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Study on Flocculation Characteristics of Potato Starch Wastewater

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Abstract: Herein, a chitosan film (CS) was modified using 2,3-epoxy-propyl trimethyl ammonium chloride (GTA) to flocculate granular pollutants in potato starch wastewater, aiming at the deficiencies of poor water solubility and weak electropositivity of the chitosan film. By examining the degree of substitution of chitosan film amino under different factors and different levels and response surface optimization tests, the optimum preparation conditions of chitosan film quaternary ammonium salt (HTCC) were obtained. Using scanning electron microscopy (SEM), Fourier infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and ^{1}H-nuclear magnetic spectroscopy, the nucleophilic substitution reaction of the GTA molecule with the hydrogen atoms in the chitosan film amino group successfully improved the water solubility and electropositivity of the chitosan film. HTCC was used to treat potato starch wastewater, and the optimal flocculation conditions were obtained. The flocculation product was recovered, and the composition analysis of the flocculation product demonstrated that HTCC-potato protein flocculation precipitate was rich in high protein, which is a good choice of feed and can realize sustainable utilization of resources.

Keywords: potato starch wastewater; chitosan film; resource utilization

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1. Introduction

Potatoes are rich in inorganic salts, vitamins, minerals, and proteins, and are becoming the fourth major staple food after rice, wheat, and corn. Moreover, it is the world's most popular non-grain food, enjoying the reputation of underground apples and second bread [1,2]. According to statistics, about 12 m^3 of high-concentration organic potato starch wastewater will be produced for each ton of potatoes that are processed [3]. The protein content of wastewater is high and nutrient content is rich, which has a certain recycling value. However, owing to the restriction of treatment technology and economic cost, wastewater is directly discharged and results in resource waste and environmental pollution [1]. Moreover, owing to the high concentration of carbohydrate, protein, and starch, chemical oxygen demand (COD) and concentration of suspended solids (SS) can reach 8000–20,000 and 3000 mg/L. If not treated and discharged into natural water bodies, black and smelly water bodies that can seriously damage the aquatic environment are formed [2,4].

The treatment of potato starch wastewater is difficult owing to its production characteristics. First, potato production is seasonal and storage time is extremely less, leading to starch production time occurring in winter every year. Low temperature is not conducive to the biochemical degradation of potato wastewater [5]. Second, the short-term discharge of potato starch wastewater is extremely large, which makes the water quality of wastewater dramatically fluctuate and not conducive to treatment [6,7]. Moreover, potato is primarily produced in northern China, and starch production is mostly performed in the rural small

workshop mode; thus, it is difficult to bear the high cost of wastewater treatment [8]. The abovementioned characteristics of potato starch production are an obstacle to wastewater treatment. The effective pretreatment of potato starch wastewater can reduce the cost of potato starch wastewater treatment, reduce the difficulty of subsequent treatment, recover protein, and subsidize the economic benefits of enterprises. It is of considerable practical significance to promote the healthy development of the potato industry [9].

Potato production is seasonal in nature and potato amylator plants are mostly operated in winter; therefore, the biological treatment of wastewater is inconvenient. The physico-chemical treatment of potato starch wastewater, such as membrane separation, air flotation, adsorption, and flocculation, was extensively examined [10]. The flocculation method stands out because of its strong impact load resistance and simple operation; moreover, the flocculation method can separate and recover non-toxic and harmless organic matter in wastewater for green and sustainable development. However, traditional flocculants such as polyaluminum chloride or polyacrylamide that are commonly used will cause secondary pollution, and the recycled materials cannot be reused [11]. At this time, chitosan film is a natural cationic polymer with biocompatibility, non-toxicity, flocculation, film formation, and other characteristics, which was extensively examined by scientists and is an excellent natural flocculant [12,13]. Studies reported that the chitosan film is poor in water solubility and has limited usage in many fields. To address this disadvantage, GTA was used to modify the chitosan film. The modification reaction is performed on the side groups while the trunk is not affected, thus preserving the inherent physical, chemical, and biological properties of the chitosan film. Furthermore, the electropositivity and water solubility are considerably enhanced [14,15].

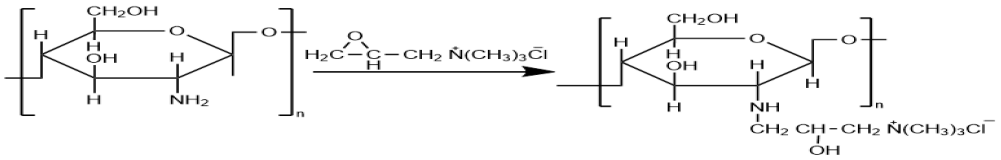
Herein, a modified chitosan film HTCC was used to treat potato starch wastewater, and the best processing conditions are reported. Flocculation is mainly divided into two stages: coagulation and flocculation. In the coagulation stage (T_0), the wastewater needs to be stirred rapidly so that the flocculant can quickly and fully contacts the wastewater, and then the speed is reduced to continue to stir for a period of time (T_1). This stage is the flocculation stage, which is to form large floc and make it easy to settle. With the protein recovery rate, COD, and turbidity removal rate as indicators, the optimal process conditions were obtained by examining the effects of process factors such as product substitution degree, HTCC dosage, pH of wastewater, flocculation temperature, coagulation stage speed, coagulation stage time, flocculation stage speed, and flocculation stage time on the treatment effect of potato starch wastewater. The variables were set as G0 and T0 in the agglomerating period and G1 and T1 in the flocculating period. Response surface tests were designed with the rate of change in floc particle size (u) as the evaluation index, and optimal dynamic conditions were obtained. Finally, the feasibility of flocculating precipitates as feed, which provides theoretical guidance for flocculating wastewater treatment in the potato starch production plant, is discussed. Herein, a chitosan film (CS) was modified as per the production characteristics of potato starch wastewater, thus aiming at obtaining granular pollutants in potato starch wastewater to flocculate granular pollutants in potato starch wastewater and recover the sediment to make feed. It is of great significance in the actual treatment and resource recycling of potato starch wastewater [16].

2. Materials and Methods

2.1. Materials Preparation

2.1.1. Preparation of Modified Chitosan Film Quaternary Ammonium Salt

Quaternary ammonium modification of the chitosan film primarily involves the interaction of amino groups in the chitosan film with GTA to perform the nucleophilic substitution reaction. The reaction equation is as follows:



A certain amount of the chitosan film was weighed and dissolved in 1% acetic acid, and then a certain amount of GTA solution was added. After evenly mixing, the pH was adjusted to neutral using a sodium hydroxide solution. After mixing with 100 mL of isopropyl alcohol, the product was added to a four-port flask and fully reacted at a certain temperature, and then separated and purified with anhydrous ethanol and acetone, respectively. Finally, the product was dried at 70 °C [17]. The optimal quaternary ammonium salt of the chitosan film was then obtained.

2.1.2. Preparation of Potato Starch Wastewater

In the lab, potato starch wastewater is prepared, and potatoes are bought from local supermarkets, washed, peeled, and cut into small pieces, then poured into a juicer and juiced according to a mass ratio of 5:1 of distilled water to potatoes. The filtrate is then filtered via six layers of gauze to produce potato starch wastewater.

