



## Preparation, characterization, and assessment of different acrylamide-based polymers by inverse emulsion polymerization for water treatment

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### Abstract

This research paper explores the production of acrylamide-based homo-polymers and copolymers via inverse emulsion polymerization with varying monomer compositions. It emphasizes enhancing flocculation and coagulation efficiency through partially crosslinking monomers, particularly ureido methacrylate (UMA). The prepared polymers and copolymers were characterized using FT-IR, SEM, and EDX spectroscopic tools. The results of flocculation efficiency demonstrated a significant improvement in flocculation when using acrylic acid as a co-monomer (96.67%) and the UMA monomer (98.62%) as compared with 97.89% related to Magnafloc® LT27AG as a commercial flocculant. Moreover, this study offers new eco-friendly based polymers, and easily recoverable potential materials aligning with sustainable development goals.

**Keywords:** polyacrylamide; water treatment; flocculating agent; Inverse emulsion polymerization

### 1. Introduction

Polyacrylamide and its derivatives play a significant role in wastewater treatment applications. These polymers are synthesized using aqueous solution polymerization and inverse emulsion polymerization methods. Inverse emulsion polymerization offers multiple advantages, including mild conditions to carry out polymerizations with high yields and the possibility to polymerize a wide range of bifunctional monomers, high molecular weight, high solid content, and straightforward post-treatment [i]. Additionally, this method enhances the solubility of acrylamide copolymers and increases their resistance to temperature, salt, and calcium [ii].

Water scarcity, driven by population growth and human activities, is a pressing global issue that challenges sustainable development [iii,iv]. To address this shortage of freshwater resources, innovative solutions are sought, including treating industrial wastewater for agricultural use [v,vi,vii]. This heightened focus on water scarcity and environmental concerns has sparked interest in clean water and clean energy technologies [viii]. Various wastewater treatment methods, such as biological

degradation, ion exchange, chemical precipitation, adsorption, reverse osmosis, coagulation, and flocculation, have been extensively studied. These methods have different performance characteristics and environmental impacts [ix].

Coagulation and flocculation are crucial stages in water treatment, used to separate suspended solids from water. In coagulation, a chemical reagent promotes floc formation by combining with colloidal solids, making them aggregate for easier removal through sedimentation. Flocculation follows, involving gentle mixing to form larger, settleable flocs for efficient removal [x,xi]. In recent years, synthetic polymers have become key coagulant aids, boosting coagulation and flocculation efficiency with promising results. These commercial organic flocculants are typically linear, water-soluble polymers made from monomers like acrylamide and acrylic acid [xii]. Flocculation is vital in industrial wastewater treatment. Inorganic coagulants, while affordable and easy to apply, have limited efficiency and can introduce residual metal concentrations. Organic polymeric flocculants have gained popularity due to their remarkable effectiveness at low dosages. They're convenient, have minimal pH impact, require

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smaller quantities, and form larger, more durable flocs and better turbidity removal performance compared to inorganic salts [xiii,xiv]. Water-soluble, long-chain polymeric flocculants are used to separate non-settling fine solids from aqueous suspensions. They have diverse applications in mineral processing, wastewater treatment, oil sand tailings dewatering, paper making, and biotechnology. High molecular weight polymers facilitate flocculation by forming bridges between particles, forming larger, more easily settleable flocs [xv]. Polyelectrolytes, including cationic and anionic counterparts, have distinct features. Nonionic water-soluble polymers may unintentionally contain ionic groups. Anionic flocculants can have 1-100% of monomer units contributing to the overall charge, often with high molecular weights[xvi].

The flocculation of suspended particles and colloids involves various mechanisms. Electrostatic attraction leads charged particles and colloids to come together through electrostatic forces, with cationic polymers interacting with negatively charged particles and anionic polymers interacting with positively charged particles. Sorption occurs as polymers containing protonated amine groups bind to particle surfaces, contributing to aggregation and flocculation. Bridging mechanisms involving high molecular weight polymers act as bridges between particles or colloids, promoting flocculation by spanning across multiple particles and aiding in their aggregation and settling. These mechanisms collectively facilitate the flocculation process, resulting in the formation of larger flocs and the removal of suspended particles and colloids [xvii,xviii].

