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PRELIMINARY STUDY ON THE PREPARATION OF A NEW FLOCCULANT AND THE APPLICATION ON TREATMENT OF POTATO STARCH WASTEWATER

XIE AN[1], LI SHUJUN[1], LIN YALING[1], YANG BINGNAN[1], YANG YANCHEN[1], LIU JING[1]

1 X. An, Chinese Academy of Agricultural Mechanization of Science, China, xiean1985@hotmail.com

1 L. Shujun, lisj@caams.org.cn

1 Y. Bingnan, yangbn@caams.org.cn

1 Y. Yanchen, caamsyyc@sina.com

1 L. Y. Yaling2008@hotmail.com

1 L Jing, hanxiucao_1983@hotmail.com

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ABSTRACT To avoid problems as complex as operation, high cost and easily caused secondary pollution by traditional flocculant in treatment of potato starch wastewater, a new green environment-friendly polymer starch flocculants, quaternary amine cationic modified starch with a high degree of substitution (DS) was prepared via the reaction of potato starch with 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride (CHPTMA) using pre-drying dry process. Through the orthogonal test, the optimal conditions for preparing the cationic starch with high DS were: cationic etherifying agent dose %5 of starch (dry base), the mole ratio of NaOH to etherification substance is1, reaction temperature is 85°, reaction time is 5 h, getting the flocculant of cationic starch with 0.3903 DS. The results showed that the flocculation effects of the flocculant of cationic starch were increased with the increasing of the DS. The average result of treatment of potato starch wastewater showed that the flocculation rate was about 10% higher than that with using traditional polyacrylamide flocculant with the same reaction time and the same dosage.

Keywords: Potato starch wastewater, Flocculant, Cationic starch

INTRODUCTION In recent years, potato starch processing industry in China developed rapidly and production capacity reached 1.15 million tons per year. However, the heavy high density organic waste water and environmental pollution in potato starch processing have not been well treated. Flocculation processes is one of the most popular wastewater treatment processes, it has high practical value in the primary treatment process and the pretreatment stage. The flocculation efficiency depends largely on the characteristics of flocculant. At present, polyaluminium chloride and polyacrylamide are widely used in the treatment of food-processing wastewater. But the aluminum ion in traditional flocculant would induce Alzheimer's disease; polyacrylamide flocculant is hard to be degraded and the monomer has virulent poison, all of the above reasons will restrict the usage of the traditional flocculation. In recent years, non-toxic, easily biodegradable, wide variety of sources of raw materials, low price of natural modified polymer flocculants were used widely and widely [2-4].

In this paper, the study was mainly on the preparation of the quaternary amino groups containing cationic starch with a high degree of substitution (DS) which was prepared via the reaction of potato starch with 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride (CHPTMA) using pre-drying dry process and the effects of the DS of cationic modified starch (CMS) in different amount of etherification substance, different reaction temperature and different reaction time. Finally, the optimal conditions for preparing the cationic modified starch with high DS were obtained through the orthogonal test. Put the cationic modified starch with different DS into the treatment of potato starch wastewater, and get the relationship between the degree of cationic modified starch flocculant and the effect of the treatment of potato starch wastewater. Under the same flocculating conditions, compare the flocculation effects of the flocculant of cationic starch and traditional polyacrylamide flocculant in the treatment of potato starch wastewater.

METHODS AND MATERIALS

Materials Potato Starch, food-grade, Huhhot Huaou Starch co,.Ltd; PotassiumBiphthalate (HOOCC6H4COOK), potassium dichromate(K2Cr2O7), guarantee reagent, 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride (CHPTMA), polyacrylamide (PAM) and poly ferric sulfate (PFS) are all technical grade; sodium hydroxide(NaOH), acetic acid (CH3COOH), grain alcohol(CH3CH2OH), silver sulfate (Ag2SO4) and oil of vitriol (H2SO4) are all analytical reagents.

HG-9023A Electric Blast Drying Oven; KXL-1010 Digesting Apparatus; KDY-9820 Automatic Kjeldahl Azotometer; TB-9820 electronic balance; motor stirrer; Toshiba S-3400-Ⅱscanning electron microscope(SEM); FTIR Spectrometer; COD571 Chemical Oxygen Demand Analyzer

Preparation of Cationic Modified Starch (CMS) with High DS The NaOH is mixed in fixed proportion with CHPTMA and little water under 10℃ in 10 min by activation reaction. Spray the activated reagent on dry potato starch, beat till smooth, pre-dry for 1h under 50℃, put thepowder starch in a airtight container, can get white solid substance under certain temperature and time.

