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Research to Synthesize Cationic Polyacrylamide Emulsion Use for Treatment Wastewater Drain from the Paper-Making Process

Nguyen Huy Tung, Nguyen Pham Duy Linh, Bui Tien Thanh*
School of Chemical Engineering, Hanoi University of Science and Technology, Ha Noi, Vietnam
**Corresponding author emails: thanhbt.buitien@gmail.com*

Abstract

Cationic polyacrylamide emulsions (CPAM) are widely applied in industries such as petroleum extraction, paper-making, cosmetics, and treatment wastewater drain from industrial process... Currently, on the market, CPAM products are very diverse, and the selected products have different characteristics such as molecular weights and cation content, depending on the needs of each field. For treatment wastewater from paper-making process, CPAM is required to have a cation degree of 30-40% and a molecular weight of 6-12 million Da. There are many studies on synthesizing CPAM, but most of them have been implemented by traditional methods, investigating each factor affecting the polymerization process of CPAM, product characteristics as well as the conversion of a synthesis reaction. However, none of them have suggested the simultaneous influence of input parameters. In this study, a new approach to finding the optimizing condition for reaction of synthesis inverse emulsion (water-in-oil) cationic polyacrylamide by using Box - Behnken model could help to find the optimizing input factors for reaction faster, saving research time for developing new products and reducing the production costs compared to traditional methods. The results of research obtained copolymers with a molecular weight of 8.042.957 Da, a cation degree of 35.68% with optimal conditions: monomer concentration of 25%, the content of cation monomer of 40.70%, and the content of initiator of 0.54%. The results of trial testing to treat the wastewater collected from the paper-making process show that the synthetic CPAM has a similar performance compared with imported CPAM on the market. The characterization of CPAM and sludge samples after treatment was analysed by: Fourier-transform infrared spectroscopy (FTIR), hydrogen magnetic resonance spectroscopy (^{1}H-NMR), dynamic light scattering method (DLS), permeation chromatography method gel (GPC), and thermal analysis method (TGA-DSC). The surface structure of the sludge was analysed by SEM images.

Keywords: Emulsions, cationic polyacrylamide, molecular weight, cationic degree, paper industry wastewater.

1. Introduction

The process of industrialization is developing rapidly. Together with that environmental pollution due to wastewater discharge from factories, and industrial zones into rivers and lakes is serious. Many countries have been promoting research activities and technological solutions for industrial wastewater treatment [1]. Wastewater treatment by mean flocculation is a commonly used process to treat wastewater from industrial factories before being discharged into the environment. The process of wastewater treatment by flocculation method usually includes technological steps such as precipitation, coagulation, flocculation, and settling [2].

In the wastewater treatment process, the flocculant is a very important agent, which affects to the quality of the output water after treatment. There are many types flocculants as polyacrylamide (PAM), polydiallyl dimethyl ammonium chloride (PDADMAC), and polyacrylic acid (PAA) and others. The flocculants help to create larger flocs, which increase the efficiency of the settling and cleaning of wastewater. Meanwhile, PAM is a polymeric material synthesized from the polymerization of commonly used acrylamide monomers. Cationic polyacrylamide (CPAM) is a derivative of PAM, synthesized from acrylamide monomer and cationic monomer, which is widely used in wastewater treatment [3]. Specifically in wastewater from the paper-making process, there are many organic components such as fibers, fillers, dyes, kaolin, and others. Therefore, the positive charge in CPAM will completely neutralize the negative charges of the mud particles, the long carbon backbone and high molecular weight of CPAM (up to several million Da) facilitate the formation of bridges through a chain bridging mechanism, it helps the settling process better [4]. The characteristic of CPAMs are normally used for treating wastewater from the paper-making process and have the cationic degree of 30 - 40%, molecular weight of 6-12 million Da.

