Preparation of Cationic Chitosan and Its Application as a Multifunctional Chemical Additive

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ABSTRACT

The cationic chitosan is prepared in this paper. This kind of cationic chitosan is a good retention aid for bleached hardwood pulp, the filler retention increased by 33.0% when the cationic chitosan (DS=1.27) dosage was 0.05%. Because many of the materials used in papermaking process are excellent microbiological nutrients, these nutrients will result in the growth of bacteria; uncontrolled growth of bacteria and fungi in the papermaking process adversely affects machine runnability. According to the standard methods of microbe growth inhibition test, cell counting was conducted after proper cultivated time. This paper explored the factors that affecting the cationic chitosan's antibacterial effect.

KEYWORDS
Cationic chitosan; preparation; retention; microbial contamination; cell counting; antibacterial effect; multifunctional chemical

INTRODUCTION

Chitosan has a wide scale of applications in the papermaking industry [1-3], but it only dissolves in acid and is restricted within narrow limits. And at the same time, papermaking operation environment is changing from acidity to neutrality and alkalescency nowadays; it is evident that it doesn't adapt the development. An yu-qin, Cao li-yun, Yang qiang have done a lot of work on the synthesis of chitosan and starch or acryl amide and their applications in the papermaking process [4-7]. Cationic chitosan has been widely used in the wastewater treatment and has a good effect [8-11]. But the utilization of cationic chitosan as a retention aid in the papermaking industry hasn't been reported. According to our research, the cationic chitosan has more positive charge, so the bonding ability between fibers and filler retention are improved greatly.

Microorganisms cause various problems in the papermaking process. Slime deposits that break loose can cause defects, holes or even sheet breaks [12]. This can have considerable impacts on the production and on paper quality, which is a key driver for printing & writing grades, tissue & towel grades, and mechanical grades, like newsprint. A major concern in board grades, especially in closed board mills, is the foul odor caused by anaerobic bacteria producing volatile fatty acid or hydrogen sulphide [13]. Across all grades, coatings and additives spoilage can be another costly result of microbial activity [14].

While most papermakers are aware of these issues, the pressure to reduce overall production costs has pushed many mills to cut the cost associated with microbial control programs [15-17]. The use of oxidizing biocides for slime control has allowed papermakers to reduce microbial deposit control costs and without negatively affecting runnability, but they can cause serious corrosion on the surface of paper machine mainframe, at the same time they are not environmental friendly. So we develop a novel chemical that has good antibacterial effect and not have adverse effect like the oxidizing biocides.

MATERIALS AND METHODS

Materials

Chitosan: commercial product, provided by one company in Shandong province
Etherifying agent: provided by one company in Shandong province
Bleached hardwood pulp: provided by one paper mill in Shandong province
Cationic chitosan: prepared by ourselves
E. coli: generously supplied by Faculty of Food Science and Bioengineering
Aspergillus's Niger: generously supplied by Faculty of Food Science and Bioengineering
Saccharomyces Cerevisiae: generously supplied by Faculty of Food Science and Bioengineering
Culture Medium：Brewis Peptone Culture Medium, Czapek Culture Medium, Malt Juice Culture Medium
Yeast Extract：Biochemical reagent, Tianjin Yingbo Chemical Reagent Co. Ltd
Peptone：Biochemical Reagent, Tianjin Yingbo Chemical Reagent Co. Ltd.
Glucose anhydrous: analytical pure, Tianjin Yongda Chemical Reagent Development Center
Agar: Tianjin Zhujiang sanitation material Co. Ltd.
Sodium Chloride: Analytical pure, Tianjin Beifangtianyi Chemical Reagent Co. Ltd.

Methods

Methods of preparing the cationic chitosan

The chitosan mixed with the Etherifying agent in the isopropyl alcohol, and stirred for a period of time at given temperature, and gained the final product. The final product was marinated by ethanol absolute and then filtrated for several times, then vacuum-dried.

Handsheet making

The bleached hardwood pulp with consistency of 0.2% was disintegrated uniformly. Appropriate dosage of cationic chitosan was added. The stock then put into FRANK machine to make handsheet.

Beating degree

Beating degree is measured through the Schopper-Riegler beating degree tester.