Dip the sample in 80% grain alcohol which contain certain acetic acid, then filtrate, clean and dry it, can get pure cationic starch.

Measurements of the DS of cationic modified starch[5] The total nitrogen concentration in CMS is analyzed by Kjeldahl method. Then use the equation（1） to calculate the DS of CMS.

$$DS=\frac{11.57\times(X_1-X_0)}{100-13.44\times(X_1-X_0)} \qquad (1)$$

In the equation, X1 stands for the nitrogen concentrations in CMS, %；X0 stands for the nitrogen concentrations in potato starch, %； 11.57, 13.44 are the reduction coefficients.

The characterization of CMS

<u>Scanning electron microscopy (SEM)</u> Sample preparation of SEM was as follow: the CMS samples were dried to constant weight. A thin layer of the sample granules was mounted on the copper sample-holder using a double sides carbon tape and coated with gold of 10 nm thicknesses to make the samples conductive. SEM studies were carried out using a scanning electron microscope (Toshiba S-3400-Ⅱ, Tokyo, Japan) at acceleration voltage of 30 kV.

<u>Infra-red spectral characterize</u> FT-IR measurements were performed on pellets of sample powder mixed with KBr. The sample quantity (between 2 and 6 mg) in KBr (200 mg) was chosen in order to optimize the pellet transmittance and to obtain a well detectable absorption.

Measurements were performed in the mid-infrared region, with a resolution of 4 cm-1, by using a FTIR Spectrometer.

Determination of the optimal conditions for getting the CMS with high DS According to documents and previous experiment, four influencing factors such as amine / starch, sodium hydroxide / amine molar ratios, reaction temperature and time were discussed on the DS of the CMS through the orthogonal test (As shown in Table 1), and get the optimal conditions for getting the CMS with high DS.

Table 1. Factors of preparation of CMS

No.	A amine / starch %	B sodium hydroxide / amine molar ratios	C reaction temperature /℃	D reaction time /h
1	45	1.0	75	3
2	50	1.2	80	4
3	55	1.4	85	5

Water quality analysis of potato starch wastewater The wastewater in this experiment came from the potato starch wastewater of Huhhot Huaou Starch co,.Ltd, it has many organic matters like protein (soluble & unsoluble) etc. The method for analyzing the main ingredients of wastewater is shown in Table 2; measurement for main emission allowance is shown in Table 3.

Table 2. The method for analyzing the main Ingredients of potato starch wastewater

No.	Ingredient	method
1	moisture	oven drying method
2	crude protein	kjeldahl
3	crude fiber	filtration method
4	starch	enzyme hydrolysis method
5	fat	Soxhlet

Table 3. Measurement and main emission allowance of potato starch wastewater

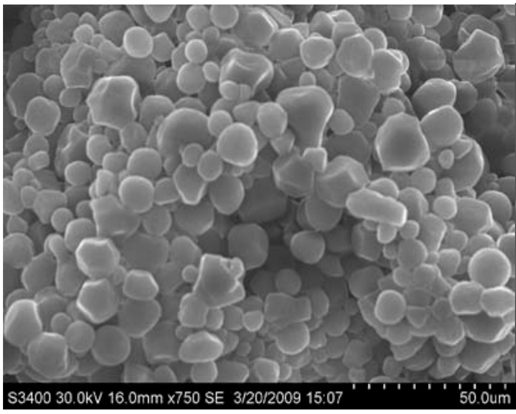
No.	Item	Measurement
1	COD_{Cr}	dichromate titration
2	BOD_5	dilution and seeding method
3	SS	gravimetric method
4	nitrogen content	distillation and titration
5	pH	

Analyze on the flocculation effects of CMS First, make the flocculant into solution with a certain concentration, as reserved. Put 150ml raw water into 250ml conical flask, add flocculant, and stir for 10min by stirrer and place for 2H. Centrifugalize 10min in the condition of 4200 RPM. Take the supematant liquid, measure COD by potassium dichromate method to observe the flocculation effects of the flocculant.