In some previous research, such as the study by author Huaili Zheng *et al*. successfully synthesized CPAM by ultraviolet light and applied CPAM in wastewater treatment containing kaolin [5]. In the

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same wastewater with high kaolin content, author Jiangya Ma *et al*. synthesized CPAM and tested flocculation with different cationic degrees [6]. Author Yufeng Wang *et al.* studied the influence of CPAM dosage on the efficiency of wastewater treatment [7]. Lihuan Mo *et al.* optimized CPAM dosage, PAC dosage, and pH on the efficiency of wastewater from the paper-making process using response surface methodology [8]. Although previous researchers have studied each input factor to CPAM copolymerization by traditional methods, none has suggested the simultaneous influence of input parameters on the characteristics of CPAM and conversion efficiency. In this study, a new approach is finding the optimizing condition for reaction by using the model Box - Behnken in Design Expert software [9, 10]. The obtained regression equations and response surface model help to find the optimizing input factors for reaction faster, saving research time for developing new products and reducing the production costs compared to traditional methods. Furthermore, the emulsion has a short shelf life, and sometimes the product may expire due to long transportation times. This method can help domestic manufacturers quickly localize their products to meet market demands instead of waiting for imports. [11].

The hydrogen magnetic resonance spectroscopy (^{1}H-NMR) and fourier-transform infrared spectroscopy (FTIR) were used to confirm the structure of the polymer. Gel permeation chromatography (GPC) and Ubbelohde viscometer were used to determine the molecular weight and molecular weight distribution of CPAM. The emulsion particle diameter and the particle size distribution were determined by dynamic light scattering (DLS). The thermal properties of the copolymers were investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

In this study, the efficiency of wastewater treatment by synthetic CPAM and commercial CPAM C4008 was analyzed by indicators of chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), and turbidity. The surface structure of the obtained sludge was analyzed by scanning electron microscopy (SEM).

2. Experiments

2.1. Materials

2.1.1. Chemicals in the synthesis of CPAM emulsions

The water phase includes acrylamide - AM (98% - Jiangsu, China), 2 - Trimethylammonioethyl methacrylate chloride - DMC (75 wt% in H_2O - Beijing, China).

The oil phase includes Isopar L, Span 80 and Tween 85 (99.5% - Jiangsu, China).

Three initiators were bought from Tokyo, Japan: azobis (isobutyramidine) dihydrochloride - V50 (98%), kali persulphate - $K_2S_2O_8$ (98%), and natri bisulfite - $NaHSO_3$ (98%).

There are also chemicals such as IPA (99%), ethanol (99,5%), I_2 (99%), KI (99%), $HgCl_2$ (99,5%), $Na_2S_2O_3.5H_2O$ (99%), starch soluble (99%), and $AgNO_3$ (99%).

2.1.2. Chemicals in wastewater treatment

The chemicals used in wastewater treatment include poly aluminum chloride (PAC, 31%), HCl 45%, H_2SO_4 50%, NaOH 32%, $Ca(OH)_2$, calcium chloride ($CaCl_2$, 99%), and commercial CPAM C4008 (molecular weight about 6 - 10 million Da, cationic degree about 30-40%, Guangdong, China).

2.2. Preparation of CPAM Emulsions

The CPAM emulsions were prepared by inverse emulsion copolymerization (Fig. 1 and Fig. 2). The reaction was conducted in reactor equipment with a mechanical stirrer, a UV lamp, a system for high-purity nitrogen, and a condenser. The reaction conditions included a temperature of 61°C, a stirring speed of 2600 rpm, reaction time of 7 hours.

Premix the materials for each phase and slowly add the oil and water phase into the reactor. Throughout the process of reaction, the nitrogen gas and the redox initiator add continuously. In the end, stop stirring and heating, and a W/O emulsion is obtained.

