

# Cationic Polyacrylamide Emulsion with Ultra-high Concentration as a Flocculant for Paper Mill Wastewater Treatment

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Cationic polyacrylamide emulsions prepared with ultra-high concentration (CPAME-uhc) have the advantages of fast dissolution, convenient operation, and low transportation cost. In order to further improve the molecular weight, solubility, and temperature/salt resistance of CPAME-uhc, in this study the preparation process of CPAME-uhc was optimized, and the effects of solubilizing agents and functional monomers on solubility and temperature/salt resistance of CPAME-uhc were evaluated. Finally, the flocculation performance of CPAME-uhc on papermaking wastewater was examined. The results showed that the molecular weight of CPAME-uhc can be increased to 14 to 15 million by process optimization, and the solubility of CPAME-uhc can be greatly increased by adding urea and Na<sub>2</sub>SO<sub>4</sub>. The temperature/salt resistance of CPAME-uhc can be improved by adding 2 wt% N,N-dimethylacrylamide, 2 wt% N-vinylpyrrolidone, and 5 wt% sodium 2-acrylamide-2-methylpropionate, based on the total monomer weight. When CPAME-uhc was added to papermaking wastewater the removal percentages of chemical oxygen demand (COD) and suspended solid (SS) were 95% and 93%, respectively. This study provides a useful reference for the preparation, optimization and application of CPAME-uhc.

*Keywords:* Polymer emulsion with ultra-high concentration; Cationic polymer; Flocculation; Paper mill wastewater

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## INTRODUCTION

Cationic polyacrylamide (CPAM) is a linear macromolecule compound. Because of its various active groups, it can adsorb many substances to form hydrogen bonds (Ma *et al.* 2017; Li *et al.* 2018). For example, it can flocculate colloids with negative charges (Xu *et al.* 2014) and has the functions of decolorization, adsorption, adhesion, and turbidity removal (Ochoa *et al.* 2006; Patel *et al.* 2011). It is widely used for treatment of papermaking wastewater having high organic impurities (Swerin 1998; Solberg and Wagberg 2003; Schwarz *et al.* 2007; Yoon *et al.* 2012), dyeing and finishing (Yang *et al.* 2013; Gupta *et al.* 2015), mineral processing (Zhou and Franks 2006; Ji *et al.* 2013), oil field (Guo *et al.* 2014; Li *et al.* 2014), food (Pinotti *et al.* 2001), and brewing industries (Liu and Jin 2009). It is used in the dewatering treatment of municipal sludge (Zheng *et al.* 2014), paper-making sludge (Wu *et al.* 2019), and other industrial sludge (Besra *et al.* 2003; Wang *et al.* 2019). Because of its wide application, it is an important synthetic water-soluble polymer.

Traditional cationic polyacrylamide powder products have many problems associated with their application, such as difficulty of dissolving, slow dissolution speed, and the need for large dissolution equipment, *etc.* The cationic polyacrylamide emulsion products obtained by conventional emulsion polymerization usually have excellent solubility and simple operation, but with low concentrations and high transportation cost. Cationic polyacrylamide emulsions with ultra-high concentration (CPAME-uhc) can obviously save transportation costs, but their molecular weight, solubility, and temperature/salt resistance need to be further improved.

Therefore, this study attempted to improve the molecular weight of CPAME-uhc by optimizing the preparation conditions. A further goal was to increase the solubility and temperature/salt resistance of CPAME-uhc by adding suitable solvents and functional monomers. The flocculation effect of the obtained CPAME-uhc on paper making wastewater is also tested. The purpose of this paper is to provide valuable reference for the preparation of high-performance CPAME-uhc and for its application in various complex industrial wastewater treatment.

## EXPERIMENTAL

### Materials

White oil and D40 oil were produced by ExxonMobil. Acrylamide, cationic monomer (DAC, 80%), and sodium 2-acrylamide-2-methylpropionate sulfonate (50%) were industrial pure and provided by Feymer (Zhangjiagang City, China). Span80, Tween 61, V50, sodium sulfate, urea, and sodium phosphate were chemical pure purchased from Beijing Chemical Reagent Company (Beijing, China). Ammonium persulfate, sodium bisulfite, phase changer TX-10, crosslinking agent (N,N-methylene sulfate) *b*iacrylamide, N, N-dimethylacrylamide, and N-vinylpyrrolidone were the analytical purities purchased from Beijing Chemical Reagent Company. The macromolecule stabilizer (22%) was self-made.

### *Preparation of CPAME-uhc*

Oil and water phases were prepared in proportion in 1000 mL beakers. The water phase was slowly poured into the oil phase by a peristaltic pump, and the mixture was emulsified for 10 min at 8000 r/min by a homogenizer. The emulsion was poured into a flask and charged with nitrogen for 1 h at a constant stirring speed of 300 r/min. The reaction was started by dropping redox initiator, and the temperature rise rate was controlled by controlling the acceleration of initiator droplets. The residual monomer was removed by dropping initiator rapidly for 3 min after the temperature no longer increased. After 30 min of heat preservation, the effective concentration of the emulsion was increased to about 60% by using the rotary distiller. Next, 1.5% phase transfer agent was added to the product to obtain emulsion products of CPAME-uhc.

### *Determination of molecular weight*

The cationic polymer emulsion was precipitated with a mixture of ethanol and acetone with a volume ratio of 1:1. The precipitates were washed repeatedly with the mixture and then filtered and dried. According to GB/T 31246 (2014), the intrinsic viscosity ( $\eta$ ) of cationic polymers was determined by an Ubbelohde viscometer and calculated using Eqs. 1 and 2,

$$M = 802 [\eta]^{1.25} \quad (1)$$

$$[\eta] = kM^\alpha \quad (2)$$

where  $\eta$  is intrinsic viscosity (mL/g),  $k = 4.75 \times 10^{-3}$  is an empirical constant, and  $\alpha = 0.80$  is an empirical constant.