RESULTS AND ANALYZIS

The characterization of cationic starch

Electron Microscopy Analysis The microstructure of the potato starch crystal structure and crystal structure after CHPTMA were examined by scanning electron microscopy under the same magnification (Figure 1 and 2). From the figures, potato starch was similar to the round spherical particles, the particles clear, plump-eared, accumulate closely; and the space between the pellets can be seem clearly. The crystal structure of CHPTMA was close-embedded state, no clear space between the pellets; clear landfill structure can be seen because there were many comb-branched monomers around the backbone of pre-gelatinized starch matrix in the vicinity, which formatted flexible components and rigid skeleton interpenetration between the structures. The close-embedded structure of hardness and softness was the reason of excellent flocculation to CMS[6].



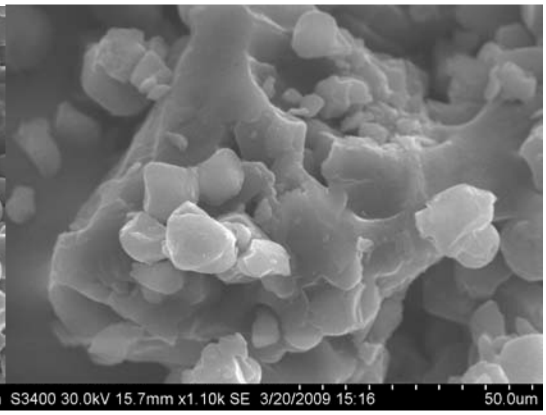


Figure 1. The microstructure of the potato starch crystal structure

Figure 2. Crystal structure after CHPTMA

Infra-red Spectral Characterize Figure 3, 4 and 5 show the FTIR Spectra of potato starch, CMS with low DS (0.0298) and CMS with high DS (0.3903).

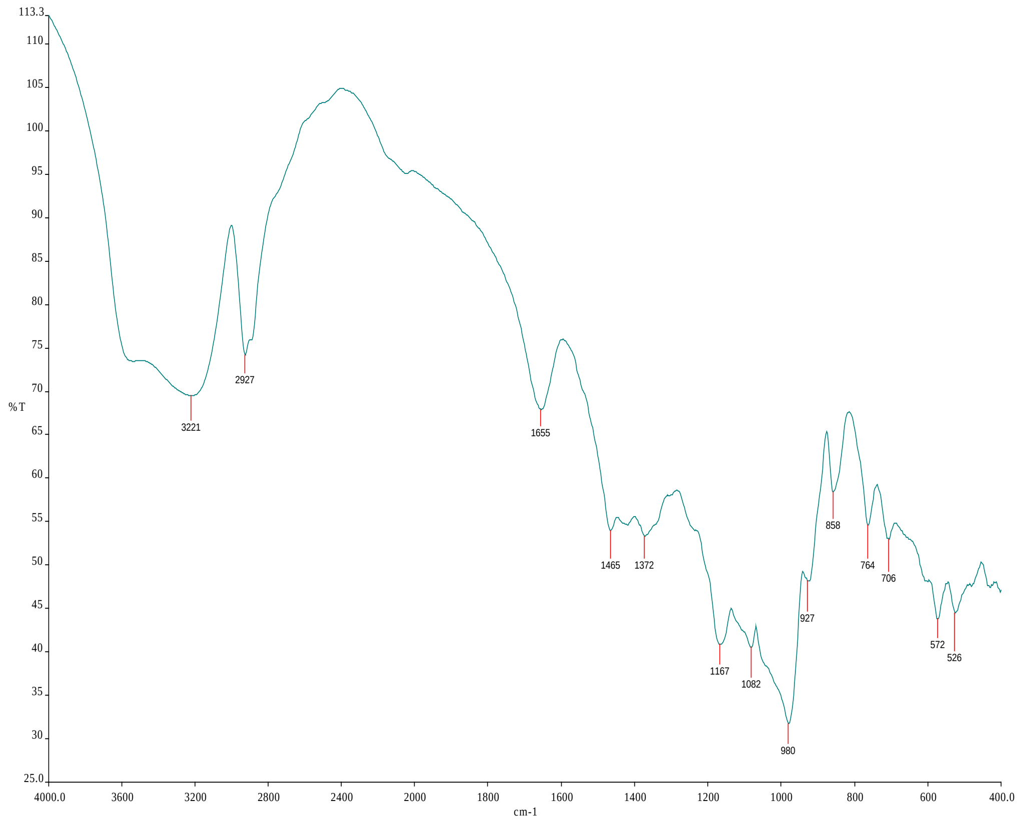


Figure 3. FTIR Spectra of potato starch

From the Figure 3, in the characteristic absorption peak of potato starch: 3221cm^{-1} is O-H stretching vibration, 2927 cm^{-1} is C-H stretching vibration and 1655 cm^{-1} is C=O stretching vibration.