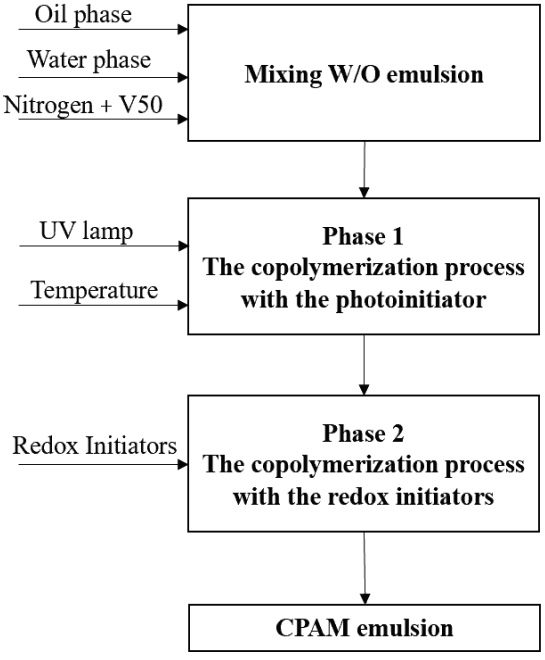


Fig. 1. CPAM emulsion synthesis process diagram

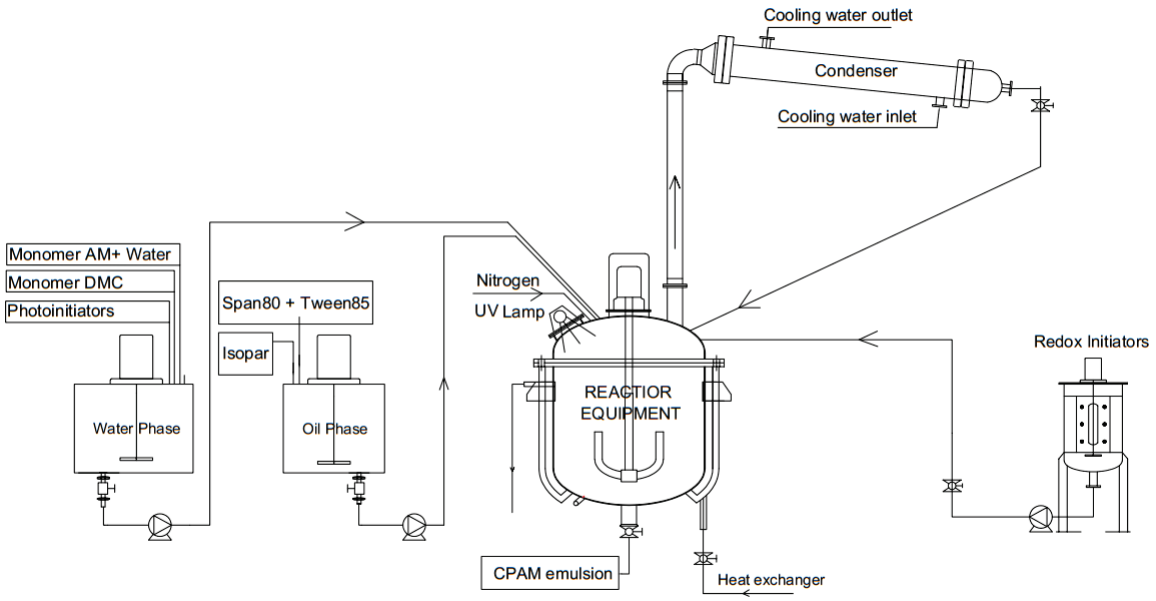


Fig. 2. CPAM emulsion synthesis equipment system

The optimizing condition is selected by using equations and response surface model of the study *"Optimization Conditions to Obtain Cationic Polyacrylamide Emulsion Copolymers with Desired Cationic Degree for Different Wastewater Treatments"* [10], as below:

$$DC = -61.08 + 1.10A + 0.65B + 202.95C + 4.34 \times 10^{-3}AB + 0.82AC + 0.48BC - 3.36 \times 10^{-2}A^2 - 1.26 \times 10^{-3}B^2 - 225.54B^2 \quad (1)$$

