mL); m was the adsorbent mass (g).

Antibacterial activity

Minimum inhibitory concentration (MIC) referred to the minimum concentration of drugs that could inhibit the growth of pathogenic bacteria in the culture medium after 18 ~ 24 h of bacteria culture in vitro, which was an important index to measure the antibacterial activity. Minimum inhibitory concentration (MIC) was separated and determined by Luria-Bertani broth dilution method after culture, and the required bacterial suspension was about 10^8~10^9 CFU/mL[29]. Serially diluted CMCDAS in the final concentration of 0 ~ 5 mg/mL was mixed with the inoculum and Luria-Bertani broth with the Luria-Bertani broth mixture without Schiff base cultured at 37 ºC for 24 h as the blank control[30]. OD_{630nm} refers to the absorbance of a solution at 630 nm.

X-ray powder diffraction

The structure of samples was characterized by XRD with Ni-filtered Cu-$K_α$ radiation at 40 kV and 40 mA. The scattered radiation was detected in the angular range of 10 ~ 80º (2θ) at the wavelength was $1.5406×10^{-10}$ m.

Fourier transform infrared spectroscopy

The samples were prepared by the potassium bromide tableting method, and then tested with the spectra being recorded from 4000 to 400 cm^{-1} with 32-scans at room temperature and the resolution of 4 cm^{-1}.

Thermo gravimetric analyzer

Thermogravimetric analysis of St, DAS and CMCDAS were performed at a 10 ºC/min heating rate in the range from 25 ºC to 800 ºC in the atmosphere of nitrogen.

Scanning electron microscope

The morphology of St, DAS and CMCDAS was characterized by the scanning electron microscope at the voltage of 5 kV. The sample was fixed on the metal sample platform with conductive adhesive, and the surface was sprayed with gold.

Energy dispersion microscope

The element characterization of Schiff alkali metal complex of chitosan dialdehyde starch was carried out under 15 kV voltage. The sample was fixed on the metal sample platform with conductive adhesive, and the surface was sprayed with gold.

Results And Discussion

X-ray powder diffraction

The XRD patterns of St, DAS and CMCDAS were shown in Fig. 1. The diffraction peaks of corn starch appeared at 15º, 17º, 18º and 23º, which belonged to typical A-type crystal structure. The patterns of DAS showed only one amorphous diffraction peak at 21º, which suggested that the oxidation of sodium periodate destroyed the intermolecular/intramolecular hydrogen bonding and the helical molecular through the transformation of C_2-C_3 bond into the aldehyde group[31]. The characteristics diffraction peak of CMCDAS was offset, irregularly broadened and slightly weakened strength than that of DAS, which indicated that the crosslink of carboxymethyl chitosan and dialdehyde starch was not only restricted the molecular movement of chitosan chain, but also destroyed the crystalline state of chitosan[32]. As a result, the oxidation and amination of starch could seriously destroy the crystalline area of starch and obviously decrease the crystallinity.

Fourier transform infrared spectroscopy

The FT-IR spectra of St, DAS and CMCDAS were shown in Fig. 2. The major peaks at 3428 cm^{-1}, 2932 cm^{-1} and 1642 cm^{-1} in the spectrum of corn starch were always attributed to the hydroxyl groups, $-CH_2$ and the amorphous region water respectively, while the distinct peaks at 1738 cm^{-1} and 878 cm^{-1} of DAS were attributed to C = O and the hemiacetal of DAS[33–35], which were conforming with previous works of corn starch and DAS. From the spectrum of CMCDAS, the peaks at 1738 cm^{-1} and 878 cm^{-1} disappeared, while the peaks at 1629 cm^{-1}, 1324 cm^{-1} and 1412 cm^{-1} appeared which were attributed to the stretching vibration peak of C = N, the out-of-plane bending vibration of O-H and C = O stretching vibration[36]. Therefore, the carboxymethyl chitosan and dialdehyde starch had been successfully crosslinked.

Thermogravimetric analyzer

There were two thermal degradation stages in the thermogravimetric curve of CMCDAS in Fig. 3. The first stage below 120 ºC was always attributed to the evaporation of bound water and adsorbed water with a small weight loss of 4.5%; and the second stage, with weight loss of 43.0% from 120 to 400 ºC, was always attributed to the decomposition of pyranose and the Schiff base structure containing unsaturated bonds and nitrogen atoms with lower energy[37, 38]. At this stage, the maximum decomposition rate temperature of carboxymethyl chitosan dialdehyde starch Schiff base was 284.5 ℃, and the maximum decomposition rate temperature of dialdehyde starch was 300.9 ℃, which was slightly lower than that of starch (T_{max}=314.6 ℃). These results indicated that Schiff base and dialdehyde starch were more easily decomposed by heating than original starch, which might be attributed to the destroyed spiral molecular structure and the changed crystalline structure of starch through by oxidation and amination reaction. At 800 ℃, the residual amount of CMCDAS was 32.9%, which was higher than that of corn starch (14.3%) and dialahyde starch (8.5%).