#### *Evaluation of solubility, temperature, and salt resistance*

The dissolution time of CPAME-uhc in deionized water was determined by the conductivity method according to GB/T 31246 (2014). CPAME-uhc was dissolved in NaCl salt with salinity of 0.5% to form a 2000 mg/L solution. The solution was aerated with nitrogen to remove oxygen and then placed in an oven at 75 °C. The bulk viscosity of the solution was measured after 0, 3, 10, 20, and 30 days of storage, and the retention values of the solution viscosity were calculated based on a viscosity of 0 days of storage.

#### *Evaluation method of flocculation performance COD removal*

The COD of wastewater, marked as  $COD_0$ , and the COD of supernatant after flocculation, marked as  $COD_1$ , were determined according to GB/T 11914 (1989). The COD removal percentage was then calculated according to Eq. 3.

$$\text{COD removal (\%)} = \left(1 - \frac{COD_1}{COD_0}\right) \times 100 \quad (3)$$

#### *SS removal*

The suspended matter content of paper-making wastewater was recorded as  $SS_0$  and determined according to the national standard GB/T 11901 (1989). The suspended matter content of supernatant after flocculation and sedimentation was recorded as  $SS_1$ . The SS removal percentage was calculated according to Eq. 4.

$$\text{SS removal (\%)} = \left(1 - \frac{SS_1}{SS_0}\right) \times 100 \quad (4)$$

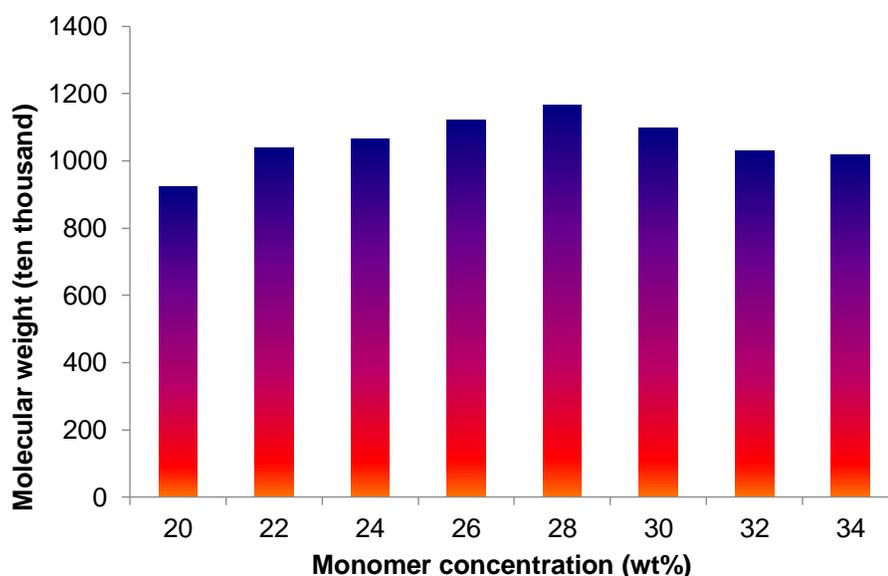
## RESULTS AND DISCUSSION

### **Effect of Monomer Concentration on Molecular Weight of CPAME-uhc**

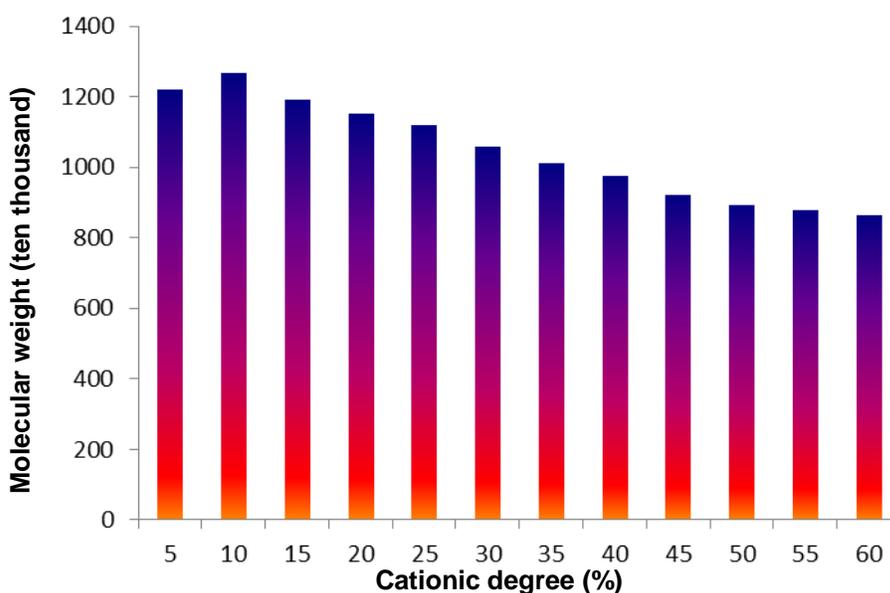
Inverse emulsion polymerization is based on each latex particle as a polymerization unit. The change of monomer concentration leads to a change in the monomer number of a single colloidal particle, thus affecting the molecular weight of the polymer (Pabon *et al.* 1999). Figure 1 shows the influence of monomer concentration on the molecular weight of CPAME-uhc.

The molecular weight of the cationic polymer emulsion increased first and then decreased with the increase of monomer concentration. The molecular weight was the largest when the monomer concentration was 28 wt% (based on the total weight of all monomers). With relatively low monomer concentration, less than 28 wt%, the molecular weight of an emulsion increased with the increase of monomer concentration. This result agrees with the mechanism of free radical polymerization. However, when the concentration of monomers was too high, greater than 28 wt%, the viscosity of the system increased greatly with the progress of polymerization. This resulted in the monomer not being able to diffuse to the active group of the increasing macromolecular chain in time; thus the degree of polymerization could not continue to increase. In addition, due to the high concentration of monomers, the reaction heat was difficult to transfer rapidly from the

viscous particles to the medium, resulting in local overheating of the reaction, which possibly led to the reduction of the molecular weight of the product. In conclusion, 28 wt% concentration was the optimum concentration for polymerization.