$$M = -4.70 \times 10^7 + 1.94 \times 10^6 A - 1.10 \times 10^5 B + 1.29 \times 10^8 C - 9.67 \times 10^7 AB + 2.68 \times 10^5 AC + 5.56 \times 10^5 BC - 3.90 \times 10^4 A^2 - 1.89 \times 10^3 B^2 - 1.51 \times 10^7 C^2 \quad (2)$$

$$H = -40.70 + 2.48A - 0.56B + 4.52 \times 10^2 C + 1.93 \times 10^{-3}AB + 1.18AC + 1.87BC - 7.01 \times 10^{-2}A^2 - 4.96 \times 10^{-3}B^2 - 5.30 \times 10^2 C^2 \quad (3)$$

where A is monomer concentration (%); B is the content of cationic monomer (%); C is the content of initiator (%).

2.3. Methods to Determine the Structure, Molecular Weight, Cation Content of CPAM and the Conversion of the Synthesis Reaction

The CPAM structure was determined by analyzing the FTIR spectrum (model IRAffinity-1S Fourier - Shimadzu, Japan) and ^{1}H-NMR spectrum (Bruker Avance Neo 600 MHz). The particle size distribution of CPAM emulsions was determined by dynamic light scattering (DLS) using the Horiba SZ-100 nanoparticle size meter. The molecular weights and molecular weight distribution of CPAM were confirmed by gel permeation chromatography - GPC (detector: RID A). The TGA - DSC was carried out on a Mettler Toledo thermal analyzer.

The molecular weight of CPAM was determined by measuring polymer solution viscosity using a Ubbelohde viscometer and calculated using the Mark Houwink - Sakurada equation:

$$\eta = K \times M^{\alpha} \quad (4)$$

where η is the characteristic viscosity of the polymer, M is the molecular weight of the polymer, and K and α are constants depending on the nature of the polymer and the solvent.

The cationic degree of the CPAM was determined by titration of the polymer solution with 0.1 M silver nitrate solution and potassium dichromate indicator until the solution changed from yellow to brick red, then the process was terminated. The calculation formula is shown as following:

$$DC(\%) = \frac{M \times N \times (V - V_0)}{W} \quad (5)$$

where M is the molecular weight of cationic monomer; N is the molar concentration of the silver nitrate solution; V and Vo are the volumes of the silver nitrate solution reacted with the sample and the blank, respectively; W is the amount of the CPAM.

The conversion of the reaction was determined by the HIP titration method. The calculation formula is as follows:

$$H(\%) = \frac{C - \frac{1}{2} \times \frac{(V_0 - V) \times N}{V_i}}{C} \quad (6)$$

where C is the volume concentration of the initial monomer; N is the concentration of the $Na_2S_2O_3$ solution (N); V_0 is the volume of $Na_2S_2O_3$ used to titrate the residual monomers in the blank sample (mL); V is the volume of $Na_2S_2O_3$ used to titrate the residual monomers in the sample (mL); and V_i is the volume of the reaction mixture at the time i (mL).

2.4. Method to Evaluate the Ability of Industrial Wastewater Treatment by CPAM Emulsion

Fig. 3 shows the flocculation mechanism using CPAM. The negative charges on the colloidal particles neutralize the positive charges on the chain of CPAM (charge neutralization mechanism). As a result, the particles are encouraged to move closer together and form clusters. Additionally, the long carbon backbone and the high molecular weight of CPAM, facilitate the formation of bridges through a chain bridging mechanism. These bridges are closed to help create large flocs, that improves the efficiency of the treatment process.