Paper physical properties

Determined according to TAPPI standard

Filler retention

Filler retention rate is calculated as the following equation [18]

$$Rt = \frac{0.94 \times (A-C) \times (1-B-D)}{(B-C) \times (1-A-D)} \times 100\%$$

A-ash content of hand sheet
B-ash content of stock
C-ash content of fiber, which is determined by TAPPI standard T413om-80
D-reduce weight after dried at (900±25)℃

Antibacterial experiment

The culture medium was sterilized at 121℃ for 40min. The experiments were carried out in 150ml medium, being inoculated with about 10^6 cells/ml. Cell cultivation was carried out at different condition that is suitable for any cells growth. E. coli was cultured at 36℃ for 24h; Aspergillus's Niger and Saccharomyces cerevisiae were cultured at 28℃ for 72h. All experiments were performed in triplicate. And calculate the antibacterial rate as Eq. (1):

$$X = (E-F)/E \times 100\%. \quad (1)$$

X-antibacterial rate, %

E-average cell counts in the control sample

F-average cell counts in the tested sample

RESULTS AND DISCUSSIONS

Retention aid experiment

Effects of different dosage of cationic chitosan on the drainage and filler retention

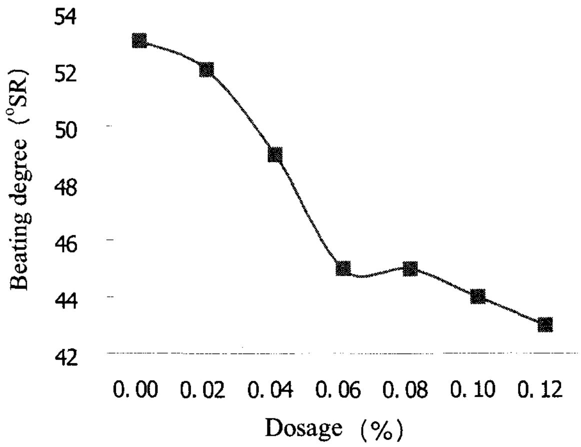

Fig. 1 Effects of different dosage of cationic chitosan on the drainage

The DS of cationic chitosan is 1.27, stock pH 8.0

Table 1 Effects of different dosage of cationic chitosan on the filler retention

Dosage (%)	Basis weight (g/m^2)	Density (g/cm^3)	Breaking length (km)	Tearing index ($mN{\cdot}m^2/g$)	Filler retention (%)
0.00	59.0	0.514	3.28	4.68	32.6
0.05	61.0	0.523	3.22	4.53	65.6
0.10	61.5	0.498	3.18	4.45	73.2
0.15	62.7	0.503	3.04	4.39	80.8
0.20	63.5	0.512	2.89	4.28	84.3

DS of cationic chitosan is 1.27; ash content of fiber is 0.47%; ash content of stock is 19.30%, $CaCO_3$ reduced weight after dried is 5.32%.

Fig. 1 and Table 1 show that the drainage ability and filler retention increase as the dosage of cationic chitosan increases, when the dosage of cationic chitosan is 0.06%, the beating degree decreases 8 °SR; but the strength properties of handsheet decrease. When the dosage of the cationic chitosan is 0.20%, the filler retention is 84.3%, but the reduction of breaking index is 11.9%. Taking every handsheet properties into consideration, the best dosage of cationic chitosan for bleached hardwood pulp is 0.05%, in this situation the filler retention is 65.6%.

Effects of different DS of cationic chitosan on the drainage and filler retention

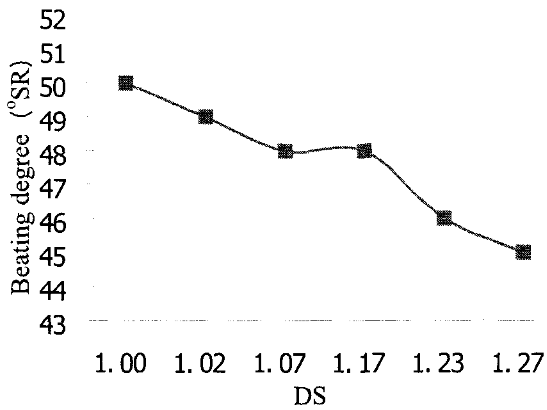

Fig. 2 Effects of different DS of cationic chitosan on the drainage
The dosage of cationic chitosan is 0.06%, stock pH 8.0