2.2. Determination Method

Substitution degree measurement: Note that 8.53 g of solid $AgNO_3$ was accurately weighed and dissolved in deionized water, and then 0.05 mol/L solution was prepared using a 1000 mL volumetric bottle, and stored in a brown bottle that was kept away from light. Finally, the accurate concentration of 0.05 mol/L of $AgNO_3$ was calibrated using the standard solution of 0.01 mol/L NaCl.

A total of 5% of K_2CrO_4 indicator was formulated.

For the indicator, 0.1 g of chitosan film quaternary ammonium salt was dissolved in 100 mL of deionized water, 5% K_2CrO_4 was used as an indicator, and 0.05 mol/L $AgNO_3$ was titrated until a brick red precipitate was obtained. Then, the degree of substitution (*DS*) was calculated as follows:

$$DS = \frac{V \cdot c/1000}{V \cdot \frac{c}{1000} + \left(m - V \cdot c \cdot \frac{M_1}{1000}\right)/M_2} \times \frac{1}{DD} \times 100\% \quad (1)$$

where V (mL) is the volume of silver nitrate solution required for titration of chitosan film quaternary ammonium salt; c (mol/L) is the concentration of silver nitrate solution used; m (g) is the mass of chitosan film quaternary ammonium salt used; and M_1 (g/mol) is the molar mass of chitosan film quaternary ammonium salt. M_2 (g/mol) is the molar mass of monochitosan film, and *DD* is the degree of deacetylation of the chitosan film raw material used.

Determination of chemical oxygen demand (COD): As per the GB11914-89 COD determination, the standard curve is obtained using the following equation: $y = 0.0002x - 0.0013$; $R^2 = 0.9992$.

Determination of turbidity: At room temperature, turn on the NTU-1000 turbidimeter for preheating and measure the turbidity directly after preheating.

Protein content was measured using the biuret method, and the standard curve was $y = 0.0053 + 0.04525x$; $R^2 = 0.999$.

Determination of particle size of flocs: At room temperature, turn on the ZETAsizer Nano ZS laser particle size meter to preheat, measure the background, then add the sample, adjust the instrument to the required test conditions, measure and record the sample particle size, and calculate the average particle size of the sample.

2.3. Characterization

A certain amount of HTCC and chitosan film samples are placed on the loading platform, sprayed with gold, and then observed using the Hitachi Regulus8100 scanning electron microscope. The instrument voltage is set to 20 kV. A certain amount of HTCC and chitosan film samples were then dried and ground, pressed with potassium bromide at a constant temperature, and then the functional groups of the two substances were characterized using a VERTEX 80 Fourier infrared spectrometer. A certain amount of HTCC was then dissolved in D_2O to obtain 5% chitosan film solution, which was tested and analyzed using the Brooke 400 M NMR instrument to obtain hydrogen spectra. A certain amount of HTCC and chitosan film samples were then dried, ground and placed on a slide, and then characterized using the Brooke D8 advance X-ray diffractometer. The test conditions were set to a scanning speed of $4^\circ \cdot min^{-1}$ and $2\theta = 5^\circ$–60°.

2.4. Study on Flocculation Kinetics

Flocculation kinetics primarily studies the influence of dynamic factors on the change in flocs' particle size, which has a great influence on the flocculation effect [18]. Von Smoluchowski proposed the discrete flocculation dynamic equation, which provided a solid foundation for this concept. Then, Stein and Camp developed the velocity gradient (G) theory, which describes the collision degree of particles in fluid with G, which is regarded as an important evaluation index in sewage treatment plants to date.

2.4.1. Determination of Velocity Gradient G

As per the book of water treatment design calculation, the calculation formula of velocity gradient G is obtained:

$$G = \sqrt{\frac{102N}{\mu V}} \tag{2}$$

where G (μm) is the velocity gradient (s^{-1});
N (min) is the power required by the stirring shaft (kW);
μ (min) is the dynamic viscosity coefficient of water (kg/(s·m));
V (min) is the volume of wastewater used for flocculation (m^3).

$$N = \frac{ykln^3\left(r_2^4 - r_1^4\right)}{408} \tag{3}$$

where y (μm) is the number of stirring blades during flocculation (each);
k (min) is the coefficient;
l (min) is the length of the slurry plate (m);
n (min) is the rotational speed (rad/s);
r_1 (min) is the difference between impeller diameter and pulp plate width (m);
r_2 (min) is the radius of the impeller.

$$k = \frac{\psi\rho}{2g} \tag{4}$$

where ψ (μm) is the drag coefficient;
ρ (min) is the density of water (1000 kg/m^3);
g (min) is gravity acceleration (m/s^2).

2.4.2. Particle Size Monitoring and Average Growth Rate Calculation of Flocs

A particle size analyzer is used to monitor the growth process of floc particles and calculate the average growth rate of particle size. The formula is as follows:

$$u = \frac{1}{n}\sum_{i=1}^{n}\frac{\Delta d_i}{\Delta t_i} \tag{5}$$

where Δd_i (μm) is the particle size difference of flocs in adjacent time;
Δt_i (min) is the time difference used to measure two adjacent times.

2.4.3. The Relationship between Average Growth Rate of Flocs and Treatment Effect

Seven groups of wastewater in the response surface test were randomly selected to measure their effluent turbidity and COD, and the relationship between the growth rate of associated floc size and the treatment effect of potato starch wastewater was analyzed.

3. Results and Discussion

3.1. Sample Characterization Analysis

The micromorphologies of chitosan film and HTCC materials were observed using scanning electron microscopy (SEM). Figure 1 shows the SEM images of chitosan film and HTCC materials obtained under the best conditions.

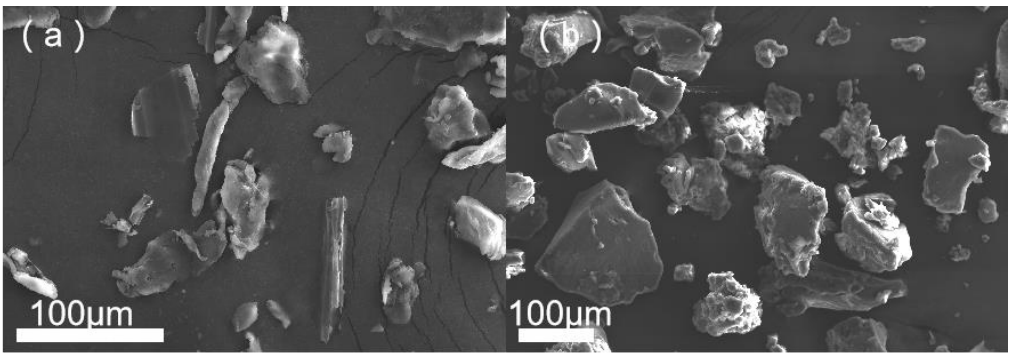


Figure 1. SEM images of CS (**a**) and HTCC (**b**).

Figure 1a shows the SEM image of chitosan film. In the SEM image of Figure 1a, it can be clearly observed that the average particle size of chitosan film is ~50 μm, which is generally small, and the particle distribution is wide, and most of the shape is a long strip. As can be seen from the SEM image in Figure 1b, the average particle size of HTCC is ~100 μm, twice as large as that of chitosan film, and most of the shapes are regular chunks. In conclusion, there are significant differences in particle size and morphology between the chitosan film and HTCC.