The untreated wastewater samples used in this study have indicators: COD of 787.2 mg/L, BOD5 of 330.9 mg/L, TSS of 7870 mg/L, and turbidity of 2617 mg/L. The wastewater samples were stirred with chemicals such as $Ca(OH)_2$ for pH adjustment and precipitation, PAC to coagulant, and CPAM for the activated flocculant process. The wastewater samples after treatment were analyzed and measured for COD (model HI 83099, Hanna Instruments), BOD5 (BOD5 meter, VelpScientipica, UK), TSS (UV Probe 254+ meter, France), and turbidity (model WGZ-2000, Chongqing, China).

The SEM images of sludge sample was observed by scanning electron microscope (model S4800, Hitachi, Japan).

3. Results and Discussion

3.1. Characteristics and Synthesis Performance

Optimal conditions were selected based on equations and response surface models comprising the monomer concentration of 25%, the content of DMC of 40.70%, and the content of the initiator of 0.54%. At that condition, the model gives prediction results M= 10,794,788 Da, DC = 40%, and H = 96.12%. At the same time, authors have experimentally verified and obtained the results in Table 1.

Table 1. The results of the CPAM synthesis

Experimental results			Predicted results		
DC (%)	M (Da)	H (%)	DC (%)	M (Da)	H (%)
35.68	8,042,957	94.05	40	10,794,788	96.12

The results show that the characteristics of CPAM obtained from the experiment have a molecular weight of 8,042,957 Da and a cation degree of 35.68%, which is equivalent to the predicted results. This means that the application of the model can help provide quickly optimizing input parameters for synthesis reaction and help to save research time and costs and satisfy diversify of the demand market.

3.2. Structure and Characterization of CPAM Copolymers

The infrared absorption bands of CPAM DC 35.68%, CPAM C4008 and the assignments are shown in Fig. 5. The $-NH_2$ group and the C=O group (the specific functional group for AM monomers) had wave numbers at about 3391 cm^{-1} and at 1659 cm^{-1}, respectively [12]. The peak with wave number 2923cm^{-1} was assigned to the $-CH_3$ and $-CH_2-$ groups [13]. The peak with wave number 1729 cm^{-1} was assigned to C=O group in the cationic monomer DMC. The peak with wave number at 1471 cm^{-1} was assigned to the $-CH_2$ group of δ - CH_2 - $N^+(CH_3)_3$ in the cationic monomer DMC [14]. The peak at 1138 cm^{-1} was assigned to $-C-O$ in the DMC. The characteristic peak at 951 cm^{-1} was for the quaternary ammonium group of DMC. The results FTIR spectra show a match for the characteristic wave numbers of functional groups of the two CPAM DC 35.68%, commercial CPAM C4008, and both of them were copolymerized from AM and DMC.