**Fig. 1.** Influence of monomer concentration on the molecular weight of CPAME-uhc. The monomer concentration is based on the total emulsion weight. The cationic degree is 20 wt% based on the total monomer weight. The cosolvent dosage is 1 wt%, and the crosslinking agent is 0.2 ppm both based on the total monomer weight. The initial temperature is 6 °C, and the maximum heating rate is 6.5 °C/min. The stirring speed is 300 r/min. The standard deviation of monomer concentration is  $\pm 0.5\%$ . The standard deviation of molecular weight is  $\pm 0.3$  million.



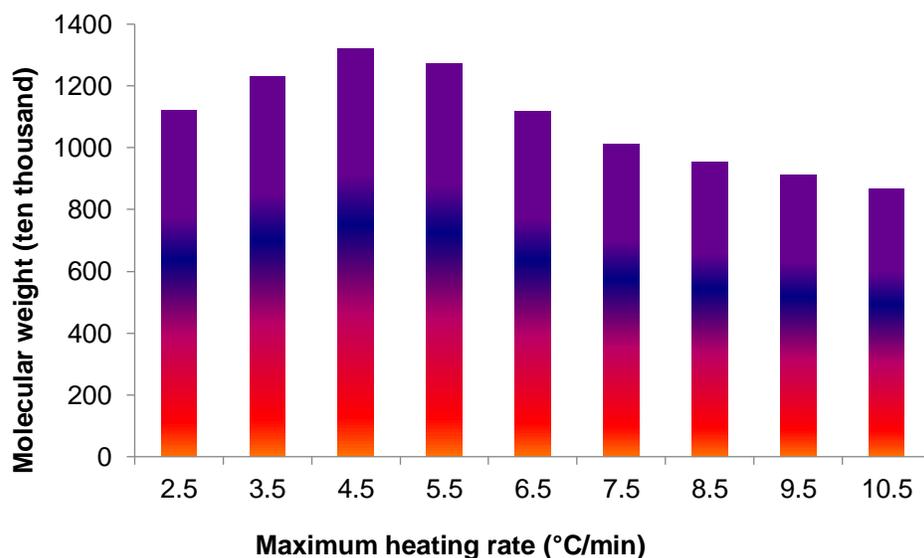
**Fig. 2.** Effect of cationic degree on molecular weight of CPAME-uhc. The monomer concentration was 28 wt% based on the total emulsion weight. The cationic degree was based on the total monomer weight. The cosolvent dosage was 1 wt%, and the crosslinking agent was 0.2 ppm, both based on the total monomer weight. The Initial temperature was 6 °C and the maximum heating rate was 6.5 °C/min. The stirring speed is 300 r/min. The standard deviation of cationic degree is  $\pm 0.4\%$ . The standard deviation of molecular weight is  $\pm 0.3$  million.

### Effect of Cationic Degree

As shown in Fig. 2, the molecular weight of CPAME-uhc decreased gradually with the increase of cationic degree, which is mainly attributable to the poor activity of cationic monomer than acrylamide monomer. With the increase of cationic monomer ratio, the monomer activity in emulsion polymerization systems decreased, so the molecular weight of the obtained product was relatively low. The molecular weight of the emulsion decreased slowly when the cationic degree was between 20% and 25%. When the cationic degree was greater than 30%, the decrease of the emulsion was more obvious. To ensure the flocculation effect of anionic garbage and other substances in wastewater, the optimum cationic degree was 25%.

### Effect of Maximum Temperature Rise Rate

The acceleration of initiator droplets affects the maximum temperature rise rate, which reflects the reaction rate. According to the theory of free radical polymerization, when the addition level of initiator is appropriate, the initial free radical concentration can activate enough active segments in the latex particles of fixed concentration systems to meet the requirement of polymer chain enlargement, so polymers with maximum molecular weight can be obtained. When the initiator is added slowly, the concentration of free radicals is too small, and the number of active chains generated is not enough to maintain the growth of long chains. This leads to the termination of some molecular chains, resulting in the low molecular weight of the polymer. When the initiator drops too fast, the free radical concentration is large and exceeds the growth demand of the original active chain. The excess part will generate a large number of new active free radical chains, resulting in the rapid concentration of monomers, so that the number of the final active free radical chains is small and the molecular weight of the polymer is low.



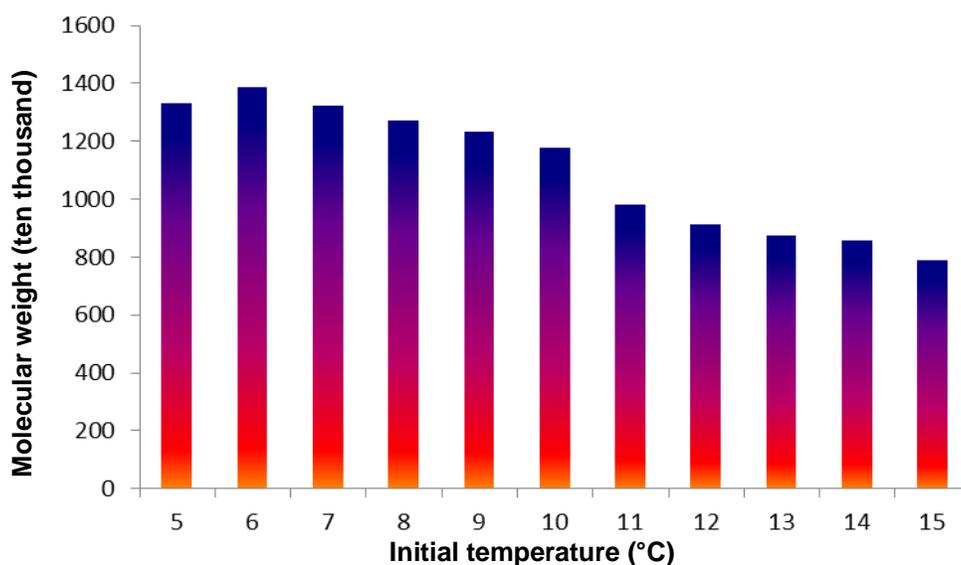
**Fig. 3.** Effect of maximum heating rate on molecular weight of CPAME-uhc. The monomer concentration was 28 wt% based on the total emulsion weight. The cationic degree was 25 wt% based on the total monomer weight. The cosolvent dosage was 1 wt%, and the crosslinking agent was 0.2 ppm, both based on the total monomer weight. The Initial temperature was 6 °C; and the stirring speed was 300 r/min. The standard deviation of maximum heating rate was  $\pm 0.1$  °C/min. The standard deviation of molecular weight was  $\pm 0.3$  million.