The chemical bond and group composition of chitosan film and HTCC materials were compared and analyzed using Fourier infrared (FTIR) spectroscopy, and infrared spectra of HTCC and chitosan film materials were obtained (Figure 2). Figure 2 shows the infrared spectra of chitosan film and HTCC. We can see that most groups do not change owing to modification, and the difference is the absorption peak of the amino group of the chitosan film. The bending vibration peak of N-H was found at 1594 cm^{-1}, but it was not found at the corresponding place of HTCC, indicating that the hydrogen atoms on the amino group were replaced in the reaction. Furthermore, the absorption peak at 1484 cm^{-1} in the HTCC map corresponds to the stretching vibration of methyl C–H; however, this peak is not present in the infrared map of chitosan film, indicating that the HTCC successfully introduced the methyl group. In conclusion, the N–H of HTCC is extremely weak, indicating that the nucleophilic substitution reaction proceeds smoothly, the degree of substitution is high, and the product is water soluble.

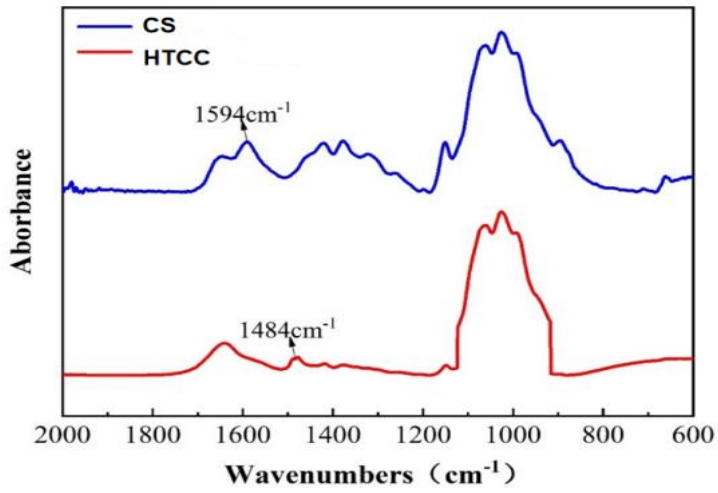


Figure 2. FTIR spectra of CS and HTCC.

Figure 3 shows the ^{1}H-NMR spectra of HTCC. Note that d = 4.70 ppm is the proton peak of D_2O, and a very strong proton peak of CH^3 (4*) on quaternary ammonium appears at 3.15 ppm, which indicates that small molecules of quaternary ammonium salt were introduced into the chitosan film. Furthermore, d = 4.70, 3.55, 3.50, 2.71, and 1.98 ppm are divided into the peaks of 1, 5, 3, 2, and 4 in the six member ring. The peak at 3.72 ppm is the signal peak of the hydrogen atom on methylene (6), which indicates that the alcohol hydroxyl group at position 6 was not substituted. The peaks at d = 4.22, 3.33, and 2.84 ppm are the signal peaks of hydrogen atoms 2*, 3*, and 1* in the small molecular quaternary ammonium salts. Furthermore, there may be a residual acetyl group in the chitosan film, and its peak is d = 1.83 ppm. To summarize, the nucleophilic substitution reaction occurred on the amino group of the chitosan film, and the ^{1}H-NMR spectra agreed with the structure of HTCC.

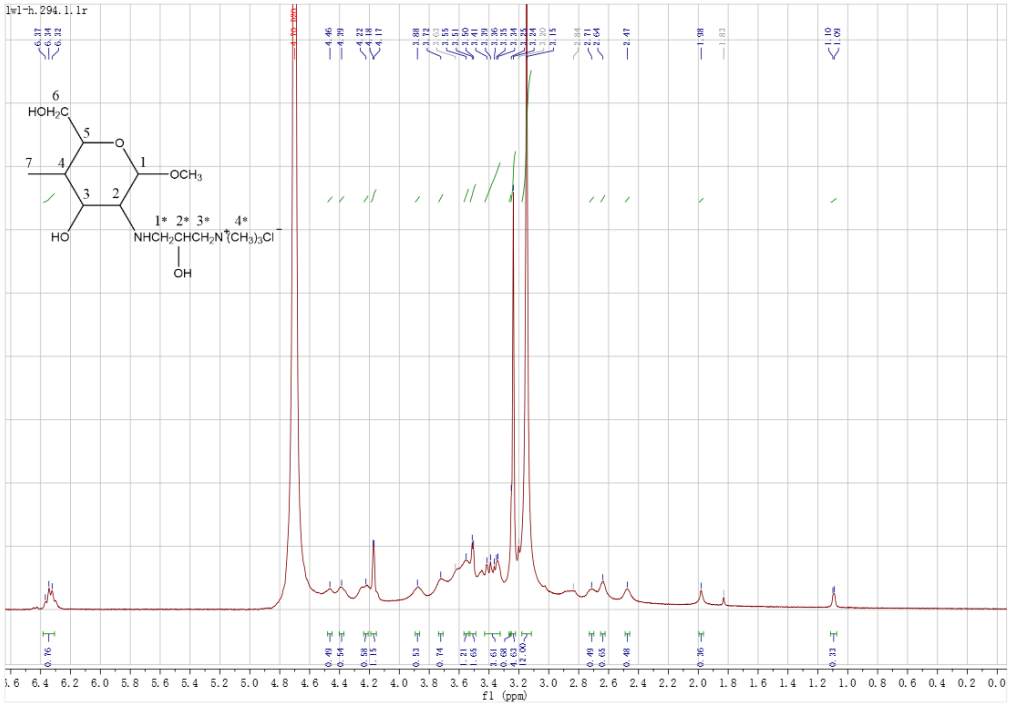


Figure 3. NMR of chitosan film quaternary ammonium salt.

X-ray diffraction (XRD) was used to analyze the structure of HTCC and chitosan film materials. The XRD patterns of HTCC samples obtained under the optimal conditions of molar ratio of reactants of 4, reaction temperature of 80 °C, pH of 7, and reaction time of 9 h are shown as follows: As can be seen from the Figure 4, the crystallinity of chitosan film is higher than that of HTCC. This is because a hydrogen bond is easy to form in the presence of both amino and hydroxyl groups, while HTCC lacks the amino group possessed by the chitosan film. The main reason why chitosan film is insoluble in water is the two strong diffraction peaks at ~10° and 20°. After modification, the diffraction peak at 10.95° of HTCC material disappeared, and the strong diffraction peak at 20.24° was considerably weakened. This is primarily attributed to the nucleophilic substitution reaction between GTA and chitosan film, which considerably weakens the generation of the hydrogen bond and reduces the crystalness of HTCC. The molecular structure becomes loose, which greatly strengthens the water solubility of modified products.

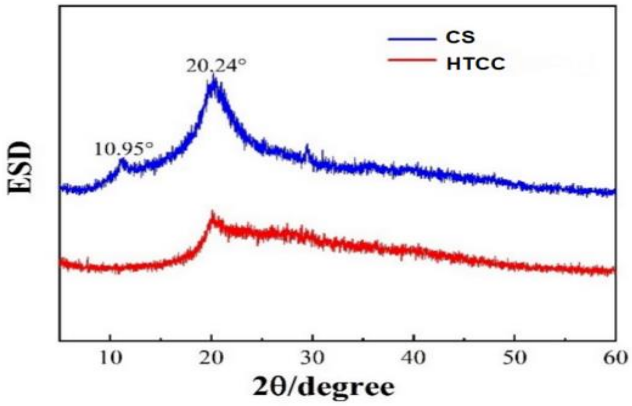


Figure 4. XRD spectrum of CS and HTCC.