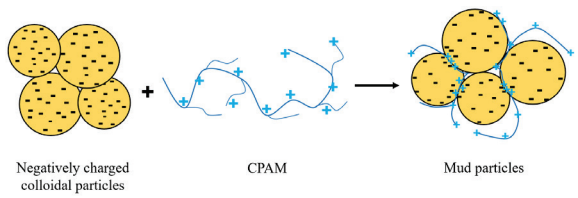


Fig. 3. Mechanism of the flocculation process by CPAM

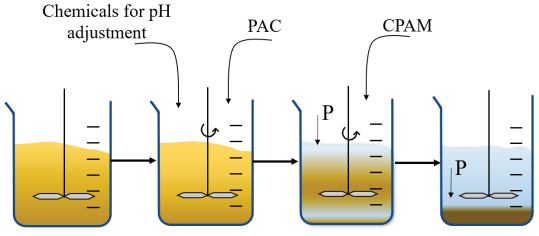


Fig. 4. Process of wastewater treatment by CPAM sample

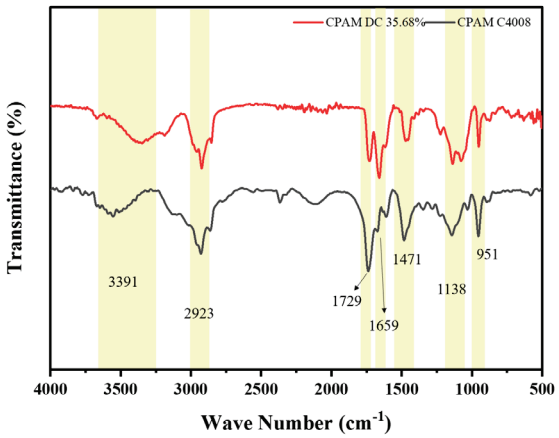


Fig. 5. FT-IR spectra of CPAM DC 35.68% and CPAM C4008

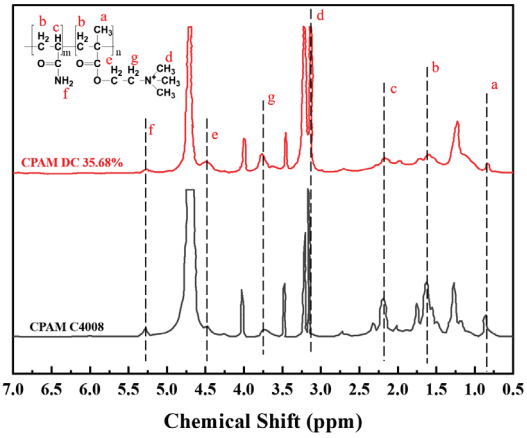


Fig. 6. ^{1}H-NMR spectra of CPAM DC 35.68% and CPAM C4008

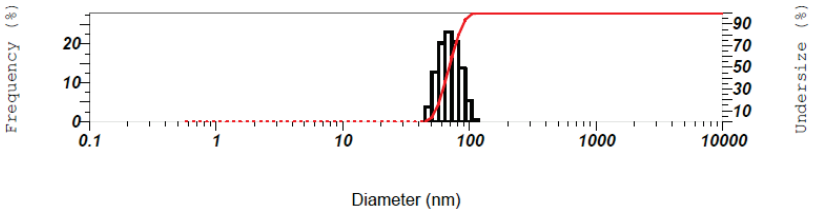


Fig. 7. DLS result of CPAM DC 35.68%

Fig. 6 shows ^{1}H-NMR spectra of CPAM DC 35.68% and CPAM C4008. The chemical shift at about δ_H = 0.834 ppm corresponds to the protons in $-CH_3(H_a)$. The two peaks of CPAM at δ_H = 1.600 ppm and δ_H = 2.166 ppm were attributed to the protons at the methylene $-CH_2-$ (H_b) and $-CH-$ (H_c) groups, respectively. The sharp peak at δ_H = 3.139 ppm was assigned to the protons of $-N^+(CH_3)_3$ (H_d) of the cation monomer DMC. The chemical shift at δ_H = 4.488 ppm was assigned to the proton of $-O=C-O-CH_2^+$ (H_e). The protons of the methylene group in $-CH_2-N^+$ (H_g) had a chemical shift at δ_H = 3.768 ppm. The chemical shift at about δ_H = 5.05 ppm was attributed to the protons of $O=C-NH_2$ (H_f). The chemical shifts from 5.6 to 6.2 ppm [15], did not show any peaks in Fig. 6, which means that the monomers reacted completely and the reactions had a high conversion rate. The ^{1}H-NMR spectral results showed that CPAM DC 35.68% was successfully synthesized by free radical polymerization from two monomers AM and DMC [5]. The molecular structure of CPAM DC 35.68% is similar to the commercial CPAM C4008.

The analysis results (Fig. 7) show that the particle size distribution ranges from 50 to 110 nm and the polydispersity (PI) is 0.415. The obtained emulsion particle has a diameter similar to other studies and the range is good to have the stable emulsion.

The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of CPAM were about 8,140,700 g/mol and 2,090,200 g/mol, respectively. The polydispersity index PDI = 3.8947 (Fig. 8), which means that the carbon backbone of the polymer is uniform.