The purpose of this study is to create various types of eco-friendly acrylamide-based homo-polymers and copolymers, utilizing different monomers with partial crosslinking properties to enhance the flocculation effect in water treatment. Additionally, materials that increase hydrogen bonds, such as the ureido group, incorporate intermolecular hydrogen bonds to improve coagulation and flocculation efficiency. These synthesized polymers are prepared through the environmentally friendly inverse emulsion polymerization technology, with variations in co-monomer type, dosage, initiator type, and reaction conditions. Furthermore, homo and copolymer emulsions are assessed as flocculants in water treatment applications, adding value through polymer

recovery. The characterization of homo-polymers and copolymers is conducted using various spectroscopy tools.

## 2. Experimental

### 2.1. Materials

In this study, various chemical materials were used in the synthesis of polymeric flocculants. These materials include Acrylamide [Am,  $\geq 99\%$ ], ammonium per sulfate [APS], potassium persulfate [KPS], sodium persulfate [SPS], and tert-butyl hydroperoxide [TBHP] were purchased from MERK, Germany. Acrylic acid [AA], methacrylic Acid [MAA], stearyl methacrylate [SMA], Ureido Methacrylate 25% in Methyl Methacrylate [UMA 25%], and Magnafloc<sup>®</sup> LT27AG were purchased from BASF, Germany. Hydrogen peroxide and Benzoyl peroxide were purchased from LOBA Chemie, India. Sodium bisulfite [SBS], purchased from Fisher Scientific, USA. Mineral oil (Liquid paraffin) was purchased from Masr Co. for petroleum, Egypt. Ammonium hydroxide (30 %) was purchased from pioneer for Chemicals-Piochem, Egypt. TRIDAC ISO6 was purchased from SASOL, Italy. Span 80 and Tween 85 were purchased from Croda, India. Distilled water [HPLC grade] was purchased from Sigma-Aldrich, Germany. All the above materials were used without any further purification.

### 2.2. Equipment

The polymerizations were conducted in a 1-liter temperature-resistant glass reactor placed in a thermostatic water bath [MEMMERT, Germany], equipped with a PTFE blade stirrer, a PTFE coated PT 100 thermometer, reflux glass condenser), pH meter [Jenway 3520, UK], Pre-emulsions were made using a high-speed mechanical mixer [BGD 750/1], mechanical stirrer [Heidolph, Germany], nitrogen tube, The polyacrylamide emulsion product was filtered using a 100-micrometer polypropylene filter.

### 2.3. Methodology

In the present study, several acrylamide-based polymers are prepared in terms of initial temperature, aqueous to oil ratio, acrylamide amount, type and dose of initiator, vinyl co-monomer, a dose of acrylic monomer, and the influence of ureido methacrylate; to investigate the properties of the polymers in terms of pre-emulsion stability, resultant colloidal polymer emulsion stability, coagulum formation, average molecular weight, and gravimetric conversion, in

addition to their evaluation as flocculating agents in water treatment.