Scanning electron microscopy

According to the SEM images of St (A), DAS (B) and CMCDAS (C and D) in Fig. 4, the surface of DAS was different with the round or irregular corn starch (Figure A), which might be caused by the collapsed or completely deformed (Figure B), the surface of CMCDAS (Figure C and D) was irregular and obvious cross-linked which was caused by the reaction of dialdehyde starch and carboxymethyl chitosan. The above phenomenon indicated that oxidation and cross-linking reaction would gradually destroy the corn starch granules structure, which was consistent with the XRD results.

Adsorption of metal ions on carboxymethyl chitosan dialdehyde starch Schiff base

Chitosan had excellent coordination ability for metal ions according to its C6 primary hydroxyl group, C3 secondary hydroxyl group and C2 amino group, and the Schiff base had excellent coordination ability and special biological activity due to its high density electron cloud formed by lone electron pair. Therefore, the carboxymethyl chitosan dialdehyde starch Schiff base (CMCDAS) would obtain good adsorption effect on metal ions according to hydrogen bonding, electrostatic action, coordination adsorption or the above ways of synergy. The adsorption capacity of carboxymethyl chitosan dialdehyde starch Schiff base on metal ions was shown in Table 1 and Fig. 5, the absorption quantity of copper, nickel, silver and zinc was 2.534 mmol/g, 2.265 mmol/g, 2.2 mmol/g and 1.386 mmol/g, respectively. As the results, the adsorption capacity on CMCDAS was basically conforming to Irving-Williams sequence which might be attributed to chelation and ion exchange based on the hydroxyl groups of polysaccharide and amino group[39].

Table 1
Adsorption capacity of carboxymethyl chitosan dialdehyde starch Schiff base on metal ions

Adsorbed metal ions	Cu	Zn	Ni	Ag
The adsorption quantity (mmol/g)	2.534	1.386	2.265	2.2
Normalized mass (%)	17.06	16.51	17.57	49.03
atomic (%)	4.24	5.37	4.90	10.98

Antibacterial activity of carboxymethyl chitosan dialdehyde starch Schiff base

As shown in Table 2 and Fig. 6, the minimum inhibitory concentrations of carboxymethyl chitosan dialdehyde starch Schiff base (N = 4.51%, N = 4.85%, N = 5.71%) against *E. coli* and *S. aureus* were > 120mg/mL, 120mg/mL and 30mg/mL, respectively. Carboxymethyl chitosan dialdehyde starch Schiff base had obvious antibacterial activity against *E. coli* and *S. aureus*, and the antibacterial effect of carboxymethyl chitosan dialdehyde starch Schiff base increased with the increase of nitrogen content.

Table 2
Minimum inhibitory concentrations of *E. coli* and *S. aureus* by carboxymethyl chitosan dialdehyde starch Schiff bases with different nitrogen contents

Carboxymethyl chitosan dialdehyde starch Schiff base with different nitrogen content	Minimum inhibitory concentration (mg/mL)	
	E. coli	*S. aureus*
N = 4.51%	> 120	> 120
N = 4.85%	120	120
N = 5.71%	30	30

Antibacterial activity of carboxymethyl chitosan dialdehyde starch Schiff base metal complex

The metal complexes of carboxymethyl chitosan dialdehyde starch Schiff base (N = 4.85%) were synthesized and their minimum antibacterial concentration were measured (Fig. 7 and Table 3). The minimum inhibitory concentrations of carboxymethyl chitosan dialdehyde starch Schiff base metal complexes (Ag, Cu, Zn, Ni) against *E. coli* were 0.94 mg/mL, 7.50 mg/mL, 15 mg/mL and 15 mg/mL, respectively, which were all higher than those of CMCDAS (120 mg/mL). The minimum inhibitory concentrations of carboxymethyl chitosan dialdehyde starch schiff base metal complexes (Ag, Cu, Zn, Ni) against *S. aureus* were 1.88 mg/mL, 7.50 mg/mL, 15 mg/mL and 15 mg/mL, respectively, which were all higher than those of CMCDAS (120 mg/mL). It was found that: (1) the schiff base metal complex of CMCDAS had better antibacterial activity than the schiff base, and the silver complex had the best antibacterial activity; (2) the metal complexes (Ag, Zn, Ni) had better antibacterial effect on *E. coli* than *S. aureus*, but the antibacterial effect against *E. coli* of copper ion complex was less than that against *S. aureus*.

The antibacterial activity of CMCDAS was enhanced by the chelated metal ions according to the increasing penetrability of metal atoms in microbial lipid membrane, which was caused by the ligand orbitals overlap and the charge sharing between donor groups and positive charge of metal ions[40].