3.2. Sample Characterization Analysis

In Figure 5, the considerable difference between the solubility of HTCC and that of chitosan film is intuitively reflected. In general, the solubility of chitosan film is the best when the pH is <5 in the acidic environment because the hydrogen bond is weakened in an acidic environment. When the pH value of the solution changes to alkaline, the chitosan film will slowly precipitate from the solution. However, HTCC modified by quaternary ammonium salt shows stable and good water solubility. HTCC still has the best water solubility in an acidic environment, but HTCC will not precipitate solution even if the solution changes to an alkaline environment. Therefore, the water solubility of chitosan film is far behind HTCC, and the application of HTCC is not limited to an acidic environment. It has a broader application prospect.

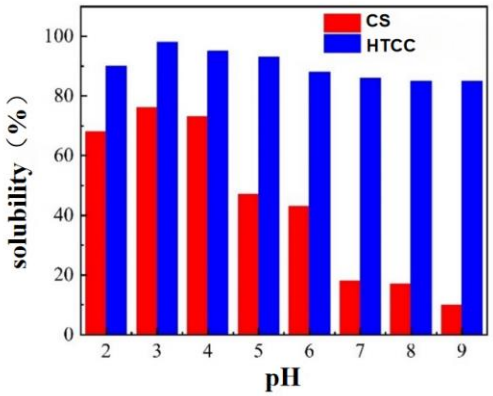


Figure 5. Comparison of water solubility between CS and HTCC.

In Figure 6, the difference in zeta potential between chitosan film and HTCC solution is considerable. As can be seen from the figure, the zeta potential of chitosan film and HTCC in acidic conditions is greater than that in neutral and alkaline environments; however, the zeta potential of HTCC is considerably greater than that of chitosan film in any environment, and the effect of pH on the zeta potential of HTCC is extremely small. These phenomena indicate that chitosan film modified by the quaternary ammonium salt successfully brings more of a positive charge. It is beneficial to neutralize protein in the potato starch wastewater and improved flocculation performance, which provides a broader prospect for green recycling wastewater treatment.

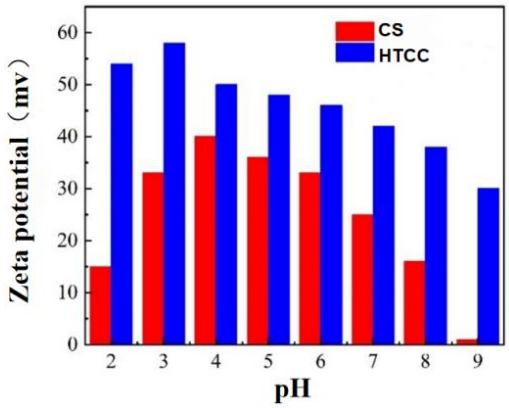


Figure 6. Comparison of positive electricity between CS and HTCC.

3.3. Optimization of Flocculation Process of Potato Starch Wastewater

The primary controllable factors in the flocculation process of potato starch wastewater are four dynamic factors: agitation rate during coagulation period, agitation time during coagulation period, agitation rate during flocculation period, and agitation time during flocculation period. Four process factors are as follows: product substitution degree, HTCC dosage, reaction temperature, and reaction pH [19,20]. This chapter primarily examines the influence of the above eight factors on turbidity, COD, and protein recovery and obtains the optimal flocculation conditions and the best effluent water quality.

Under the conditions of 500 rpm, stirring time is 2 min in the holding period, 120 rpm, stirring time is 6 min in the flocculating period, HTCC dosage is 0.5 g/L, temperature is 20 °C and pH is 6. Seven levels of product substitution degree were selected as 25%, 47%, 64%, 72%, 80%, 90%, and 98% to explore the effect of product substitution degree on potato starch wastewater treatment [21]. Figure 7 shows that with an increase in substitution degree, the removal rates of turbidity, COD, and protein all synchronously rise, which can be roughly divided into three stages. First, when the degree of substitution is <64%, chitosan film is basically insoluble in water owing to too-low substitution at this time, and the positive charge in the solution is less, and therefore, it cannot electroneutralize the negatively charged particles in the wastewater, thus resulting in poor wastewater treatment effect. When the degree of substitution is >64%, the water solubility of the product begins to show, and it can gradually dissolve in the water, obtain more positive charge, and considerably increase the removal rates of turbidity, COD, and protein. When the degree of substitution is >90%, the treatment effect of HTCC on wastewater is basically unchanged, and the treatment effect of wastewater is the best primarily because HTCC can be completely dissolved in water. Note that it can play its role of macromolecules, net trapping, bridging, electric neutralization of impurities in water, and obtain high turbidity, COD, and protein removal rate. Therefore, 98% was selected as the optimal degree of substitution as per the single-factor experimental analysis.

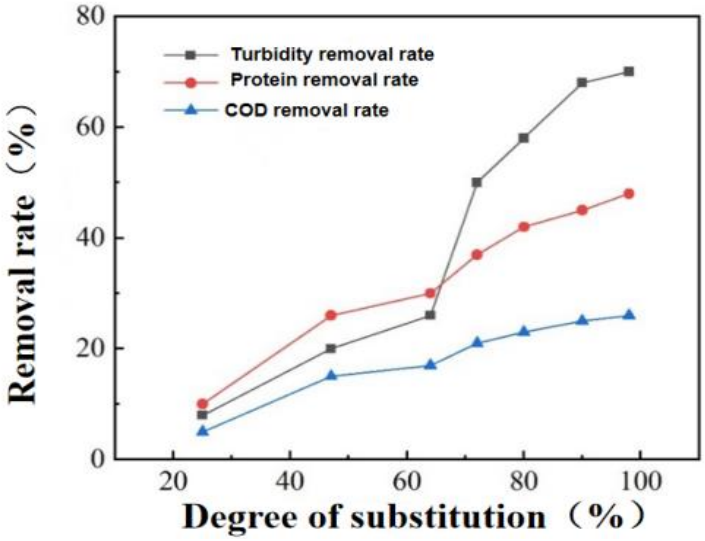


Figure 7. Effect of substitution degree on treatment effect.

Under the conditions of 98% HTCC substitution degree, 2 min is the stirring time in the holding agglomeration period, 120 rpm is the stirring time in the flocculation period, 6 min is the stirring time, 0.5 g/L is the HTCC dosage, 20 °C is the temperature, and pH is 6. Seven stirring speeds of 300, 350, 400, 450, 500, 550, and 600 rpm were selected during the agitating period to explore the effect of product substitution degree on the treatment effect of potato starch wastewater. Figure 8 shows that the overall trend is that the removal rates of turbidity, COD, and protein increase first and then decrease as the stirring speed increases during the coagulation period, and the optimal treatment effect is obtained at 350 rpm. If the agitating speed is too low, the flocculant cannot spread to the whole solution system quickly and evenly, resulting in the treatment effect not being very good. However, when the agitating speed is >350 in the agitating period, although the flocculant is fully mixed, the flocculating mass completed by flocculation will disperse owing to the excessive shear force, which reduces the treatment effect. Therefore, as per the single-factor experimental analysis, the stirring speed during the coagulation period was selected as 350 rpm.