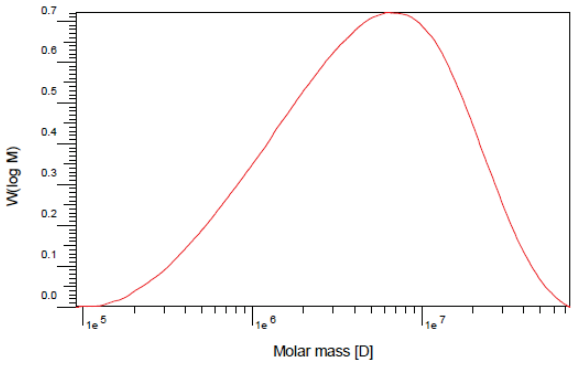


Fig. 8. Molecular weight distribution of CPAM DC 35.68% by GPC

The CPAM DC 35.68% sample was subjected to thermal analysis (TGA - DSC), and obtained the TGA - DSC graph as shown in Fig. 9. The TGA curve shows the three stages of thermal decomposition of the sample. In the first stage, the temperature was from 25 to 210 °C, the mass is reduced by about 10.17%, this is attributed to the evaporation of moisture of water and volatile impurities present in CPAM. In the second stage, in the temperature range from 210 to 340 °C, the CPAM structure began to be destroyed due to thermal decomposition leading to the amide process of the $-NH_2$ group in AM and $-CH_3$ group of the quaternary ammonium group in the DMC. This results in a mass reduction of CPAM of about 38.81%. Finally, in the

third stage of TGA, as the temperature increases, the carbon backbone structure (-C-C-) of CPAM decomposes into CO_2 and some other compounds, resulting in a weight loss of about 43.17%.

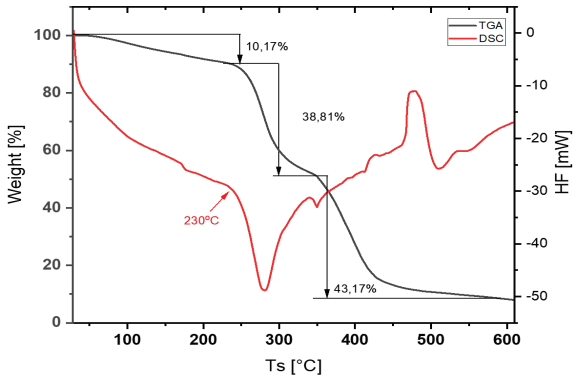


Fig. 9. TGA - DSC data of CPAM DC 35.68%

The DSC curve shows the glass transition temperature of CPAM at about 230 °C and as the temperature continues to increase, the sample decomposes. The glass transition temperature of CPAM DC 35.68% is equivalent to the results in the study of author Junren Zhu (P(AM-DMC-DAC) with *Tg* = 218.76 °C) [16]; author Bao Yu Gao synthesized P(AM-DMDAAC-BA) with *Tg* = 269.15 °C [17].

3.3. Comparison synthetic CPAM and commercial CPAM in paper-making wastewater treatment

Normally, the flocculants dosing range for wastewater treatment from 20 to 120 mg/L [18]. In this work, the dosage of CPAM is 45-75 mg/L, which was used to examine and evaluated.

In Fig. 10, at the dosing range of flocculant of 60-65 mg/L, the floc is large enough to precipitate, settle and give good wastewater treatment efficiency with the best values: COD of 25-26 mg/L, BOD5 of 19-21 mg/L, TSS of 20-25 mg /L, and turbidity of 12-15 mg/L. At this CPAM dosage range, the floc is large enough to precipitate and settle. In the low dosage of CPAM from 45 to 60 mg/L, the neutralization of flocculant is insufficient to the negative charge of sludge particles, thus resulting in small flocs. In other cases, overdosage CPAM (greater than 65mg/L), makes the colloidal system excess positive charge, causing the sludge particles to re-stabilize and reduce sludge separation efficiency. The formation of small suspended flocs leads to low wastewater treatment efficiency [19].