Table 3
Minimum inhibitory concentrations of *E. coli* and *S. aureus* for different carboxymethyl chitosan dialdehyde starch Schiff base metal complexes

Carboxymethyl chitosan dialdehyde starch Schiff base and its metal complexes	**Minimum inhibitory concentration (mg/mL)**	
	E. coli	***S. aureus***
CMCDAS (N = 4.85%)	120	120
Copper ion complex	7.50	7.50
Zinc ion complex	15	30
Nickel ion complex	15	30
Silver ion complex	0.94	1.88

Conclusion

Carboxymethyl chitosan dialdehyde starch Schiff base and its metal complexes were synthesized by crosslinking reaction and chelating reaction based on dialdehyde starch, carboxymethyl chitosan and metal ions, and then characterized by XRD, SEM, TGA and FT-IR.

The antibacterial activities of carboxymethyl chitosan dialdehyde starch Schiff base and its metal complexes against *E. coli* and *S. aureus* were determined. The minimum inhibitory concentrations of carboxymethyl chitosan dialdehyde starch Schiff base metal complexes (Ag, Cu, Zn, Ni) against *E. coli* were 0.94 mg/mL, 7.50 mg/mL, 15 mg/mL and 15 mg/mL, respectively, which were all higher than those of CMCDAS (120 mg/mL), and then, the minimum inhibitory concentrations of carboxymethyl chitosan dialdehyde starch Schiff base metal complexes (Ag, Cu, Zn, Ni) against *S. aureus* were 1.88 mg/mL, 7.50 mg/mL, 15 mg/mL and 15 mg/mL, respectively, which were all higher than those of CMCDAS (120 mg/mL). It was found that: (1) the Schiff base metal complex of CMCDAS had better antibacterial activity than the Schiff base, and the silver complex had the best antibacterial activity; (2) the metal complexes (Ag, Zn, Ni) had better antibacterial effect on *E. coli* than *S. aureus*, but the antibacterial effect against *E. coli* of copper ion complex was less than that against *S. aureus*.

From the results, the carboxymethyl chitosan dialdehyde starch Schiff base metal complexes displayed better antibacterial effect against *E. coli* and *S. aureus* than carboxymethyl chitosan dialdehyde starch Schiff base, which was caused by the ligand orbitals overlap and the charge sharing between donor groups and positive charge of metal ions according to the increasing penetrability of metal atoms in microbial lipid membrane.