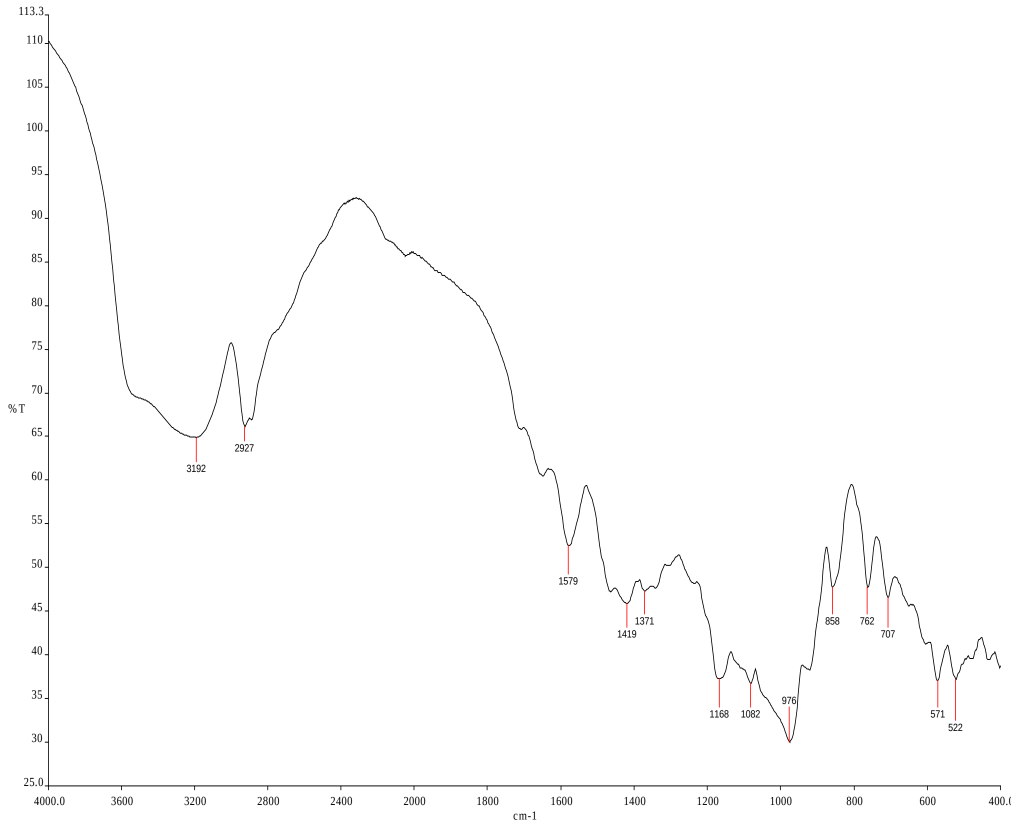


Figure 4. The FTIR Spectra of CMS(DS:0.0298)