Figure 3 shows that the molecular weight of CPAME-uhc increased first and then decreased while the maximum heating rate increased. The highest molecular weight of emulsion was obtained when the maximum heating rate was 4.5 to 5.5 °C/min.

### Effect of Initial Temperature

Generally speaking, if the initial temperature is low, the reaction speed will be slow, which will affect the polymerization efficiency. When the initial reaction temperature is too high, excessive initial active free radical chains will be produced, resulting in a low molecular weight of the polymer.

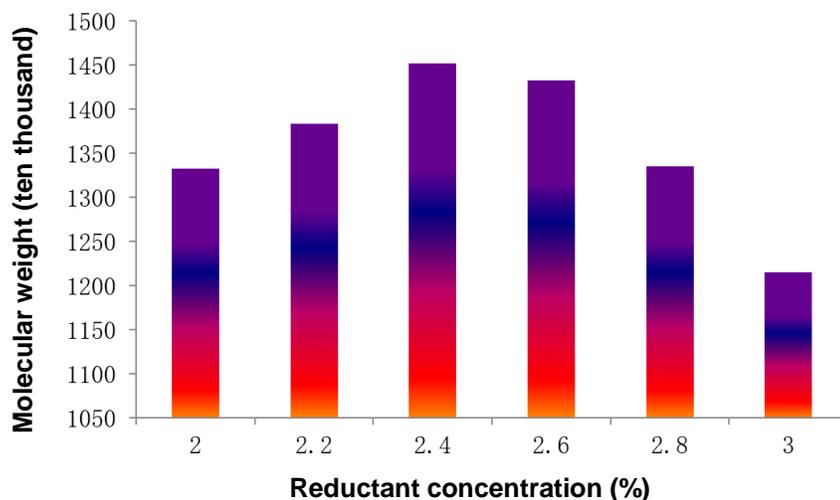
Figure 4 shows that if the initial temperature was below 10 °C, it had little effect on the molecular weight of the CPAME-uhc. Considering the reaction efficiency, the optimum initial temperature was between 6 and 8 °C.



**Fig. 4.** Effect of initial temperature on molecular weight of CPAME-uhc. The monomer concentration was 28 wt% based on the total emulsion weight. The cationic degree was 25 wt% based on the total monomer weight. The cosolvent dosage was 1 wt%, and the crosslinking agent was 0.2 ppm, both based on the total monomer weight. The maximum heating rate was 4.5 °C/min, and the stirring speed was 300 r/min. The standard deviation of initial temperature was  $\pm 0.1$  °C. The standard deviation of molecular weight was  $\pm 0.3$  million.

### Effect of Reductant Concentration

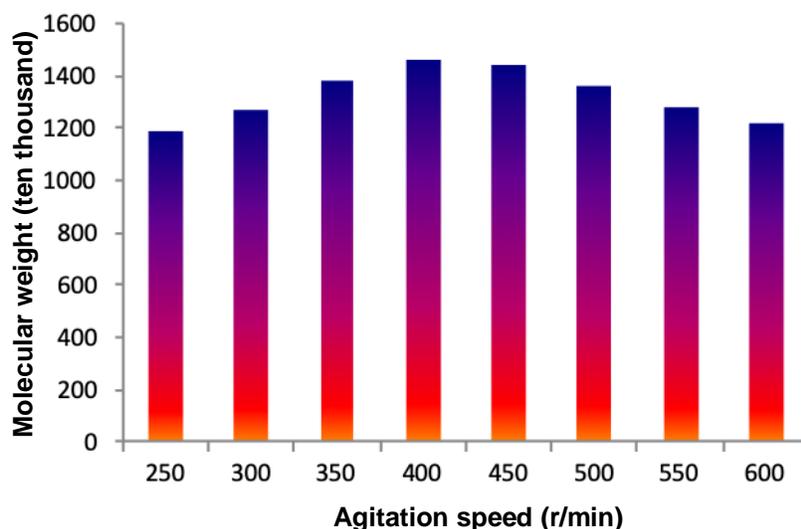
According to the mechanism of free radical polymerization, the appropriate amount of reductant and oxidant is beneficial to the preparation of high molecular weight products. Therefore, the effect of reducing agent concentration on the molecular weight of super high concentrated cationic emulsions was investigated under constant oxidant concentration of 3% and the same injection level of oxidant and reducing agent. Figure 5 shows that when the reducing agent concentration was 2.4% and 2.6%, the molecular weight of the CPAME-uhc was the highest. Therefore, the optimum range of reductant concentration was between 2.4% and 2.6%.



**Fig. 5.** Effect of reductant concentration on molecular weight of CPAME-uhc. The monomer concentration was 28 wt% based on the total emulsion weight. The cationic degree was 25 wt% based on the total monomer weight. The cosolvent dosage was 1 wt%, and the crosslinking agent was 0.2 ppm, both based on the total monomer weight. The initial temperature was 7 °C, and the maximum heating rate was 4.5 °C/min. The stirring speed was 300 r/min. The standard deviation of reductant concentration was  $\pm 0.1$  °C. The standard deviation of molecular weight was  $\pm 0.3$  million.