Declarations

Declaration of competing interest

Authors hereby declare that no conflicts of interest exist

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Figures

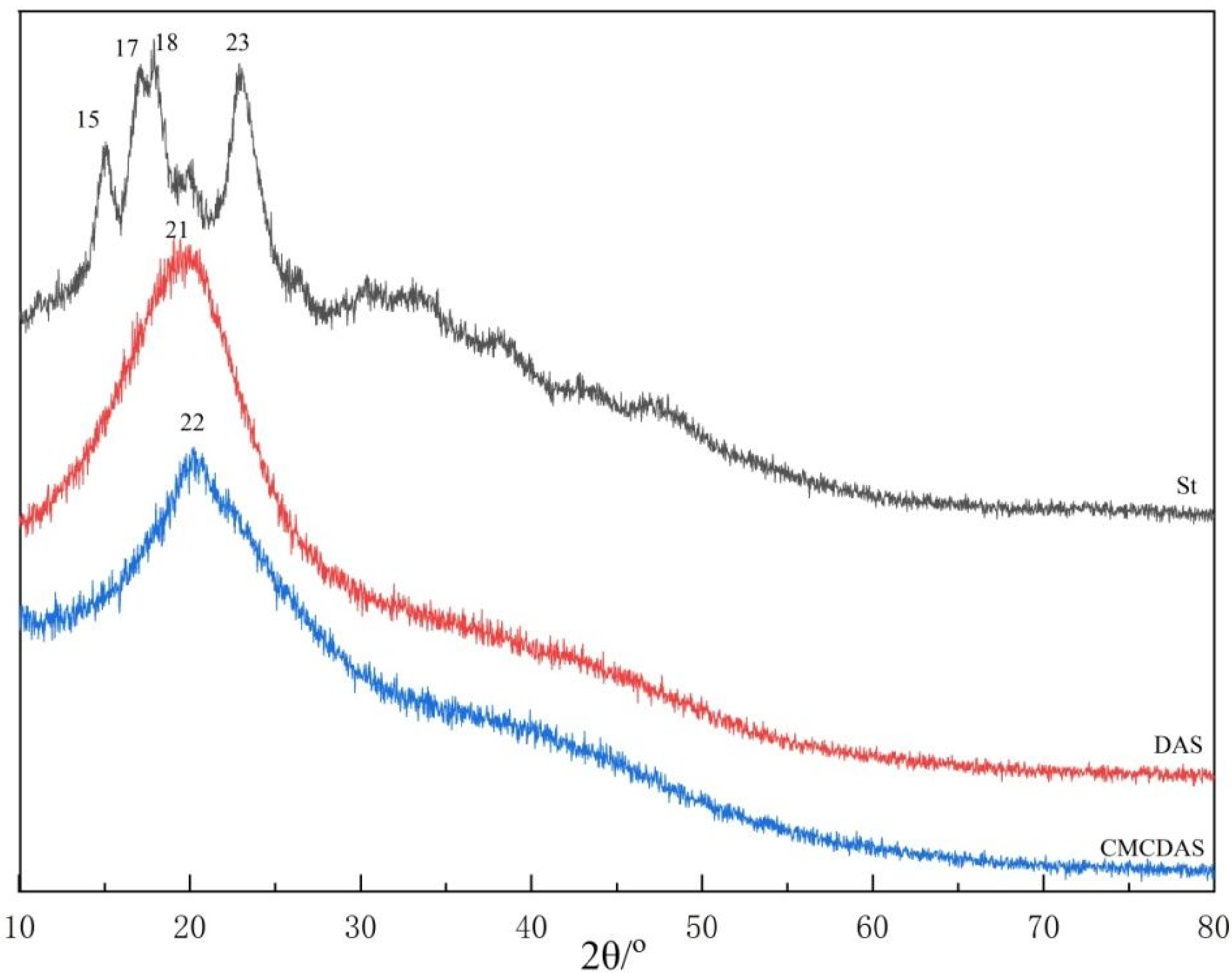

Figure 1

The power X-ray diffraction patterns of corn starch (St), dialdehyde starch (DAS) and carboxymethyl chitosan dialdehyde starch (CMCDAS)

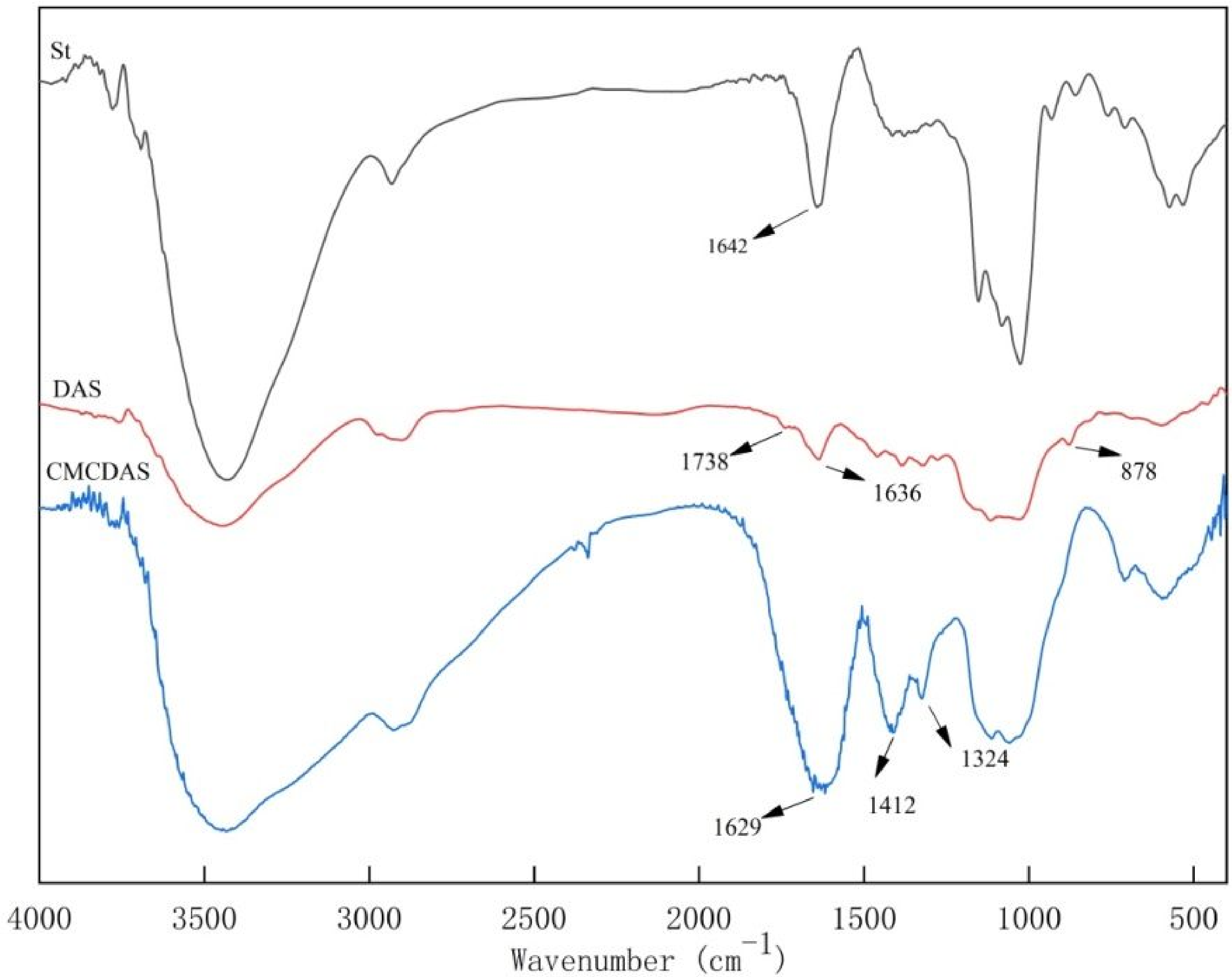

Figure 2

The FT-IR spectra of corn starch (St), dialdehyde starch (DAS) and carboxymethyl chitosan dialdehyde starch (CMCDAS)