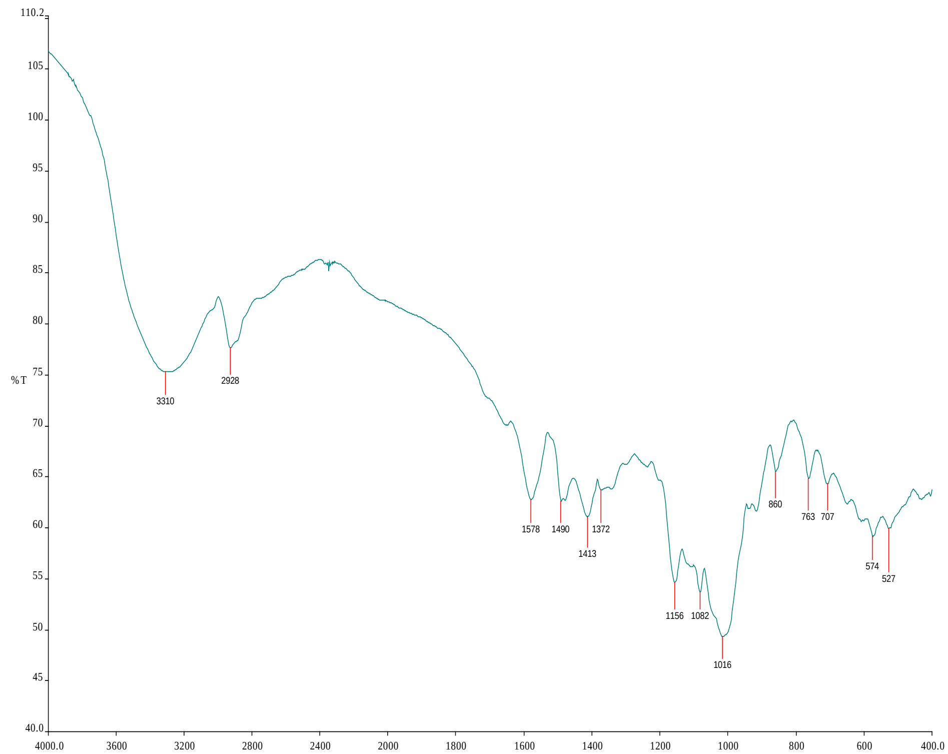


Figure 5. The FTIR Spectra of CMS(DS:0.3903)

Compare to the characteristic absorption peaks of FT-IR about potato starch, there were 1419 cm^{-1}, 1579 cm^{-1} and 2397 cm^{-1} in the FT-IR of CMS which presented the hydrocarbon bond stretching vibration of quaternary ammonium group, N-H deformation vibration and NH+ vibration, respectively. All of these characteristic peaks indicated there took places between CHPTMA and potato starch, and the quaternary ammonium groups had successfully linked to the native starch, which produced the CMS and proved the pre-drying preparation of a high DS of CMS is feasible.

The FT-IR of two degrees (0.0298 and 0.3903) of substitution of CMS had same spectra, except of the intensity of 1419 cm^{-1} were different which may be due to there were much more quaternary ammonium groups in the high degree of CMS.

Results of the orthogonal test According to the factors which influence the DS of CMS during the preparation of CMS, design the orthogonal test, the results are as shown below:

Table 4. Results of the orthogonal test

No.	A	B	C	D	N %	DS
1	1(45%)	1(1.0)	3(85℃)	2(4h)	1.679	0.2508
2	2(50%)	1(1.0)	1(75℃)	1(3 h)	1.476	0.2105
3	3(55%)	1(1.0)	2(80℃)	3(5 h)	1.903	0.2929
4	1(45%)	2(1.2)	2(80℃)	1(3 h)	0.327	0.0378
5	2(50%)	2(1.2)	3(85℃)	3(5 h)	1.288	0.1802
6	3(55%)	2(1.2)	1(75℃)	2(4 h)	1.076	0.1433
7	1(45%)	3(1.4)	1(75℃)	3(5 h)	0.571	0.0697
8	2(50%)	3(1.4)	2(80℃)	2(4 h)	0.263	0.0298
9	3(55%)	3(1.4)	3(85℃)	1(3 h)	1.131	0.1543
K_1	0.3583	0.7542	0.4235	0.4026		
K_2	0.4205	0.3613	0.3605	0.4239		
K_3	0.5905	0.2538	0.5853	0.5428		
k_1	0.1194	0.2514	0.1412	0.1342		
k_2	0.1402	0.1204	0.1202	0.1413		
k_3	0.1968	0.0846	0.1951	0.1809		
R	0.0774	0.1668	0.0749	0.0467		

From the Table 4 result of test No.3 is the best. The optimal preparation process conditions are: CHPTMA accounted for 55% of the amount of dry starch, the mole ratio of sodium hydroxide and CHPTMA is 1.0, reaction temperature is 80℃, and the reaction time is 5 hours. The final DS of CMS is 0.2929.

By analyzing K value, the optimal preparation process conditions are: CHPTMA accounted for 55% of the amount of dry starch, the mole ratio of sodium hydroxide and CHPTMA is 1.0, reaction temperature is 85℃, and the reaction time is 5 hours. The final DS of CMS is 0.3903.