### Effect of Stirring Speed

The effect of stirring rate on the dispersion of monomer aqueous solution in continuous oil phase is inevitable because the inverse emulsion is not a thermodynamically stable system (Tamsilian *et al.* 2016). The stirring speed can increase the collision between the latex particles and initiate the diffusion of the system.



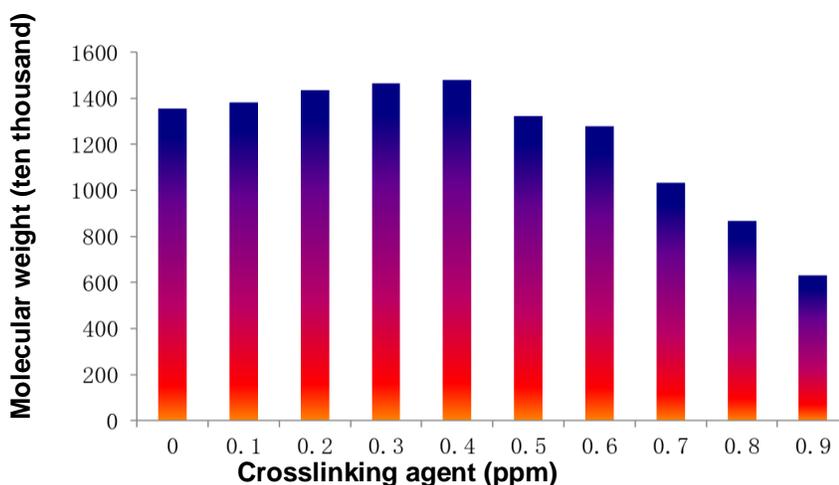
**Fig. 6.** Effect of stirring speed on molecular weight of CPAME-uhc. The monomer concentration was 28 wt% based on the total emulsion weight. The cationic degree was 25 wt% based on the total monomer weight. The crosslinking agent was 0.2 ppm, and the cosolvent dosage was 1 wt%, both based on the total monomer weight. The Initial temperature was 7 °C, and the maximum heating rate was 4.5 °C/min. The standard deviation of agitation speed was  $\pm 10$  r/min. The standard deviation of molecular weight was  $\pm 0.3$  million.

Figure 6 shows that the molecular weight of the polymer was increased gradually by increasing the stirring speed from 250 r/min to 400 r/min. The increase of stirring speed can help heat transfer and initiator diffusion, which is conducive to the production of high molecular weight products by polymerization. However, when the stirring speed is too high (Barari *et al.* 2011), the latex particles may be dispersed into too small particles, thus affecting the monomer volume required for chain growth, resulting in a decrease in the molecular weight of the product. In addition, rapid stirring may involve a large amount of air. Oxygen inhibits polymerization, leading to chain termination reaction, which could cause the reduction of the molecular weight of the polymer (Benda *et al.* 2001). Thus, the chosen stirring speed was 400 r/min.

### Effect of Crosslinker Dosage

The functional groups in the crosslinking agent molecule, mainly reactive bifunctional groups, react with the macromolecule chemicals and cross-link the macromolecules through the crosslinking agent as a bridge to form a larger molecular structure polymer (Wu *et al.* 2012). The cross-linking agent MBA has two identical and very active reactive functions. It can make the polymer rapidly and efficiently change from a linear structure to a bulk network structure (Cao *et al.* 1999) and further increase the molecular weight of the product.

As shown in Fig. 7, the molecular weight of super high concentrated cationic emulsions increased first and then decreased with the increase of crosslinking agent dosage. When the amount of crosslinking agent was 0.4 ppm, the molecular weight of CPAME-uhc was the highest. When the amount of crosslinking agent exceeded 0.6 ppm, the molecular weight of cationic polymer emulsion decreased obviously. When the concentration of crosslinking agent was too large, the solubility of some polymers decreased due to the excessive crosslinking point and the dense cross-linking network, leading to inaccurate determination of molecular weight and low molecular weight measurement results.



**Fig. 7.** Effect of crosslinking agent dosage on molecular weight of CPAME-uhc. The monomer concentration was 28 wt% based on the total emulsion weight. The cationic degree was 25 wt% based on the total monomer weight. The cosolvent dosage was 1 wt% based on the total monomer weight. The dosage of crosslinking agent also based on the total monomer weight. The Initial temperature was 7 °C, and the maximum heating rate was 4.5 °C/min. The stirring speed was 400 r/min. The standard deviation of crosslinking agent was  $\pm 0.01$  ppm. The standard deviation of molecular weight was  $\pm 0.3$  million.

**Table 1.** Effect of Compound Use of Cosolvent on the Properties of CPAME-uhc

Cosolvent (%)			Monomer Concentration (%)	Cationic Degree (%)	Max. Heating Rate (°C/min)	Initial Temperature (°C)	Crosslinking Agent (ppm)	Molecular Weight (ten thousand)	Dissolution Time (s)
CO(NH <sub>2</sub> ) <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>3</sub> PO <sub>5</sub>							
—	—	—	28	25	4.5	8.0	0.2	1153	25
1	—	—	28	25	4.5	8.0	0.2	1176	21
2	—	—	28	25	4.5	8.0	0.2	1215	19
3	—	—	28	25	4.5	8.0	0.2	1332	18
—	1	—	28	25	4.5	8.0	0.2	1307	19
—	2	—	28	25	4.5	8.0	0.2	1363	17
—	3	—	28	25	4.5	8.0	0.2	1322	16
—	—	1	28	25	4.5	8.0	0.2	1285	22
—	—	2	28	25	4.5	8.0	0.2	1240	20
—	—	3	28	25	4.5	8.0	0.2	1200	19
1	2	—	28	25	4.5	8.0	0.2	1430	15
2	1	—	28	25	4.5	8.0	0.2	1373	16
1	—	2	28	25	4.5	8.0	0.2	1325	19
2	—	1	28	25	4.5	8.0	0.2	1365	18
—	1	2	28	25	4.5	8.0	0.2	1346	18
—	2	1	28	25	4.5	8.0	0.2	1316	17

The standard deviation of molecular weight was  $\pm 0.3$  million. The standard deviation of dissolution time was  $\pm 1$  s.