### 2.3.1. The detailed synthetic procedure:

The preparation of high molecular weight polyacrylamides is strongly influenced by temperature, type of initiator, concentration of the initiator, and concentration of the monomer<sup>[xx]</sup>. The synthetic procedure described involves the preparation of high molecular weight polyacrylamides using a water-soluble redox and initiator system<sup>[xx]</sup>. The procedure is performed at a constant aqueous to oil ratio of 70:30<sup>[xxi]</sup>. In the 1-liter reactor vessel, the oil phase: 240 g liquid paraffin, as the continuous phase, 35 g Span80 and 15 g Tween85 are mixed together using a high-speed mechanical stirrer till complete homogeneity, and the aqueous phase: 150 g of acrylamide (Am) then add 550 g of distilled water (in a separate vessel) are slowly added to the oil phase at 2000 RPM under continuous nitrogen purging, for 30 minutes till the formation of a stable pre-emulsion<sup>[xxii]</sup>. Moreover, the pre-emulsion is purged with nitrogen for an additional 30 minutes before initiation. The reaction condition is Stirring at 400 rpm; and, maintaining the temperature of the water bath at 60 °C<sup>[xxiii]</sup>. Then, add the initiator: 10 g of ammonium persulfate 5 % solution (APS) and reducing agent: 2 g of sodium bisulfite SBS 5 % solution are added. The reaction is monitored until the temperature begins to increase, indicating that polymerization has started. Once the

reaction reaches its maximum peak and begins to decrease, the cooling process is started by using a water bath to a temperature of 25°C. After polymer formation, an inverting surfactant, TRIDAC ISO6 (6 g), is added to convert the emulsion to an O/W emulsion. The properties of the resultant polymer are then evaluated in terms of pre-emulsion stability, resultant colloidal polymer emulsion stability, coagulum formation, average molecular weight, and gravimetric conversion, in addition to their evaluation as flocculating agents in water treatment. The feed composition data of preparation PAm is listed in Table 1.

#### 2.3.1.1. Study the initial temperature at which the reaction begins by using redox system ( $T_{1-5}$ )

In this series of experiments, the goal is to study the impact of initial temperature on the molecular weight of the resulting polyacrylamide when using a redox initiator system. The temperature range selected for this study is between 45-60 °C, with five different temperatures tested (55, 50, 47, 46, and 45 °C), and the polymers produced are referred to as  $T_{1-5}$  polymers in addition to at 60 °C namely PAm that mentioned in first synthetic procedure. Where, the reaction at low temperatures is beneficial to produce a polymer with a high molecular weight acrylamide<sup>[xxiv]</sup>. The preparation as described in the procedure above is summarized in Table 1.

**Table 1 The feed composition data for the PAm and ( $T_{1-5}$ ) series**

Phase	Material	Amount (g)					
		PAm	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>	T <sub>5</sub>
Aqueous phase	Acrylamide	150	150	150	150	150	150
	Distilled water	550	550	550	550	550	550
Oil phase	Liquid paraffin	250	250	250	250	250	250
	Span 80	35	35	35	35	35	35
	Tween 85	15	15	15	15	15	15
Initiator	SBS	0.2	0.2	0.2	0.2	0.2	0.2
	APS	0.45	0.45	0.45	0.45	0.45	0.45
Reaction conditions	Temperature °C	60	55	50	47	46	45
	Stirring rate (RPM)	400	400	400	400	400	400

#### 2.3.1.2 Study the aqueous to oil ratio

In this series of experiments, the aqueous to oil ratio is varied while keeping the rest of the conditions constant. The  $A_{1-3}$  polymers are prepared with Aq/Oil ratios of 75/25, 80/20, and 85/15,

respectively. The goal is to study the effect of the Aq/Oil ratio on the stability of the pre-emulsion and the molecular weight of the resulting polyacrylamide<sup>[xxv]</sup>. Table 2 provides the amounts of materials and reaction conditions used for each of the  $A_{1-3}$  polymers.

Table 2 the feed composition data for the (A<sub>1-3</sub>) series.

Phase	Material	Amount (g)			
		T <sub>3</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>
Aqueous phase	Acrylamide	150	150	150	150
	Distilled water	550	600	650	700
Oil phase	Liquid paraffin	250	200	150	100
	Span 80	35	35	35	35
	Tween 85	15	15	15	15
Initiator	SBS	0.2	0.2	0.2	0.2
	Aps	0.45	0.45	0.45	0.45
reaction conditions	Temperature	47	47	47	47
	Stirring rate (RPM)	400	400	400	400

### 2.3.1.3 Study the concentration of monomer (Am<sub>1-4</sub>)

Table 3 describes a series of experiments in which different polyacrylamides, Am<sub>1-4</sub>, are prepared with increasing concentrations of acrylamide monomer.