By analyzing R value, the factors which influence the DS of CMS from high to low are: sodium hydroxide/CHPTMA molar ratios, CHPTMA/dry starch, reaction temperature and reaction time.

Analyzing of potato starch wastewater Table 5 and Table 6 are the wastewater of potato starch production and the main indicators of sewage. As can be seen from Table 5 that the protein content of starch wastewater is very high-up 2.19%.So it leads to COD values up to 49000 mg/L (Table 6). Although it is a non-toxic waste, the protein is very easy spoilage and Fermentation stink. That is the main sources of pollution of potato production and processing of wastewater.

Although the molecular weight of the protein of potato starch production wastewater is very large, it is able to maintain a stable soluble. The colloidal particle is with the same electric charge .They are mutually exclusive; at the same time, a number of hydrophilic groups of protein surface form a layer of film and take part in isolation between the colloidal particle [6], the joint action of two factors lead to its sinking difficult to unite into a group. So, if we remove the hydration film and offset charge, the protein will precipitate from solution.

Table 6. Ingredient of potato starch wastewater

No.	Ingredient	content
1	moisture	96%
2	crude protein	2.19%
3	crude fiber	0.052%
4	starch	1.0g/100ml
5	fat	0.002%

表7马铃薯淀粉生产废水主要排污指标

Table 7. The main indicators of sewage of potato starch wastewater

No.	Ingredient	content
1	COD_{Cr}	49000 mg/L
2	BOD_5	5551-1000 mg/L
3	SS	3370 mg/L
4	nitrogen content	20.28 mg/L
5	pH	6.0

Evaluation of the flocculation performance of novel cationic starch After compounding with a different DS of CMS flocculant and traditional cationic polyacrylamide and PFS, it deals with potato starch to product wastewater. After a certain period of time, we determine the COD removal efficiency of potato starch wastewater. The results as shown in the table:

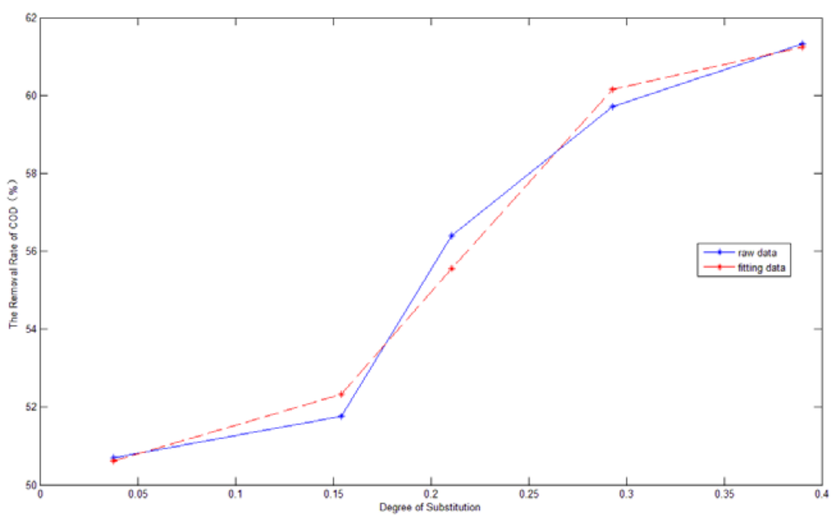


Figure 6. The relationship of the removal rate of COD and DS of the CMS

As shown on Figure 6, the removal rate of COD of the wastewater rises when the DS of the CMS get higher. Because only the charge density increase, the charge-neutralizing ability would add, when the DS of the CMS get higher, the ability of adsorption of flocculation is also increase so the higher DS the better flocculating effect. The cubic curve fitting of the DS of CMS and the COD removal efficiency of potato starch wastewater can be got. The equation can be got form MATLAB as follow:

$$Y = -1005.5X^3 + 650.8X^2 - 79.1X + 52.7 \qquad (2)$$

In the equation, X stands for the DS of CMS; Y stands for the COD removal efficiency of potato starch wastewater, %; 1005.5 , 650.8, 79.1, 52.7 are the reduction coefficients.