## Performance Optimization of CPAME-uhc

### *Solubility enhancement*

To solve the poor solubility of the CPAME-uhc after thickening, some dissolving aids, such as sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), urea ( $\text{CO}(\text{NH}_2)_2$ ), or sodium phosphate ( $\text{Na}_3\text{PO}_5$ ), can be added without affecting the performance and quality index of the product. These additives improve the temperature resistance of CPAME-uhc. For example,  $\text{CO}(\text{NH}_2)_2$  can weaken or block the formation of dipole or hydrogen bonds between  $-\text{CONH}_2$  in the dissolution process of CPAME-uhc and inhibit the association of polyacrylamide (PAM) molecules.  $\text{Na}_2\text{SO}_4$  is a strongly polar material with high water solubility. Its presence in cationic emulsion particles enhances the hydration of colloidal particles and forms sponge holes on the surface of PAM in colloidal particles. These factors improve the dissolution rate of CPAME-uhc. The solubilization mechanism of  $\text{Na}_3\text{PO}_5$  is similar to that of  $\text{Na}_2\text{SO}_4$ . Therefore, a product with good solubility and high molecular weight can be obtained by mixing urea with  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_3\text{PO}_5$ , or both.

Table 1 shows that although the action mechanism of  $\text{Na}_3\text{PO}_5$  and  $\text{Na}_2\text{SO}_4$  is the same, the  $\text{Na}_3\text{PO}_5$  was less effective than the  $\text{Na}_2\text{SO}_4$ . When the dosage of  $\text{CO}(\text{NH}_2)_2$  was 1% and the dosage of  $\text{Na}_2\text{SO}_4$  was 2%, the CPAME-uhc had the highest molecular weight and good solubility. Therefore, adding 1%  $\text{CO}(\text{NH}_2)_2$  and 2%  $\text{Na}_2\text{SO}_4$  increased the molecular weight of the CPAME-uhc and improved its solubility.

### Optimization of Temperature and Salt Resistance

With the rapid development of modern industry, the composition of industrial wastewater is becoming more complex, and the water quality is getting worse (Liu *et al.* 2014). Especially for wastewater with high salt concentration, the polymer chains of common cationic polymers will curl, and the viscosity is greatly reduced, which does not meet the requirements of modern industrial wastewater treatment.

**Table 2.** Temperature and Salt Resistance of CPAME-uhc

Sample	Cross-linking agent /ppm	DA /%	VP /%	AMS /%	Viscosity Retention / %				Molecular weight (x 10,000)
					After 3 days	After 10 days	After 20 days	After 30 days	
1	0.2	0	0	0	90.3±0.5	78.1±0.3	63.8±0.4	58.6±0.2	1351
2	0.2	1	1	1	95.7±0.5	85.6±0.3	75.6±0.4	65.5±0.2	1384
3	0.2	2	2	2	97.6±0.5	88.9±0.3	78.3±0.4	66.9±0.2	1319
4	0.2	2	2	3	97.9±0.5	89.1±0.3	78.5±0.4	67.2±0.2	1276
5	0.2	2	2	4	98.2±0.5	89.2±0.3	78.6±0.4	67.4±0.2	1256
6	0.2	2	2	5	98.4±0.5	89.4±0.3	79.1±0.4	67.5±0.2	1212
7	0.2	2	2	6	98.5±0.5	89.5±0.3	79.2±0.4	67.3±0.2	1167
8	0.2	2	2	7	98.4±0.5	89.5±0.3	79.0±0.4	67.4±0.2	1125
9	0.2	3	3	5	98.8±0.5	90.1±0.3	80.5±0.4	68.6±0.2	967
10	0.2	4	4	5	99.1±0.5	90.5±0.3	81.2±0.4	69.2±0.2	653

Note: The concentration of salt solution is 5000 mg/L. Viscosity test condition: 0# rotor, 6 rotations, 75 °C solution, concentration is 2000 mg/L. The standard deviation of molecular weight is ±0.3 million.

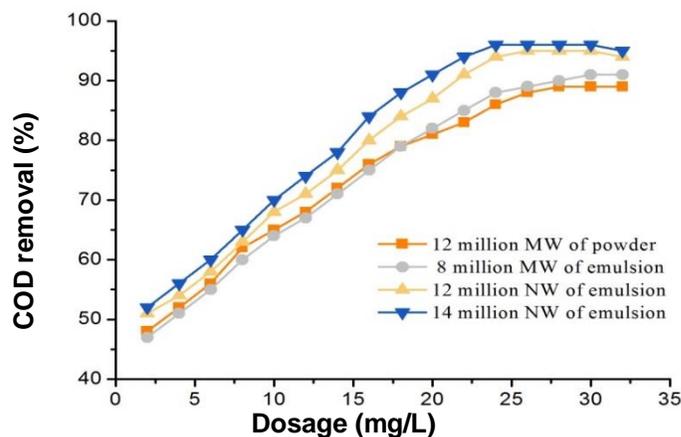
To satisfy the requirements of various inferior wastewater treatments, it is necessary to improve the salt and temperature resistance of flocculants. The introduction of thermostable and salt-resistant functional molecules, as well as long chain side groups and rigid or flexible side groups in polymers, can achieve the goal of hydrolysis resistance and hard chain breaking of polymers at high temperature and high salinity. In this paper, the improvement effects of temperature-resistant monomers dimethylacrylamide (DA), vinylpyrrolidone (VP), and salt-resistant monomers 2-acrylamide-2-methylpropionic sulfonate (AMS) were considered.