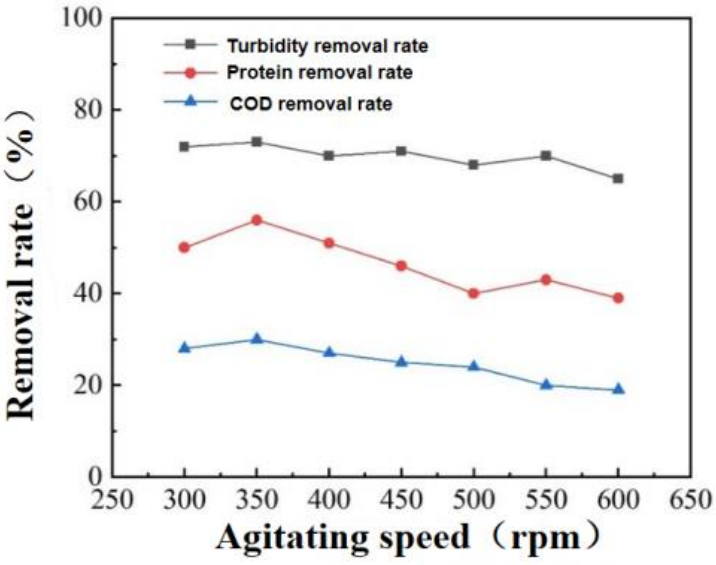


Figure 8. Effect of stirring speed on treatment effect during coagulation.

When the degree of substitution is 98% HTCC, the stirring speed is 350 rpm in the holding period, 120 rpm in the flocculation period, the stirring time is 6 min, the dosage of HTCC is 0.5 g/L, the temperature is 20 °C, and pH is 6. The agitating time of the agitating period was selected as 1, 2, 3, 4, 5, 6, and 7 min to explore the effect of agitating time on the treatment effect of potato starch wastewater.

Figure 9 shows that the removal rates of turbidity, COD, and protein present a linear pattern of first increasing and then decreasing with increase in stirring time in the coagulation period, and the optimal treatment effect is obtained at the stirring time of 3 min. If the agitating time is extremely short, the flocculant does not evenly spread to the whole solution system and the rapid agitation ends, thus resulting in a poor treatment effect. However, when the agitating time is >3 min, the formation of floc is affected by the long time of fast stirring, and therefore, it is necessary to identify the right time. As per the single-factor experiment, the agitating time was selected as 3 min.

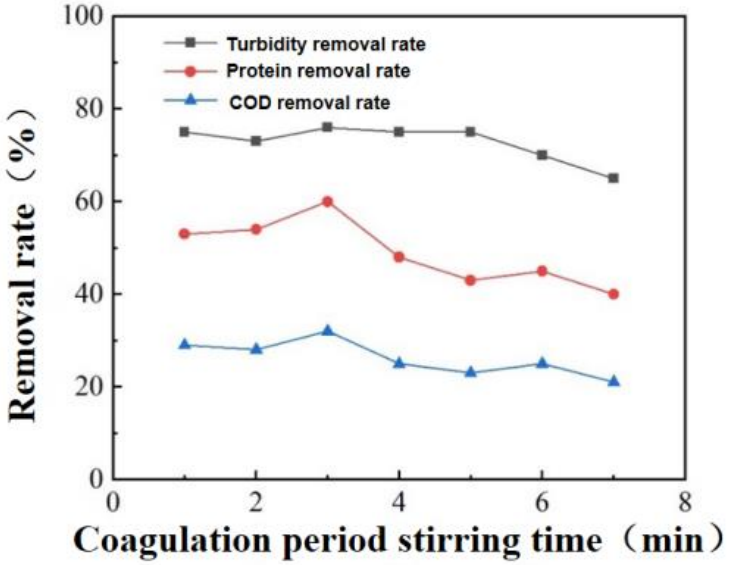


Figure 9. Effect of mixing time in coagulation period on treatment effect.

When the substitution degree is 98% HTCC, the stirring speed in the holding period is 350 rpm, the stirring time in the holding period is 3 min, the stirring time in the flocculation period is 6 min, the HTCC dosage is 0.5 g/L, the temperature is 20 °C, and the pH is 6. To explore the effect of stirring speed on potato starch wastewater treatment, seven levels of stirring speed in flocculation period were selected as 25, 50, 75, 100, 125, 150, and 175 rpm. Figure 10 shows the removal rates of turbidity, COD, and protein present a parabolic shape, and the optimal wastewater treatment effect is achieved when the stirring speed is 75 rpm during the flocculation period. When the speed is extremely small, the flocculation process is about equal to the natural sedimentation, which makes the collision between particles insufficient and creates a lack of effective flocculation reaction, which leads to the wastewater treatment effect being not very good. When the speed of flocculation is too high, the flocculant is easy to dissipate, and the wastewater treatment effect is not good. Therefore, based on single-factor experimental analysis, 75 rpm was selected as the stirring speed during flocculation.

When the degree of substitution is 98% HTCC, the stirring speed in the holding period is 350 rpm, the stirring time in the holding period is 3 min, the stirring speed in the flocculation period is 75 rpm, the dosage of HTCC is 0.5 g/L, the temperature is 20 °C, and the pH is 6. The stirring time of the flocculation period was selected as 3, 6, 9, 12, 15, 18, and 21 min to explore the effect of stirring time of flocculation period on the treatment effect of potato starch wastewater. Figure 11 shows that the removal rates of turbidity, COD, and protein reached a stable level at ~12 min of agitation time. Therefore, 12 min was selected

as the stirring time during the flocculation period as per the results of the single-factor experiment.

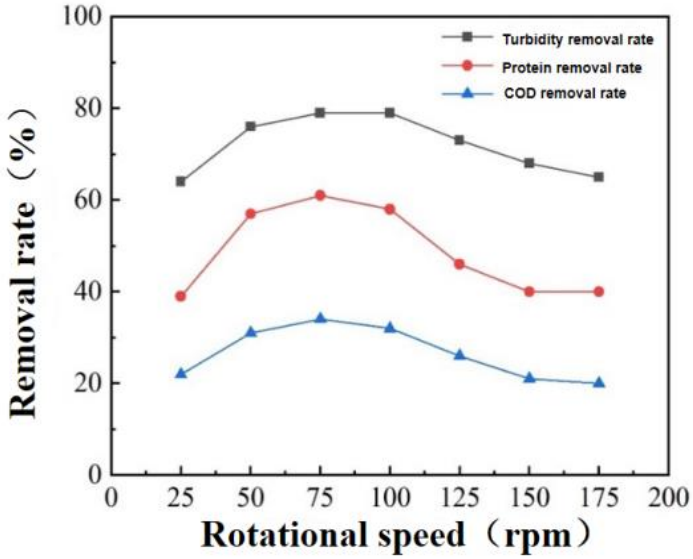


Figure 10. Effect of stirring speed on treatment effect in flocculation period.

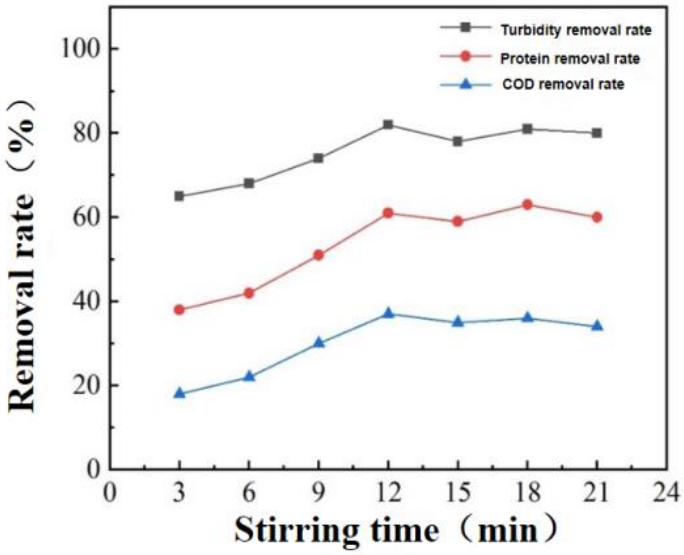


Figure 11. Effect of mixing time in flocculation period on treatment effect.