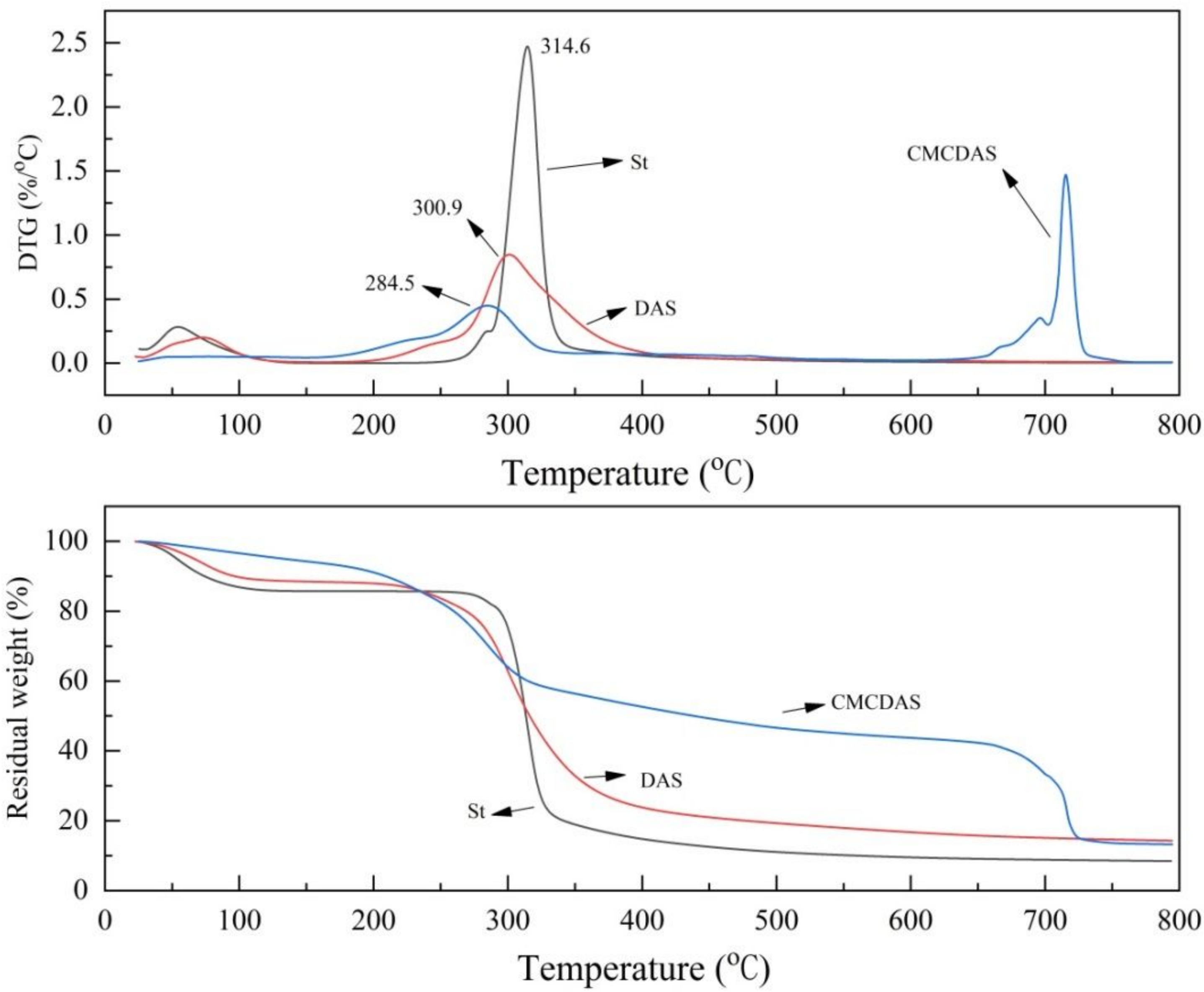

Figure 3

Thermogravimetric curves of corn starch (St), dialdehyde starch (DAS) and carboxymethyl chitosan dialdehyde starch (CMCDAS)