As shown in Table 2, the temperature and salt resistance of the emulsion increased significantly after the addition of heat and salt resistant monomers. When the dosage of DA and VP was more than 2%, the molecular weight of the product decreased due to excessive crosslinking, although the temperature and salt resistance improved. When the dosage of DA and VP was 2%, the dosage of crosslinking agent was 0.2 ppm, and the dosage of AMS was 5%, the molecular weight of the product decreased slightly, but the temperature and salt resistance of the product obviously improved.

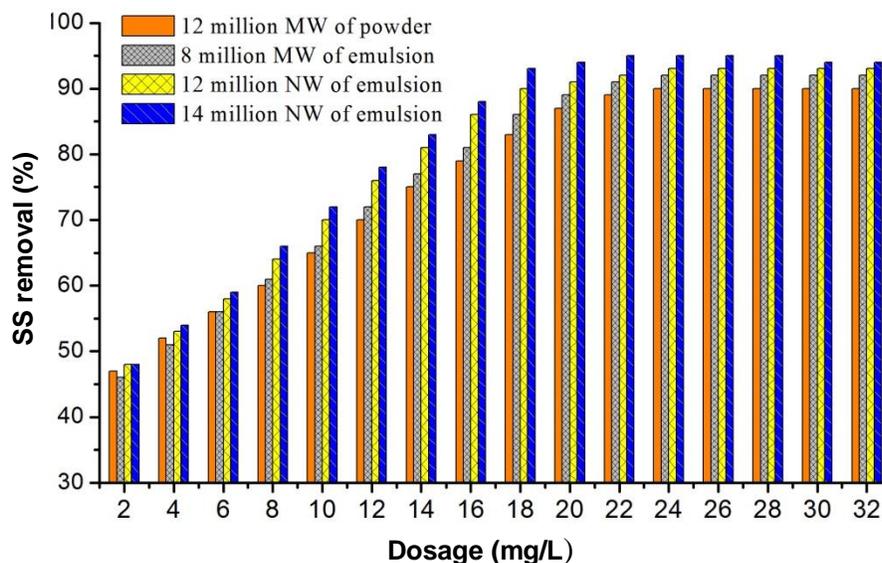
### Flocculation Performance for Paper Mill Wastewater

The indices of wastewater from a paperboard factory were as follows: COD<sub>0</sub> was 3856.8 mg/L, SS<sub>0</sub> was 1.53%, pH value was 7.76, wastewater color was yellowish, and suspended matter was white. The ultra-high concentration cationic polymer emulsion samples with molecular weights of 8 million, 12 million, and 14 million were compared with the commercially available cationic polyacrylamide dry powder with a cationic degree of 25% and a molecular weight of 1200. The results are shown below.

According to Figs. 8 and 9, the flocculation performance of emulsion cationic polymer was better than that of dry powder under the same molecular weight and dosage. The mechanism on the flocculation process could be explained as follows (Razali *et al.* 2011): the cationic polyacrylamide has a certain proportion of cationic groups (about 25%) and a long molecular chain. In the flocculation process of papermaking wastewater, the cation groups at one end of the cationic acrylamide chain adsorbs the anionic colloidal particles in the wastewater, and the groups at the other end can stretch to adsorb other colloidal particles, thus forming the aggregation of "colloidal particles polymer colloidal particles".



**Fig. 8.** COD removal of papermaking wastewater by different cationic polymers. The standard deviation of dosage was  $\pm 0.1$  mg/L. The standard deviation of cod removal was  $\pm 2\%$ .



**Fig. 9.** SS removal from paper mill wastewater by different cationic polymers. The standard deviation of dosage was  $\pm 0.1$  mg/L. The standard deviation of COD removal was  $\pm 2\%$ .

Polymer chains act by means of adsorption bridging between colloids. The emulsion cationic polyacrylamide generally has better flocculation effect than dry powder products with the same molecular weight. The main reason is that the molecular chain distribution of emulsion polymer is narrower, and the bridging effect of its long molecular chains is more balanced, so the bridge continuous cropping is better. In addition, the cationic polyacrylamide emulsion with high molecular weight has better flocculating effect, which may be due to the greater bridging effect of the high molecular weight cationic polymer chain (Wong *et al.* 2006). That is to say, when the same treatment effect is achieved, the required amount of cationic polyacrylamide emulsion with high molecular weight is less. Moreover, the COD removal and SS removal percentages increased rapidly with the increase of polymer solution dosage. When the dosage exceeded 20 mg/L, the COD removal and SS removal percentages increased slowly (Vanderhoff 1993). The main reason was that most of the suspended particles in the wastewater were flocculated and settled under the action of polymer bridging after charge adsorption, while the remaining small amount of suspended particles could hardly settle by increasing the dosage of flocculant. Furthermore, it should be noted that when the dosage of CPAME-uhc with molecular weight of 14 million is too high, the flocculation effect of papermaking wastewater will decrease slightly. This might be due to excessive flocculation when the amount of high molecular weight emulsion product is too large, resulting in loose flocs, which is unfavorable to the settling of particles in wastewater. Therefore, for the papermaking wastewater in this study, it is suggested that the dosage of CPAME-uhc with molecular weight of 14 million is 22 mg/L-24 mg/L. Another thing to be noted is that the residual monomer content of cationic polyacrylamide flocculant prepared before was more than 1000 ppm, which was more toxic, limiting its application in drinking water and other fields. However, high concentration emulsion polymerization can reduce residual monomer to below 250 ppm by adding a certain amount of initiator after completion of the reaction, which achieves the standard of drinking water and can be widely applied in various fields.