The goal of this study is to determine the effect of

Table 3 the feed composition data for the (Am<sub>1-4</sub>) series

Phase	Material	Amount (g)				
		A <sub>2</sub>	Am <sub>1</sub>	Am <sub>2</sub>	Am <sub>3</sub>	Am <sub>4</sub>
Aqueous phase	Acrylamide	150	175	200	225	250
	Distilled water	650	625	600	575	550
Oil phase	Liquid paraffin	150	150	150	150	150
	Span 80	35	35	35	35	35
	Tween 85	15	15	15	15	15
Initiator	SBS	0.2	0.2	0.2	0.2	0.2
	Aps	0.45	0.45	0.45	0.45	0.45
reaction conditions	Temperature	47	47	47	47	47
	Stirring rate (RPM)	400	400	400	400	400

### 2.3.1.4 Influence of the type of initiator (namely IN<sub>1-5</sub>) on the properties of PAM

One of the most important factors being studied is the type of initiator, as it strongly affects the molecular weight of the resulting polymer and all other factors kept constant. This series represents a study on the influence of the type of initiator on the properties of polyacrylamide (PAM) by using different initiators, namely sodium persulfate (IN<sub>1</sub>), potassium persulfate (IN<sub>2</sub>), hydrogen peroxide (IN<sub>3</sub>), benzoyl peroxide (IN<sub>4</sub>) and tert-Butyl hydroperoxide (IN<sub>5</sub>). The study was carried out according to the method described above. The feed composition data are summarized in Table 4.

increasing the monomer concentration on the molecular weight of the resulting polymers at constant Aq/Oil ratios. The table lists the materials and amounts used in each of the four experiments, as well as the reaction conditions (temperature and stirring rate).

### 2.3.1.5 Optimization of potassium per-sulfate as initiator (namely P<sub>1-4</sub>) on the properties of PAM

It was previously mentioned that the concentration of the thermal initiator was considered one of the main factors affecting the molecular weight of the resulting polymer [xxvi], in this series of experiments in which different concentrations of potassium persulfate (0.35, 0.4, 0.5, and 0.55) namely (P<sub>1-4</sub>) are used as the initiator to prepare polyacrylamides (PAM) with the aim of optimizing the properties of the resulting polymer with desired properties.

The amounts of other material and reaction conditions are kept constant across all experiments. The study was carried out according to the method described above and the feed composition data were summarized in Table 5.

Table 4 the feed composition data for the (IN<sub>1-5</sub>) series

Phase	Material	Amount (g)					
		Am <sub>3</sub>	IN <sub>1</sub>	IN <sub>2</sub>	IN <sub>3</sub>	IN <sub>4</sub>	IN <sub>5</sub>
Aqueous phase	Acrylamide	225	225	225	225	225	225
	Distilled water	575	575	575	575	575	575
Oil phase	Liquid paraffin	150	150	150	150	150	150
	Span 80	35	35	35	35	35	35
	Tween 85	15	15	15	15	15	15
Initiator	SBS	0.2	0.2	0.2	0.2	0.2	0.2
	APS	0.45	-	-	-	-	-
	SPS	-	0.45	-	-	-	-
	KPS	-	-	0.45	-	-	-
	Hydrogen per oxide	-	-	-	0.45	-	-
	Benzoyl peroxide	-	-	-	-	0.45	-
	tert-Butyl hydroperoxide	-	-	-	-	-	0.45
reaction conditions	Temperature	47	47	47	47	47	47
	Stirring rate (RPM)	400	400	400	400	400	IN <sub>(4)</sub>