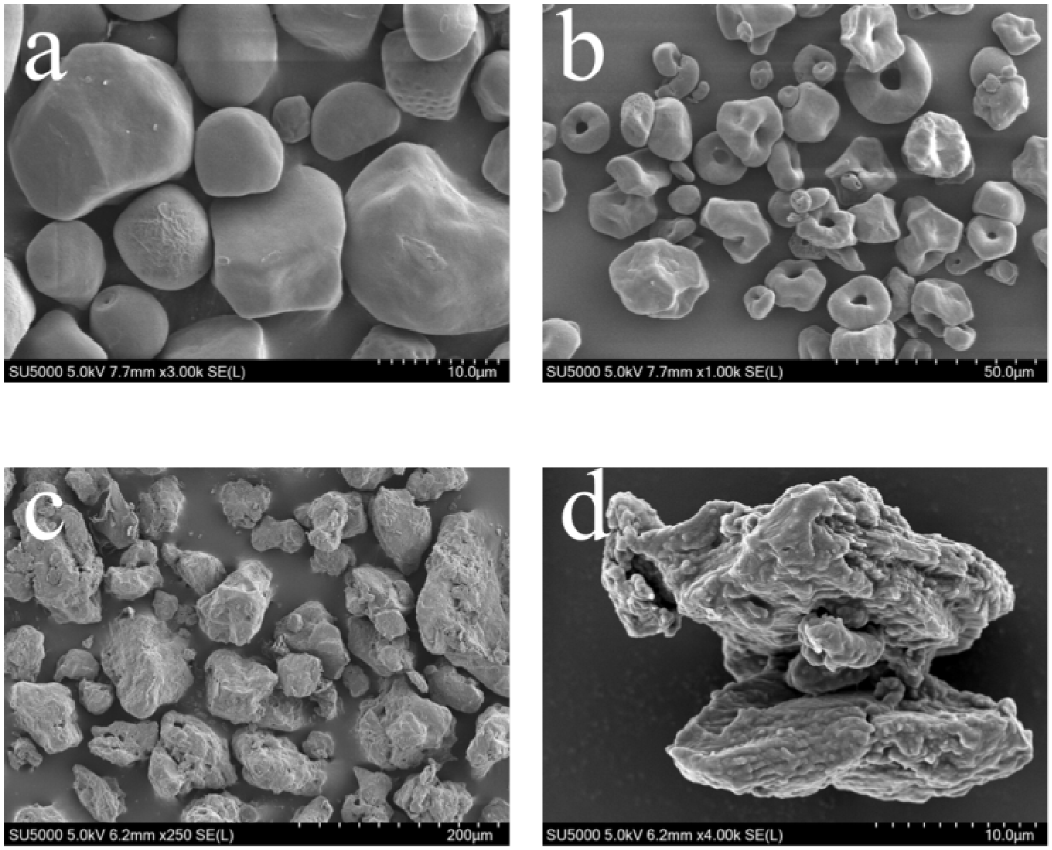

Figure 4

The SEM images of (a) corn starch, (b) dialdehyde starch, (c, d) carboxymethyl chitosan dialdehyde starch