Table 2 Effects of different DS of cationic chitosan on the filler retention

DS	Basis weight (g/m²)	Density (g/cm³)	Breaking length (Km)	Tearing index (mN·m²/g)	Filler retention (%)
0.96	60.7	0.516	3.02	4.35	48.7
1.02	61.5	0.512	3.12	4.43	52.8
1.17	61.3	0.509	3.18	4.45	59.3
1.23	60.5	0.498	3.25	4.50	63.2
1.27	61.0	0.523	3.22	4.53	65.6

The dosage of cationic chitosan is 0.05%; other condition is same to Table 1

It can be seen from Fig. 2 that the beating degree (°SR) of stock reduces continually as the DS of cationic chitosan increases, the higher the DS of cationic chitosan is, the more positive charge the cationic chitosan has, so the drainage effect is better. Table 2 shows that the filler retention is improved greatly as the DS of the cationic chitosan increase. The possible explanation for this is the positive charge of cationic chitosan enhanced when the DS increases, so the cationic chitosan can perform a better function in the filler retention. When the DS of cationic chitosan is 1.27, the highest filler retention is 65.6%.

Effects of stock pH on the drainage and filler retention

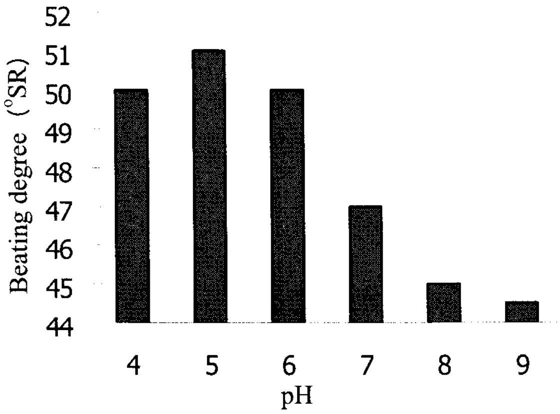

Fig. 3 Effects of stock pH on the drainage

The DS of cationic chitosan is 1.27, the dosage is 0.06%

Table 3 Effects of stock pH on the filler retention

pH	Basis weight (g/m^2)	Density (g/cm^3)	Breaking length (Km)	Tearing index ($mN{\cdot}m^2/g$)	Filler retention (%)
6	60.5	0.518	3.20	4.57	51.7
7	61.2	0.513	3.17	4.48	64.6
8	61.5	0.509	3.18	4.43	65.4
10	62.3	0.523	3.09	4.38	67.3

The dosage of cationic chitosan is 0.05%; the DS of cationic chitosan is 1.27;other condition is same to Table 1

pH can change the dynamic electricity of the stock. Fig. 3 shows that the beating degree of the stock decreases as the pH value increase, when the pH of stock is alkaline, the beating degree is lowest, and the drainage effect is best. Table 3 shows that the higher the pH of the stock, the better the filler retention. When the pH is greater than 7, the filler retention exceeds 64%, so we can deem the cationic chitosan can perform well in the condition of neutrality and alkalescency. Nowadays the papermaking industry follows the tide of these, so it can expect a bright future for a wide use in papermaking industry.

Effects of $Al_2(SO_4)_3$ on the drainage and filler retention

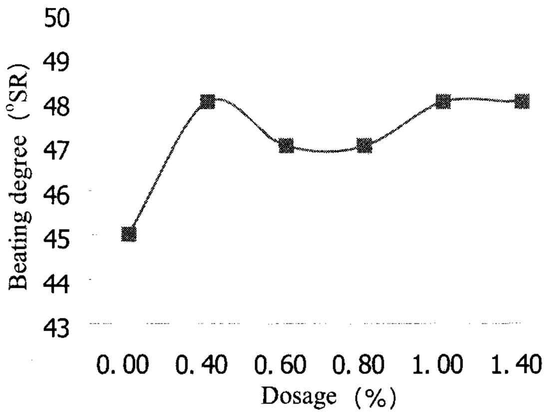

Fig. 4 Effects of $Al_2(SO_4)_3$ on the drainage

The DS of cationic chitosan is 1.27, the dosage is 0.06%

Table 4 Effects of $Al_2(SO_4)_3$ on the filler retention

Dosage (%)	Basis weight (g/m^2)	Density (g/cm^3)	Breaking length (Km)	Tearing index($mN \cdot m^2/g$)	Filler retention (%)
Control	59.0	0.514	3.28	4.68	32.6
0	61.0	0.523	3.22	4.53	65.6
0.5	61.9	0.528	3.15	4.60	66.8
1.0	62.1	0.517	3.14	4.97	68.1
1.5	61.5	0.513	3.01	4.83	66.5