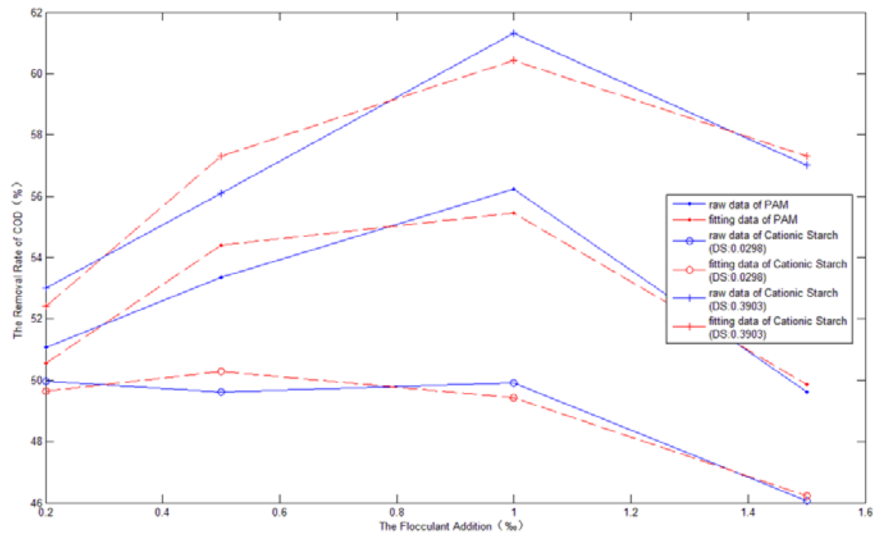


Figure 7. The flocculation effects of different flocculats

As shown on Figure 7, the flocculation effects of the PAM treatment of potato starch wastewater was worse than the CMS with a higher DS, but better than the CMS with a lower DS. That is because the tree kinds of flocculation were all the cationic type, it can adsorb potato protein particles being neutralized by the electricity, putting up bridge, get up flocculation effect, reduce COD. When the flocculation were added over the maximum concentration, the flocculating effect went down, the reason is that as more CMS was put in the water, the density of the positive charge in the solution was raised, and the potato protein particles got positive charge by adsorption, and lead the charge repulsion, reduce the flocculation effect. The conic curve fitting of the amount of flocculation in CMS and the COD removal efficiency of potato starch wastewater can be got. The equation can be got form MATLAB as follow:

$$Y = -12.5Z_1^2 + 25Z_1 + 47.9 \qquad (3)$$

In the equation, Z1 stands for the amount of flocculation in CMS (DS: 0.3903) ; Y stands for the COD removal efficiency of potato starch wastewater, %; 11.57, 13.44 are the reduction coefficients.

$$Y = -13.3Z_2^2 + 22Z_2 + 46.6 \qquad (4)$$

In the equation, Z2 stands for the amount of cationic PAM; Y stands for the COD removal efficiency of potato starch wastewater, %; 13.3 , 22, 46.6 are the reduction coefficients.

$$Y = -4.7Z_3^2 + 5.4Z_3 + 48.7 \qquad (5)$$

In the equation, Z3 stands for the amount of flocculation in CMS (DS: 0.0298) ; Y stands for the COD removal efficiency of potato starch wastewater, %; 4.7 , 5.4, 48.7 are the reduction coefficients.

CONCLUSION The CMS flocculants with high DS obtained via pre-drying dry process has a wide range of sources of raw materials, simple preparation procedure, low cost and it's non-toxic as well as easily degradable.

By orthogonal experiment, the optimal preparation process conditions of obtaining CMS with a higher DS are: CHPTMA accounted for 55% of the amount of dry starch, the mole ratio of sodium hydroxide and CHPTMA is 1.0, reaction temperature is 85℃, and the reaction time is 5 hours.

The flocculation experiments of the wastewater of potato starch production showed that when used as a flocculant, the cationic starch with a high DS has much greater flocculating effect in the experiments than that with a lower DS.

When the cationic starch's DS is 0.3903 by adding volume of 1.0 ‰, the initial wastewater pH is 6.0, and PFS compound when used, the removal rate of COD in the wastewater comes up to 64.32%.

When dosage is the same as in the case, its flocculating effect of handling potato starch wastewater is about 10% higher than the traditional polyacrylamide flocculant on average.

At the same time, compared with polyacrylamide, CMS with high DS also has advantages like non-toxic, easily biodegradable, wide variety of sources of raw materials, low cost and so on.

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