When the degree of substitution is 98% HTCC, the stirring speed in the coagulation period is 350 rpm, the stirring time in the coagulation period is 3 min, the stirring speed in the flocculation period is 75 rpm, the stirring time in the flocculation period is 12 min, the temperature is 20 °C, and the pH is 6. Note that seven levels of HTCC dosage were selected as 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, and 1.75 g/L to explore the effect of HTCC dosage on potato starch wastewater treatment. Figure 12 shows that with increase in dosage, the removal rates of turbidity, COD, and protein present a parabolic shape. When the dosage is <1 g/L, because the dosage is too small to completely flocculate the pollutants in the water, the removal rate of various items will rise with the increase in the dosage. When the dosage was >1 g/L, the removal rate remained stable at the best level, but the dosage was 1.75 g/L, and the removal rate reduced. Therefore, based on the single-factor experimental results, the dosage of HTCC was selected as 1.0 g/L.

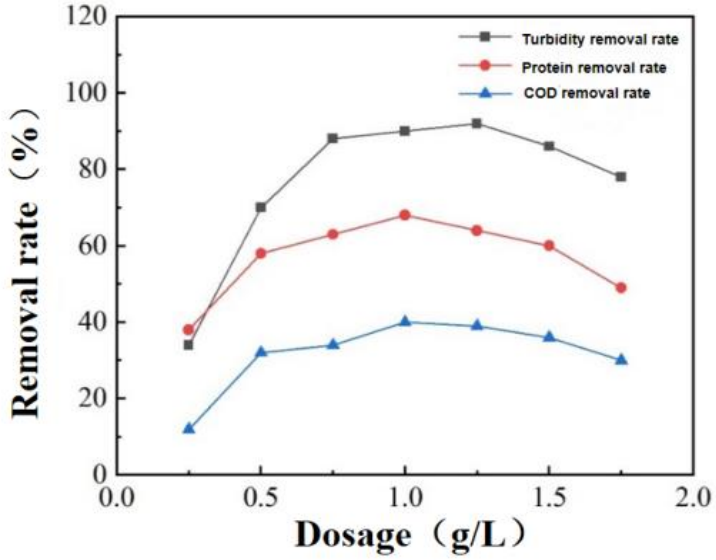


Figure 12. Effect of dosage on treatment effect.

When the degree of substitution is 98% HTCC, the stirring speed in the coagulation period is 350 rpm, the stirring time in the coagulation period is 3 min, the stirring speed in the flocculation period is 75 rpm, the stirring time in the flocculation period is 12 min, the HTCC dosage is 1.0 g/L, and the pH is 6. Seven levels of reaction temperature were selected as 10°C, 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, and 70 °C to explore the effect of reaction temperature on the treatment effect of potato starch wastewater. Figure 13 shows that temperature has little effect on turbidity, while the removal rates of COD and protein first increase and then decrease. The removal effect is best when the reaction temperature is ~40 °C. The main reason is that at a low temperature, the dynamic viscosity coefficient of water is large, the molecular thermal motion is reduced, and the collision between particles is reduced, which makes the wastewater treatment effect not good. When the temperature is too high, the high temperature will weaken the hydrogen bond between HTCC molecules, reduce the bridging effect of HTCC net, and reduce the removal rate of various items. Therefore, according to the results of the single-factor experiment, the reaction temperature was selected as 40 °C.

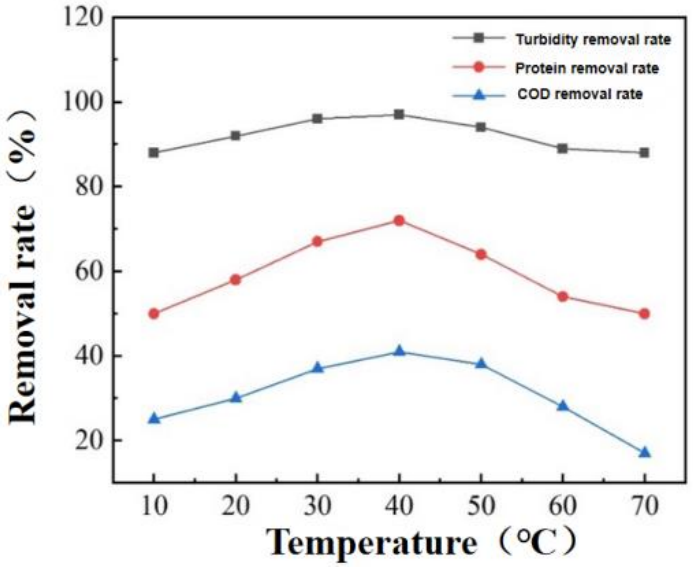


Figure 13. Effect of reaction temperature on treatment effect.

When the degree of substitution is 98% HTCC, the stirring speed in the holding period is 350 rpm, the stirring time in the holding period is 3 min, the stirring speed in the flocculation period is 75 rpm, the stirring time in the flocculation period is 12 min, the HTCC dosage is 1.0 g/L, and the reaction temperature is 40 °C. The pH levels of 3, 4, 5, 6, 7, 8, and 9 were selected to explore the effect of pH on the treatment effect of potato starch wastewater. Figure 14 shows that pH has a great impact on the removal rates of COD, turbidity, and protein, and peaks appear in the two places where pH is 4 and 8. The reason is that a pH of ~4 happens to be the isoelectric point of protein in potato starch wastewater, and the protein automatically precipitates from the solution, thus increasing the removal rate. When the pH is 7, the distance from the isoelectric point is far away, and the solution has the largest electronegative property. When the pH is >7, the negative electricity of the solution will change to the positive electricity, i.e., the treatment effect of cationic flocculant HTCC decreases. Therefore, pH 7 was selected according to the results of the single-factor experiment.

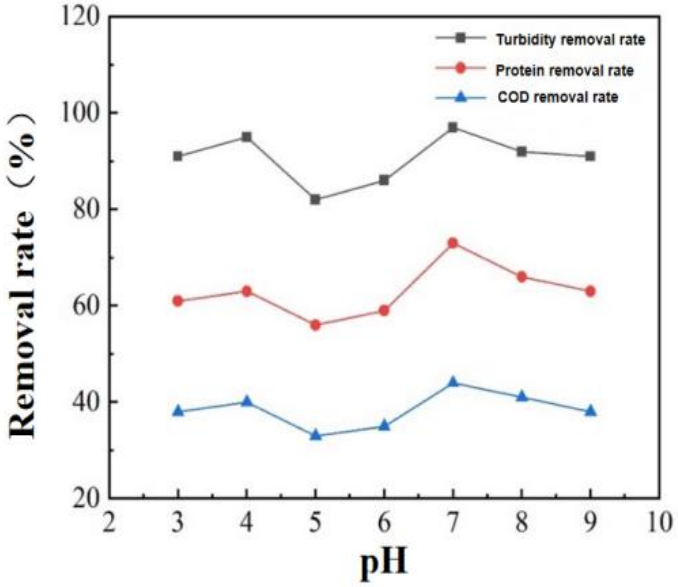


Figure 14. Effect of reaction pH on treatment effect.