Control is no addition of any chemical in the stock; the dosage of cationic chitosan is 0.05%; the DS of cationic chitosan is 1.27;other condition is same to Table 1

Fig. 4 shows that the addition of $Al_2(SO_4)_3$ has little effect on the drainage. On the contrary, the beating degree will increase. Table 4 shows the filler retention increases at the beginning and then decrease, the tear index has an increase trend. This can be considered the addition of $Al_2(SO_4)_3$ has a good effect on the filler retention and at the same time can improve the paper strength properties. When the dosage of $Al_2(SO_4)_3$ is 1.0% can gain a better paper strength and filler retention.

Antibacterial effect experiment

Antibacterial rate of different concentration of cationic chitosan

Table 5 Antibacterial rate of different concentration of cationic chitosan

Dosage/%	E. Coli		Aspergillus's Niger		S. Cerevisiae	
	cell counts	antibacterial rate	cell counts	antibacterial rate	cell counts	antibacterial rate
Control	1.04×10^6	0	5.8×10^5	0	1.10×10^6	0
0.02	9.0×10^4	91.35%	5.1×10^5	12.07%	4.0×10^5	63.64%
0.04	5.0×10^4	95.19%	4.5×10^5	22.41%	3.3×10^5	70.00%
0.06	2.0×10^4	98.08%	4.0×10^5	31.03%	2.3×10^5	79.09%
0.08	1.0×10^4	99.04%	3.3×10^5	43.10%	2.0×10^5	81.82%
0.10	0	100%	2.7×10^5	53.45%	1.3×10^5	88.18%

Control: no addition of cationic chitosan in the sample. DS of cationic chitosan is 1.23; E. Coli: 24h, 35℃, pH: 7.0; Aspergillus's Niger: 72h, 28℃, pH: 7.0; S. Cerevisiae: 72h, 28℃, pH: 7.0

Table 5 shows the antibacterial ability of cationic chitosan increases as the concentration rise. Because more cationic chitosan can wrap the bacterial and form a tight membrane on the surface, there will be no nutrition provision for the bacterial growth, and in this way we can achieve the antibacterial goal. Cationic chitosan has a good effect on the E. Coli. and S. Cerevisiae, but its effect for the Aspergillus's Niger is just to a certain extent and cannot completely control its growth. In our experiment, we choose cationic chitosan's concentration 0.06% for E. Coli, 0.10% for Aspergillus's Niger and S. Cerevisiae.

Antibacterial rate of different substitute degree of cationic chitosan

Table 6 Antibacterial rate of different substitute degree of cationic chitosan

DS	E. Coli		Aspergillus's Niger		S. Cerevisiae	
	cell counts	antibacterial rate	cell counts	antibacterial rate	cell counts	antibacterial rate
Control	1.04×10^6	0	5.8×10^5	0	1.10×10^6	0
1.00	1.0×10^5	90.38%	4.6×10^5	20.69%	4.3×10^5	60.91%
1.06	7.7×10^4	92.60%	4.2×10^5	27.59%	3.7×10^5	66.36%
1.17	5.3×10^4	94.90%	3.7×10^5	36.21%	3.0×10^5	72.72%
1.23	2.0×10^4	98.08%	3.0×10^5	48.27%	2.6×10^5	76.36%
1.27	3.0×10^4	97.11%	3.3×10^5	43.10%	2.9×10^5	73.64%

Control: no addition of cationic chitosan in the sample. E. Coli: 24h, 35℃, 0.06%, pH: 7.0; Aspergillus's Niger: 72h, 28℃, 0.10%, pH: 7.0; S. Cerevisiae: 72h, 28℃, 0.10%, pH: 7.0

Table 6 shows as the substitute degree (DS) of the cationic chitosan increase, the antibacterial ability increase at the beginning and then decrease. The proper explanation for this phenomenon is as the DS increasing, the cationic chitosan will have more positive charge, it will easily combine with the bacterial due to its negative charge on its surface, so the antibacterial rate increase steadily. But when the DS increase further, the antibacterial effect has a trend of decrease. Because the cationic chitosan's antibacterial ability partly come from the amido of the chitosan, and the other part from the quaternary ammonium salt, so when the DS increases, more quaternary ammonium salt will substitute the amido of the chitosan, and impact the best proportion of amido and quaternary ammonium salt, result in the decrease of the antibacterial effect. We choose the DS 1.23 in our experiment.