### Micromorphology and Chemical Structure of CPAME-uhc

Figure 10 shows the scanning electron microscopy (SEM) images of latex particles with magnification of 15,000 times (left) and 20,000 times (right). As shown in Fig. 10, the latex particles were regular spheres with a diameter of 200 nm to 500 nm, and no defective latex particles were found. This result indicates that the CPAME-uhc produced by the emulsion system in this paper had good stability (Zheng *et al.* 2013).

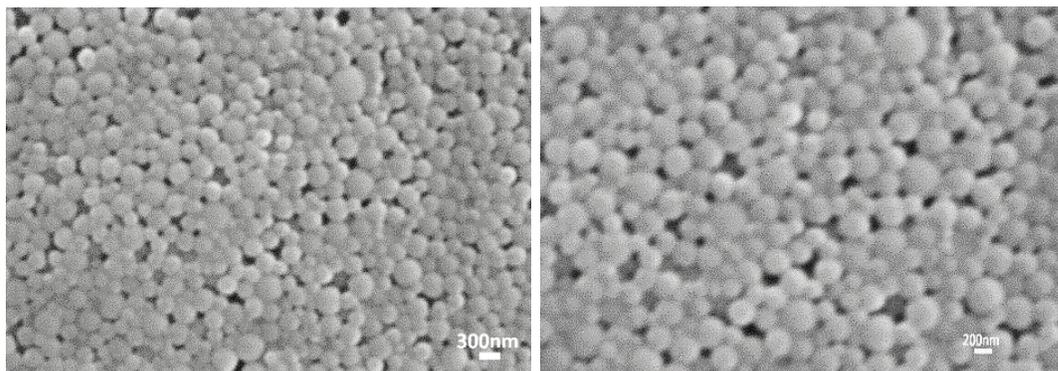


Fig. 10. Micromorphology of CPAME-uhc with different magnification times

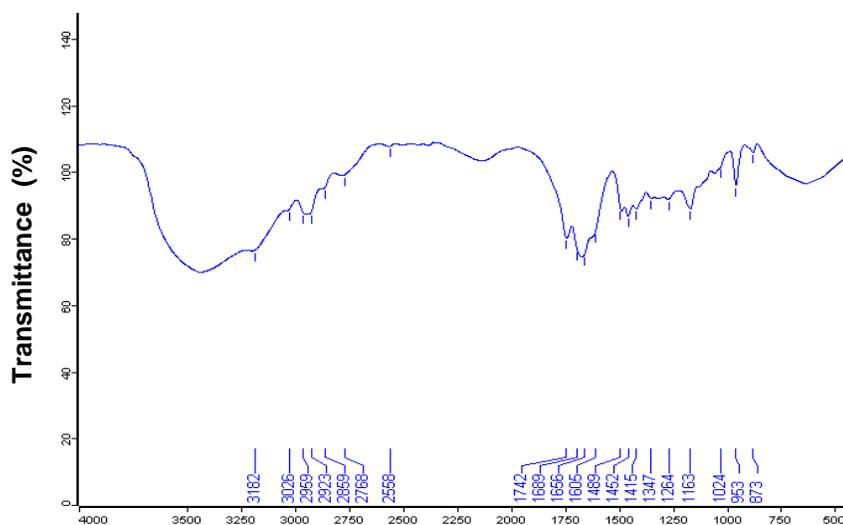


Fig. 11. FT-IR of CPAME-uhc

The cationic polymer emulsion with a concentration of 60% was precipitated by a mixture of ethanol and acetone with a mass ratio of 1:1. After drying, the chemical structure of the polymer emulsion was characterized by FT-IR, as shown in Fig. 11. The absorption peak near  $3400\text{ cm}^{-1}$  was the characteristic absorption peak of free- $\text{NH}_3$ . The absorption peak at  $2959\text{ cm}^{-1}$  represents the antisymmetric stretching vibration absorption peak of methylene. The absorption peak at  $2859\text{ cm}^{-1}$  was the symmetrical stretching vibration absorption peak of methylene. The absorption peak at  $1742\text{ cm}^{-1}$  was the characteristic absorption peak of DAC ( $\text{C}=\text{O}$  stretching vibration absorption in  $\text{COOCH}_2$ ). The absorption peak at  $1689\text{ cm}^{-1}$  was the characteristic absorption peak of amide group ( $\text{C}=\text{O}$ ). The absorption peak at  $1605\text{ cm}^{-1}$  was ( $\text{N-H}$ ) bending vibration absorption peak. The absorption peak at  $1454\text{ cm}^{-1}$  was methylene deformed vibration absorption. The absorption peak at  $1163\text{ cm}^{-1}$  was the asymmetric stretching vibration absorption peak of

C-O-C in-COOCH<sub>2</sub>. The absorption peak at 953 cm<sup>-1</sup> was quaternary ammonium group. From the above infrared characteristic peaks, it could be speculated that the super high cationic polymer emulsion was a copolymer of cationic DAC monomer and acrylamide.

## CONCLUSIONS

1. In this study, the factors affecting the polymerization process of CPAME-uhc were studied. The performance of the emulsion product were optimized. The morphology and chemical structure of the emulsion were characterized. The results showed that the ideal polymerization process was: monomer concentration 28%, cationic degree 25%, maximum temperature rise 4.5 to 5.5 °C, initial temperature 6 to 8 °C, stirring speed 400 r/min, crosslinking agent 0.4 ppm, and reductant concentration 2.4 to 2.6%.
2. Adding 1% urea and 2% Na<sub>2</sub>SO<sub>4</sub> can greatly improve the solubility of CPAME-uhc. When 2% dimethylacrylamide amine, 2% vinylpyrrolidone, and 5% sodium 2-acrylamide-2-methylpropionate were added, the temperature and salt resistance of the emulsion product increased.
3. The obtained CPAME-uhc had a COD removal of 95% and a SS removal of 93% for papermaking wastewater, which meets the requirements of sewage discharge.
4. The latex particles in the emulsion were regular spheres with a diameter of 200 nm to 500 nm. FT-IR analysis showed that the product was a copolymer of cationic DAC monomer and acrylamide.

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