The single-factor experiment optimizes the optimal treatment conditions of potato starch wastewater. When the degree of substitution was 98% HTCC, the stirring speed was 350 rpm in the holding stage, the stirring time was 3 min in the holding stage, the stirring speed was 75 rpm in the flocculating stage, the stirring time in the flocculating stage was 12 min, the dosage of HTCC was 1.0 g/L, the reaction temperature was 40 °C, and the reaction pH was 7. At this time, the effluent index is as follows: COD is 4560 mg/L, protein concentration is 560 mg/L, turbidity is 10 NTU, ammonia nitrogen is 45 mg/L, and total phosphorus is 50 mg/L.

3.4. Study on Flocculation Kinetics

Design-Expert 12 was used to draw the response surface diagram of the test results. The following figure shows the response surface model of four factors affecting the growth rate of flocculant particle size: velocity gradient G_0 (A) and T_0 (B) in the coagulation period, velocity gradient G_1 (C) in the flocculation period, and time T_1 (D) in the flocculation period. The pairwise interaction affecting the outcome of the reaction can be easily visualized.

With G_1 fixed at 300 s^{-1} and T_1 at 12 min, the interaction diagram of G_0 and T_0 was drawn (Figure 15). In the AB interaction surface, when T_0 was fixed, the growth rate of particle size demonstrated a trend of gentle rise first and then decrease as G_0 increased from 2400 to 3200 s^{-1}. This is because when G_0 is <2800 s^{-1}, the flocculation process will lack power, the flocculant cannot quickly and evenly spread to the whole solution system,

the proteins cannot all contact, and then flocculation occurs. Therefore, the particle size growth rate is slowed down. The figure shows that the maximum value of T_0 is about 2.5–3.5 min, and G_0 is within the range of 2400–2800 s^{-1}. Finally, according to the contour line with elliptical contour and the p value of AB = 0.0036 < 0.05, the velocity gradient G_0 and time T_0 of the condensation period have an extremely significant interaction with the growth rate of particle size.

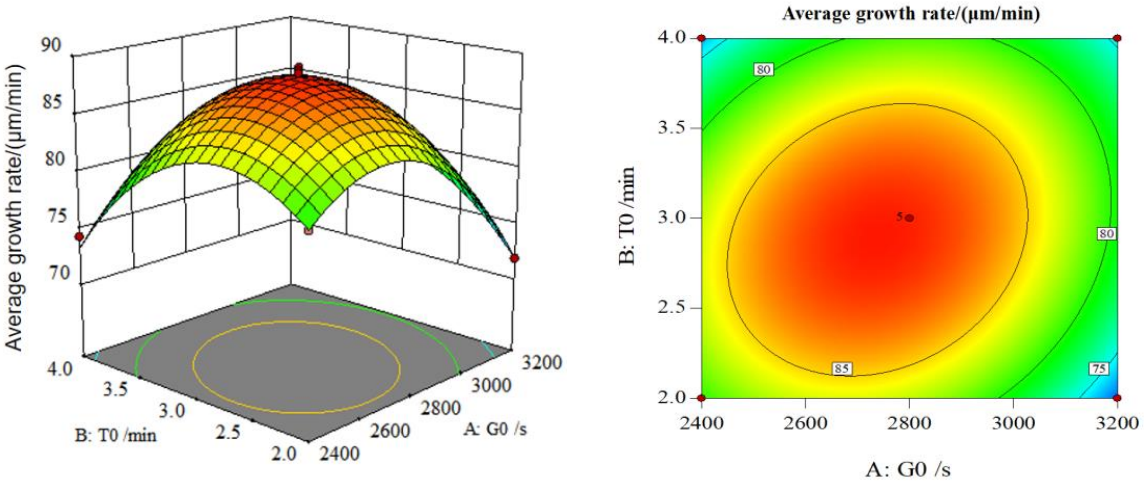


Figure 15. Effect of interaction between G_0 and T_0 on average growth rate.

When T_0 is fixed at 3 min and T1 is fixed at 12 min, the AC interaction diagram is drawn (Figure 16). In the AC interaction surface, when G_0 is fixed at a certain point, the growth rate of particle size increases first and then gently decreases with the increase in G_1. When G_1 is low, the growth rate of particle size increases first and then decreases with the increase in G_0. With the increase in G_0, the growth rate of particle size remains flat and then decreases. The figure shows that when G_0 is ~2600–3000 s^{-1} and G_1 is about 250–350 s^{-1}, the growth rate of particle size is the highest. Finally, the contour line with oval contour and the p value of AC = 0.0179 < 0.05 indicate that there is a significant interaction between G_0 and G_1.

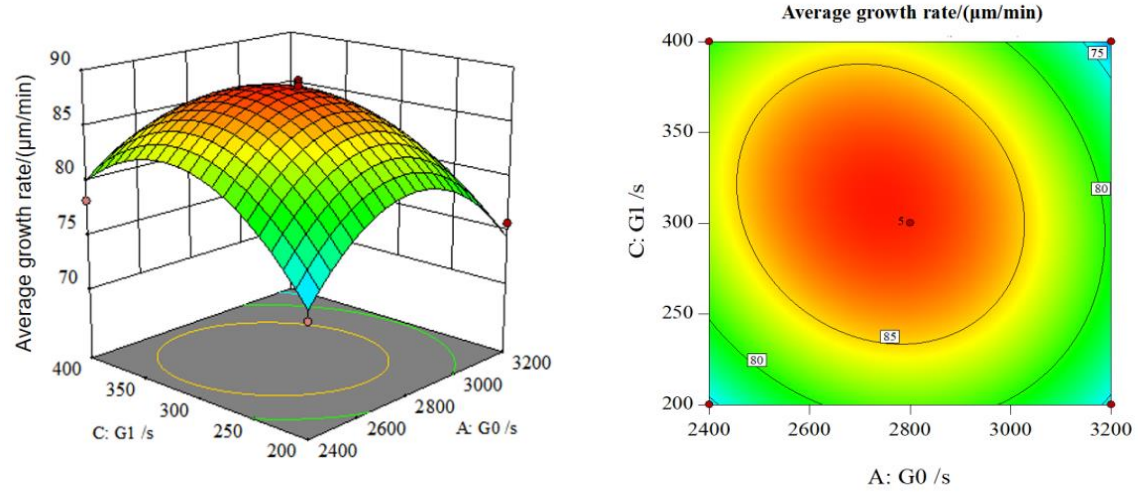


Figure 16. Effect of interaction between G_0 and G_1 on average growth rate.

Fixed T_0 at 3 min and G_1 at 300 s^{-1}. The AD interaction diagram is drawn as shown in Figure 17. In the AD interaction surface, when G_0 is low, particle size growth rate presents a trend of first flattening and then decreasing with the increase in T1. When G_0 is high, particle size growth rate presents a trend of first increasing and then decreasing with the

increase in T_1. When T_1 is low, with the increase in G_0, the growth rate of particle size first kept flat and then decreased. When T_1 is large, the growth rate of particle size first increased and then decreased with the increase in G_0. When G_0 was about 2600–2800 s^{-1} and T_1 was 11–13 min, the particle size growth rate reached the maximum. Finally, the contour with oval contour and AD p value = 0.0036 < 0.05 indicates that G_0 and T_1 have significant interaction.