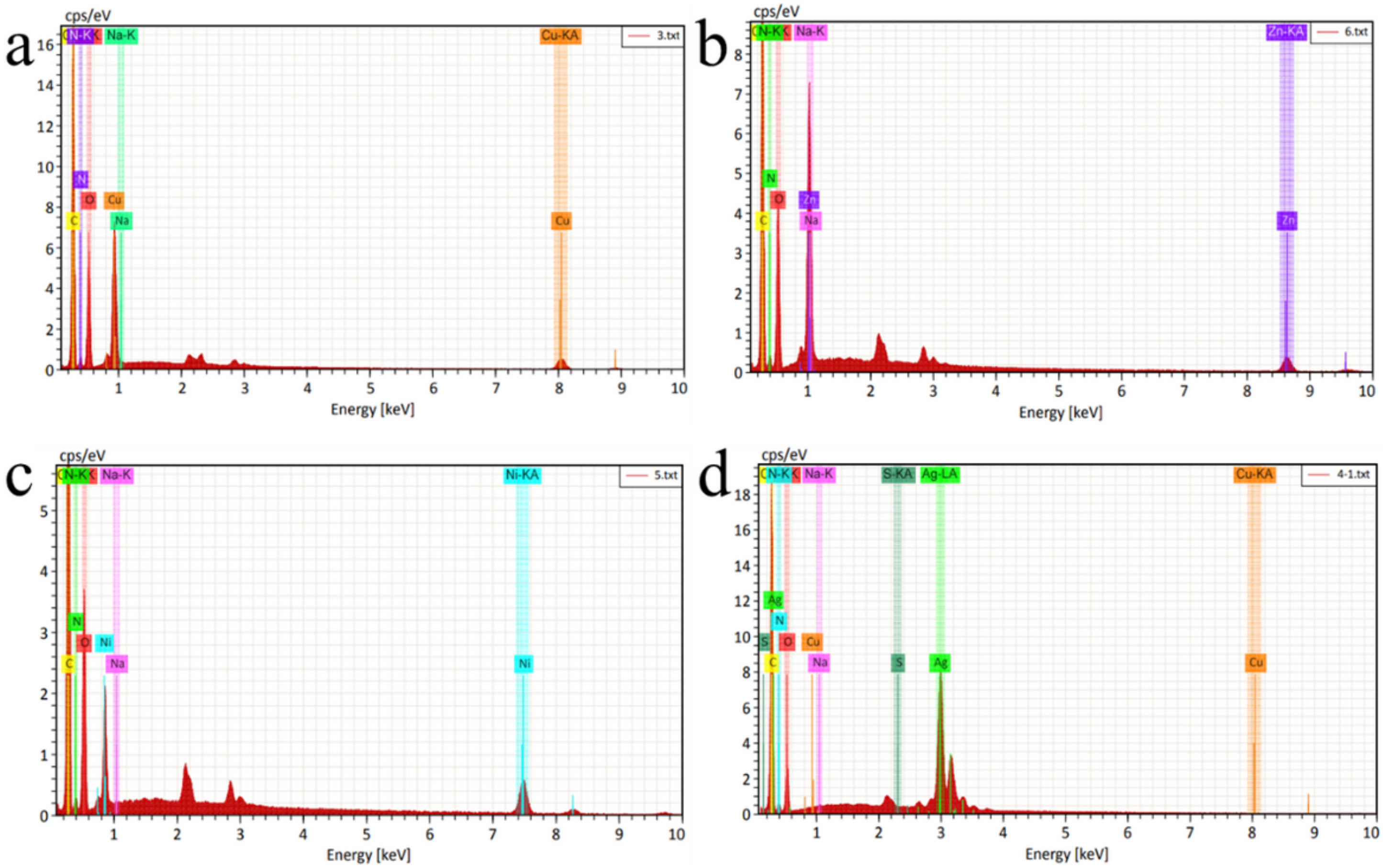

Figure 5

The EDS spectrum of carboxymethyl chitosan dialdehyde starch Schiff base metal complex (a) CMCDAS-Cu, (b) CMCDAS-Zn, (c) CMCDAS-Ni, (d) CMCDAS-Ag