Antibacterial rate of cationic chitosan in different pH

Microorganism growth needs a proper pH environment, because the concentration of H^+ affects the microorganism absorbs nutrition and its biochemical reaction.

Modified chitosan's antibacterial effect comes from two sides, namely, the NH^{3+} on the chitosan and the quaternary ammonium salt after modification. In acidic condition, NH^{3+} on the chitosan can absorb the cell which surface has negative charge through static induction, and this process will be good for the antibacterial effect. But in the alkaline condition, the modified chitosan can be neutralized, reaction equation as follows: $R_4N^+Cl^-+NaOH= R_4N^+OH^-+NaCl$, so the antibacterial effect of cationic chitosan can reduce dramatically. At the same time, because the acetic acid also has antibacterial effect to some extent, so in the acidic condition, we will have a higher antibacterial rate.Table7 shows that the cationic chitosan has a good antibacterial effect on all the three samples, although its effect on the Aspergillus's Niger shows not as good as the other two, the antibacterial rate can also reach 60% at the acid test

Table 7 Antibacterial rate of cationic chitosan in different pH

pH	E. Coli		Aspergillus's Niger		S. Cerevisiae	
	cell counts	antibacterial rate	cell counts	antibacterial rate	cell counts	antibacterial rate
Control	1.04×10^6	0	5.8×10^5	0	1.10×10^6	0
5.5	1.3×10^4	98.75%	2.3×10^5	60.34%	1.7×10^5	84.55%
6.0	1.7×10^4	98.37%	2.7×10^5	53.45%	2.0×10^5	81.82%
6.5	2.0×10^4	98.08%	2.7×10^5	53.45%	2.1×10^5	80.91%
7.0	2.0×10^4	98.08%	3.0×10^5	48.27%	2.6×10^5	76.36%
7.5	3.0×10^4	97.11%	3.7×10^5	36.21%	2.8×10^5	74.55%
8.0	4.3×10^4	95.87%	4.0×10^5	31.03%	2.8×10^5	74.55%

Control: no addition of cationic chitosan in the sample. DS of cationic chitosan is 1.23, E. Coli: 24h, 35℃, 0.06%; Aspergillus's Niger: 72h, 28℃, 0.10%; S. Cerevisiae: 72h, 28℃, 0.10%

Antibacterial rate of cationic chitosan in different temperature

Table 8 Antibacterial rate of cationic chitosan in different temperature

Temperature	E. Coli		Aspergillus's Niger		S. Cerevisiae	
	cell counts	antibacterial rate	cell counts	antibacterial rate	cell counts	antibacterial rate
Control	1.0×10^6	0	5.8×10^5	0	1.10×10^6	0
20℃	1.7×10^4	99.12%	2.7×10^5	53.45%	2.0×10^5	81.82%
25℃	2.0×10^4	99.12%	3.0×10^5	48.27%	2.3×10^5	79.09%
30℃	2.0×10^4	98.90%	3.0×10^5	48.27%	2.6×10^5	76.36%
35℃	2.0×10^4	98.08%	3.0×10^5	48.27%	1.9×10^5	82.73%
40℃	1.3×10^4	98.75%	3.2×10^5	44.83%	2.0×10^5	81.82%

Control: no addition of cationic chitosan in the sample. DS of cationic chitosan is 1.23, E. Coli: 24h, 0.06%; Aspergillus's Niger: 72h, 0.10%, pH: 7.0; S. Cerevisiae: 72h, 0.10%, pH: 7.0

Different microorganisms have different optimum temperature for their culture. Table 8 shows that the temperature has a little effect on the antibacterial ability.

Antibacterial rate of cationic chitosan in different ions

Addition 0.20mol/L NaCl、$MgCl_2$、$CaCl_2$ to the cationic chitosan solution, and then testing its antibacterial ability after 1h.