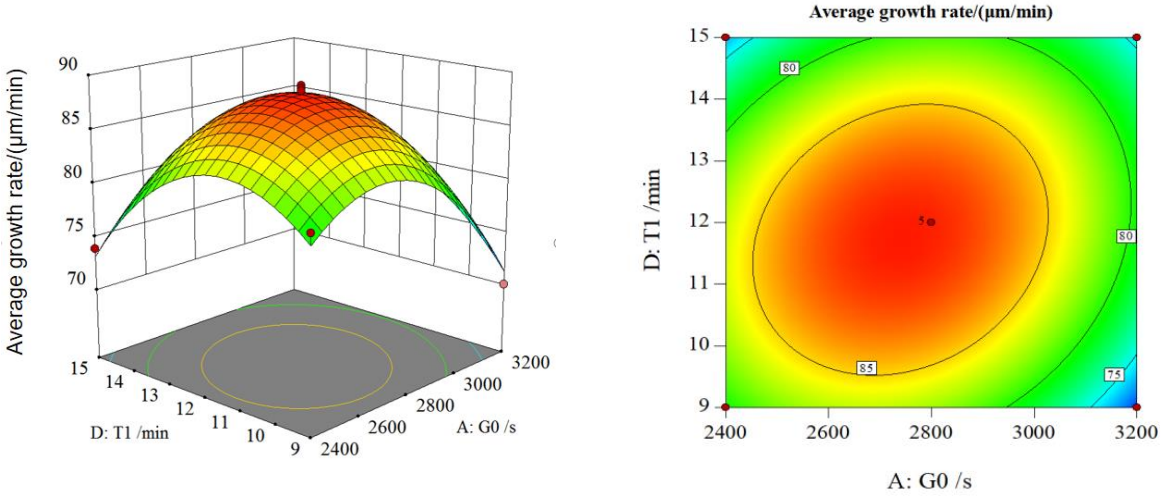


Figure 17. Effect of interaction between G_0 and T_1 on average growth rate.

With G_0 fixed at 2800 s^{-1} and T_1 at 12 min, the BC interaction diagram is shown in Figure 18. On the BC interaction surface, with the increase in G_1, the growth rate of particle size first increases and then decreases. When G_1 is low, the growth rate of particle size first flattens and then decreases with the increase in T_0. The growth rate of particle size increased first and then decreased, indicating that there was a significant interaction between G_1 and T_0. Considering only the interaction between the two, the particle size growth rate reaches the maximum when T_0 is about 2.5–3.5 min and G_1 is about 250–350 s^{-1}. The interaction between BD and CD was not significant, which is consistent with the results of variance analysis.

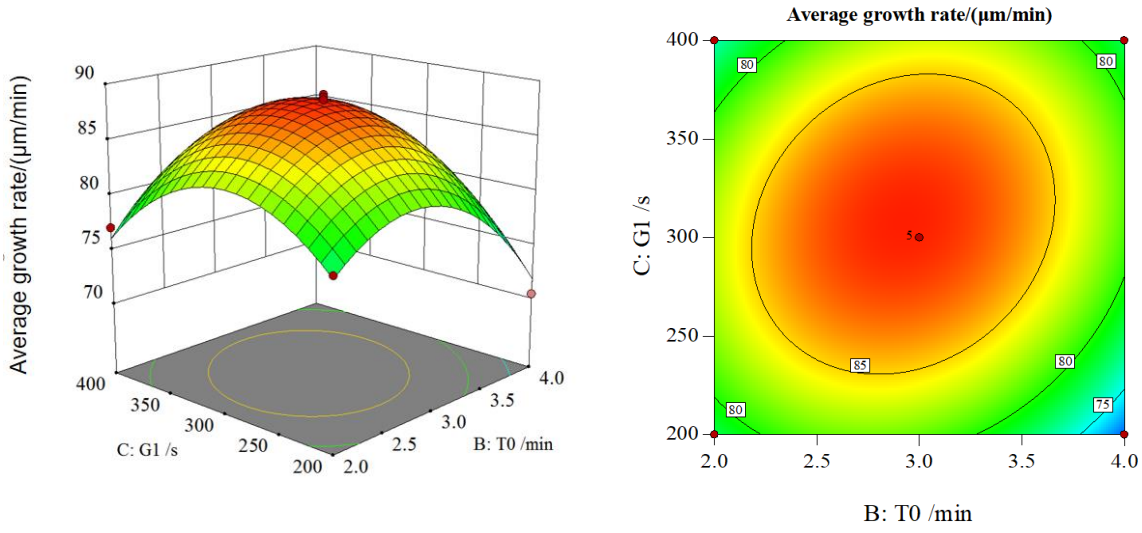


Figure 18. Effect of interaction between G_1 and T_0 on average growth rate.

With the maximum particle size growth rate as the optimization target, the experiment was optimized by Design-Expert 12, and the predicted particle size growth rate was 88.638 μm/min. The predicted values of the four factors were 2725.811/s for G_0, 2.881 min

for T0, 309.303/s for G_1, and 11.671 min for T_1. To determine the accuracy of the model, optimized parameters were used for verification tests. The experimental parameters were set as G_0 at 2700/s, T0 at 2.9 min, G_1 at 310/s, and T_1 at 11.7 min. The average growth rate of particle size was 88.56 ± 0.46 μm/min, which was not significantly different from the predicted value of 88.638 μm/min. This shows that the optimized process parameters of this model are reliable. At this time, potato wastewater treatment effect is the best.

3.5. Reuse of Flocculation Products

The components of the flocculated products recovered from flocculation were analyzed, and the important indexes of feed measured according to GB14924.3-2010 [22] are listed in Table 1. As shown in the table, the contents of calcium, total phosphorus, crude protein, lysine, and methionine all meet the national standard, indicating that the flocculation product has the potential to be transformed into feed.

Table 1. Analysis table of the flocculation product feed index.

	Calcium g/kg	Total Phosphorus mg/L	Crude Protein mg/L	Lysinemg/L	Methionine mg/L
Measured value	12	8	280	15.6	10.2
Standard value	≥10	>6	≥160	≥13.2	≥7.9

4. Conclusions

In summary, chitosan film modified by GTA was HTCC, which successfully improved the electropositivity and water solubility, and improved the flocculation effect. As the raw material is natural organic polymer material, the recycled organic matter is green, non-toxic and harmless, can be used as feed or fertilizer, greatly subsidizing the economic benefits of enterprises, and can promote the potato industry towards a healthy ecological development, but because chitosan can also be used in high-precision equipment production, the price is expensive, and a major difficulty in future focus is how to produce food-grade chitosan in large quantities, make its price popular, obtain a wider range of uses, and contribute to the construction of a green society.

Author Contributions: Y.W. and J.Z. (Writing—review and editing): preparation, creation and/or presentation of the published work by those from the original research group, specifically critical review, commentary or revision–including pre- or post-publication stages. H.Y. (Formal analysis): application of statistical, mathematical, computational, or other formal techniques to analyze or synthesize study data. S.Y. and G.L. (Conceptualization): ideas; formulation or evolution of overarching research goals and aims. Z.L. and J.W. (Resources): provision of study materials, reagents, materials, patients, laboratory samples, animals, instrumentation, computing resources, or other analysis tools. All authors have read and agreed to the published version of the manuscript.

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