Fig. 11 shows the efficiency of wastewater treatment from a paper production line with CPAM DC 35.68% and commercial CPAM C4008 at a flocculant dosage of 65 mg/L. The result is equivalent processing efficiency, large flocs, and good settling capacity. The treated water was clear and reached the target values [20].

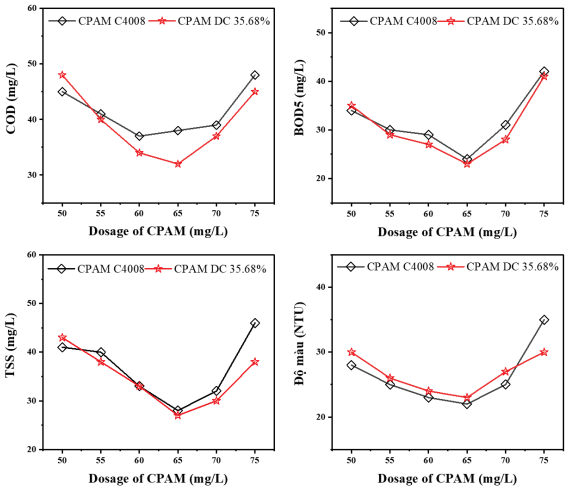
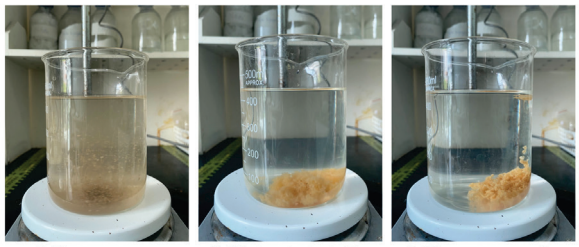


Fig. 10. Wastewater treatment results using CPAM DC 35.68% and commercials CPAM C4008



A. Raw wastewater | B. Wastewater treated by CPAM DC 35.68% | C. Wastewater treated by C4008

Fig. 11. Wastewater samples obtained after treatment with CPAM DC 35.68% and commercial CPAM C4008

The SEM image (Fig. 12) shows the structure of two sludge samples obtained after treatment with CPAM DC 35.68% and commercial CPAM C4008 with similar surface structures. The result shows the synthesis CPAM DC 35.68% and commercial CPAM C4008 have similar ability for release water from the mud and good treatment for waste water from paper-making process.

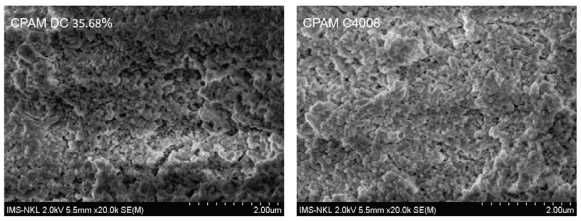


Fig. 12. SEM images of sludge samples treated with CPAM DC 35.68% and commercials CPAM C4008

4. Conclusion

The synthesis of CPAM DC 35.68% was successful by using reverse emulsion polymerization at condition monomer concentration of 25%, monomer cation content of 40.7%, initiator content of 0.54%, speed stirring at 2600 rpm, reaction temperature of 61 °C, and reaction time of 7 hours. Results analyzed by ^{1}H−NMR, FTIR, DLS, GPC, and TGA - DSC confirmed that the CPAM were synthesized

successfully. These results show the structure of CPAM DC 35.68% equivalent to commercial product. The obtained emulsion shows good efficiency to treat wastewater treatment from the paper-making process. The results of this study have important implications for the production of CPAM by using experimental planning and response surface model, enabling quick response to market demand, cost reduction, and overcoming the limitations associated with imported CPAM emulsions, particularly their short shelf life when subjected to extended shipping times.

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