Table 5 shows, as the Na^+, Mg^{2+}, Ca^{2+} concentration increases, the antibacterial effect of the cationic chitosan decrease, because the cationic chitosan and the metal ions form chelates. So in the environment that has lots of Na^+, Mg^{2+}, Ca^{2+}, we should consider the decrease of the cationic chitosan's antibacterial effect. Because of the ion radius, charge density difference among different ions, the chelation will be different, and this will result in different antibacterial ability.

Table 9 Antibacterial rate of cationic chitosan in different ions

Ion	E. Coli		Aspergillus's Niger		S. Cerevisiae	
	cell counts	antibacterial rate	cell counts	antibacterial rate	cell counts	antibacterial rate
Control	1.0×10^6	0	5.8×10^5	0	1.1×10^6	0
No addition	2.0×10^4	98.08%	3.0×10^5	48.27%	2.6×10^5	76.36%
Na^+	2.1×10^5	79.81%	4.6×10^5	20.69%	5.8×10^5	47.27%
Mg^{2+}	1.6×10^5	84.62%	4.2×10^5	27.59%	4.9×10^5	55.45%
Ca^{2+}	1.2×10^5	88.46%	3.8×10^5	34.48%	5.1×10^5	53.64%

Control: no addition of cationic chitosan in the sample. No addition: No addition of ions; DS of cationic chitosan is 1.23, E. Coli: 24h, 35℃, 0.06%; Aspergillus's Niger: 72h, 28℃, 0.10%, pH: 7.0; S. Cerevisiae: 72h, 28℃, 0.10%, pH: 7.0

Antibacterial rate of cationic chitosan in different heat treatment condition

We treat the cationic chitosan solution at 80℃、100℃、 120℃ for 30 minutes, then quickly placed them into the water bath, adopting the same the method as before, taking the cationic chitosan without heat treatment as the control sample, comparing the antibacterial rate.

Table 10 Antibacterial rate of cationic chitosan in different heat treatment condition

Temperature	E. Coli		Aspergillus's Niger		S. Cerevisiae	
	cell counts	antibacterial rate	cell counts	antibacterial rate	cell counts	antibacterial rate
Control	1.0×10^6	0	5.8×10^5	0	1.1×10^6	0
Comparison	2.0×10^4	98.08%	3.0×10^5	48.27%	2.6×10^5	76.36%
80℃	5.0×10^5	51.92%	4.5×10^5	22.41%	7.0×10^5	36.36%
100℃	7.5×10^5	27.88%	5.0×10^5	13.79%	8.5×10^5	22.73%
120℃	8.5×10^5	18.27%	5.3×10^5	8.60%	9.7×10^5	11.82%

Control: no addition of cationic chitosan in the sample. Comparison: No addition of ions; DS of cationic chitosan is 1.23, E. Coli: 24h, 35℃, 0.06%; Aspergillus's Niger: 72h, 28℃, 0.10%, pH: 7.0; S. Cerevisiae: 72h, 28℃, 0.10%, pH: 7.0

As the table 10 shows, the antibacterial ability decreases dramatically when the heat treatment intensity increases, so the heat treatment has a notable effect on the antibacterial rate. This because the cationic chitosan will be easily decomposed in the higher temperature, leading to more useless decomposition, so the antibacterial effect decreases.

CONCLUSIONS

1. The cationic chitosan is a good drainage and filler retention aid for bleached hardwood pulp. The filler retention increased by 33.0% when the dosage is 0.05%.
2. The DS of cationic chitosan also affects the drainage and filler retention. The higher the DS of cationic chitosan is, the better the performance in the wet end of papermaking.
3. The chitosan has a better performance in neutrality and alkalescency condition.
4. $Al_2(SO_4)_3$ is a good cofactor for the cationic chitosan. It will have good filler retention and paper strength when the $Al_2(SO_4)_3$ dosage is 1.0%.but it has negative effect on the draingage.
5. The antibacterial ability of cationic chitosan increases as the concentration rise.
6. When the substitute degree (DS) of the cationic chitosan increases, the antibacterial ability increases at the beginning and then decreases.
7. The cationic chitosan has a good antibacterial effect on all the three samples.
8. In the lower temperature(lower than 40℃), the temperature has a little effect on the antibacterial ability.
9. As the Na^+, Mg^{2+}, Ca^{2+} concentration increases, the antibacterial effect of the cationic chitosan decrease.
10. In the higher temperature (between 80℃ and 120℃), the antibacterial ability decreases dramatically when the heat treatment intensity increases.

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