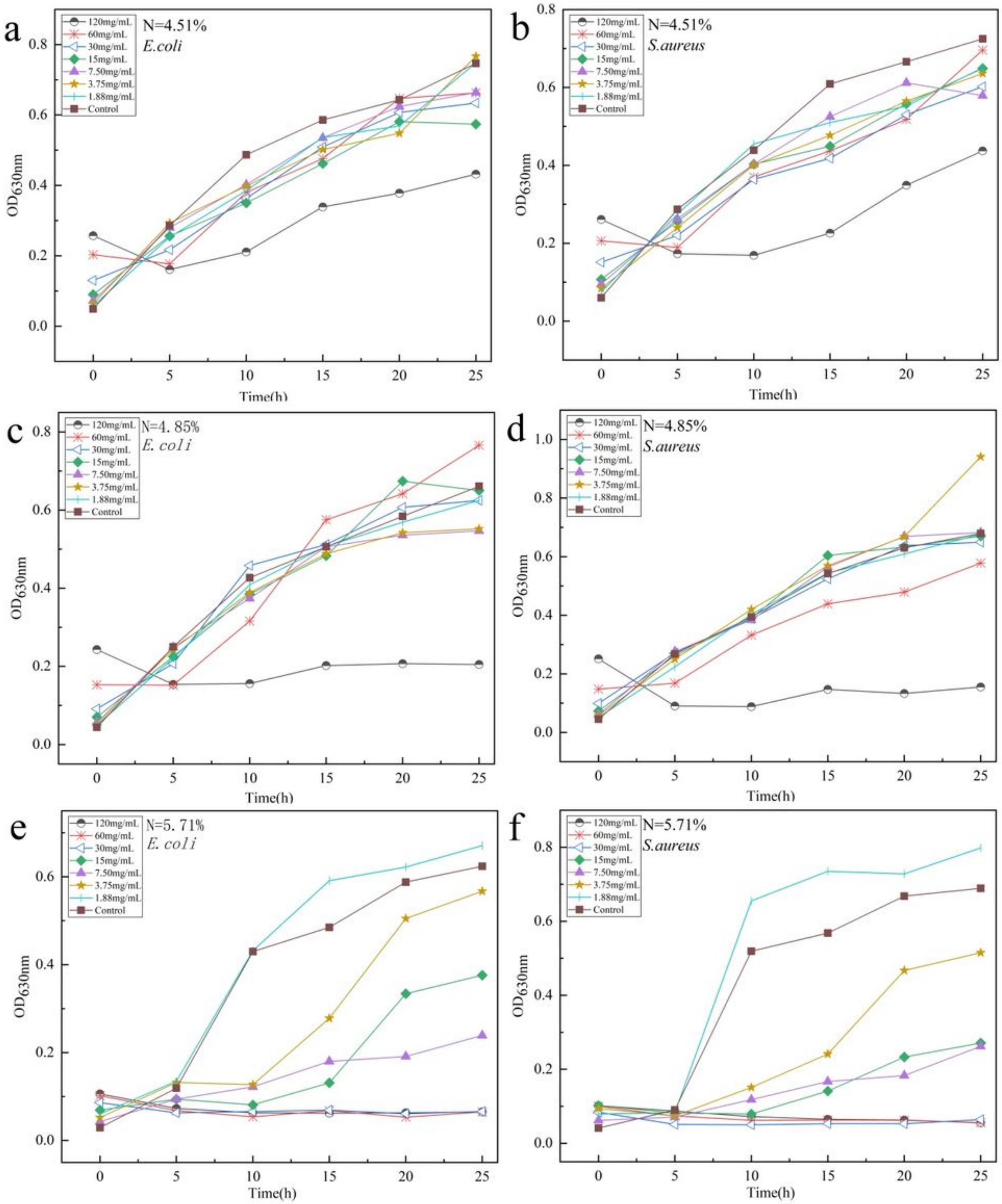

Figure 6

E. coli and *S. aureus* growth curves at different concentrations of carboxymethyl chitosan dialdehyde starch

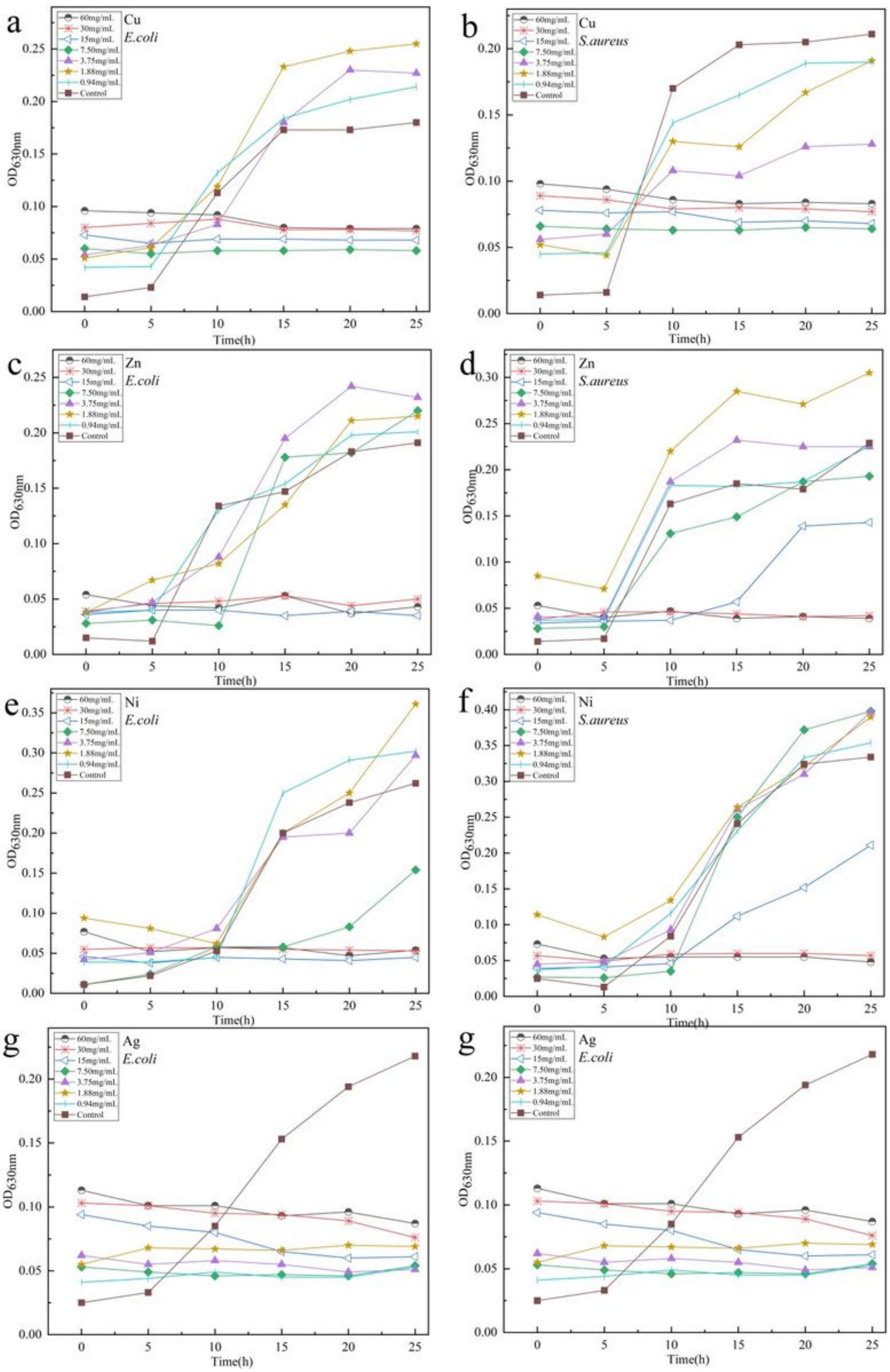

Figure 7

E. coli and *S. aureus* growth curves at different concentrations of carboxymethyl chitosan dialdehyde starch schiff base metal complex