Table 5 the feed composition data for the (P<sub>1-4</sub>) series

Phase	Material	Amount (g)				
		IN <sub>1</sub>	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>
Aqueous phase	Acrylamide	225	225	225	225	225
	Distilled water	575	575	575	575	575
Oil phase	Liquid paraffin	150	150	150	150	150
	Span 80	35	35	35	35	35
	Tween 85	15	15	15	15	15
Initiator	SBS	0.2	0.2	0.2	0.2	0.2
	KPS	0.45	0.35	0.4	0.50	0.55
reaction conditions	Temperature	47	47	47	47	47
	Stirring rate (RPM)	400	400	400	400	400

### 2.3.1.6 Influence of the type of vinyl co-monomer (namely M<sub>1-3</sub>) on the properties of PAM

The study aims to investigate the effects of incorporating another monomer with acrylamide as the main monomer on the properties of the resulting polymers in terms of the quantitative conversion of the monomer into a polymer and the efficiency of the resulting polymers as flocculating agents in water treatment are studied. However, the acrylamide to monomer ratio is 90:10 [xxvii], where the acid monomer is neutralized by ammonium hydroxide [xxviii]. Acrylic (M<sub>1</sub>) and methacrylic acid (M<sub>2</sub>) will be studied as water-soluble monomers and stearyl methacrylate (M<sub>3</sub>) as an oil-soluble monomer with the constant of the aqueous /oil ratio and total monomer content as shown in Table 6.

### 2.3.1.7 Optimization of acrylic acid as co-monomer (namely AA1-4) on the properties of PAM

This series of experiments aims to optimize the use of acrylic acid as a co-monomer in the synthesis of polyacrylamide (PAM) to improve the flocculating efficiency of the resulting polymer. Acrylic acid is added at different concentrations (25, 30, 35, and 40 g) namely AA<sub>1-4</sub> which the percentage of acrylic acid (11.11, 13.3, 15.5, and 17.7 %) respectively from total monomer while maintaining a constant total monomer content. The aqueous phase is prepared by neutralizing the added acrylic acid with ammonium hydroxide solution, and the oil phase preparation is kept constant. The reaction conditions, including temperature and stirring rate, are also kept constant for all samples, the feed composition data for the preparation is listed in Table 7.

Table 6 the feed composition data for the (M<sub>1-3</sub>) series.

Phase	Material	Amount (g)			
		P <sub>2</sub>	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>
Aqueous phase	Acrylamide	225	202.5	202.5	202.5
	Acrylic acid	-	22.5	-	-
	Methacrylic acid	-	-	22.5	-
	Distilled water	575	575	575	597.5
Oil phase	Stearyl methacrylate	-	-	-	22.5
	Liquid paraffin	150	150	150	122.5
	Span 80	35	35	35	35
	Tween 85	15	15	15	15
Initiator	KPS	0.4	0.4	0.4	0.4
	SBS	0.2	0.2	0.2	0.2
reaction conditions	Temperature	47	47	47	47
	Stirring rate (RPM)	400	400	400	400

Table 7 The feed composition data for the (AA<sub>1-4</sub>) series

Phase	Material	Amount (g)				
		M <sub>1</sub>	AA <sub>1</sub>	AA <sub>2</sub>	AA <sub>3</sub>	AA <sub>4</sub>
Aqueous phase	Acrylamide	202.5	200	195	190	185
	Acrylic acid	22.5	25	30	35	40
	Ammonium hydroxide (30%)	4.5	5	6	7	8
	Distilled water	575	570	569	568	567
Oil phase	Liquid paraffin	150	150	150	150	150
	Span 80	35	35	35	35	35
	Tween 85	15	15	15	15	15
Initiator	SBS	0.2	0.2	0.2	0.2	0.2
	KPS	0.4	0.4	0.4	0.4	0.4
reaction conditions	Temperature	47	47	47	47	47
	Stirring rate (RPM)	400	400	400	400	400

### 2.3.1.8 Studying the influence of ureido methacrylate on the properties of PAM

In the present series, different experiments namely U<sub>1</sub>, U<sub>2</sub>, U<sub>3</sub>, U<sub>4</sub>, and U<sub>5</sub>, were performed by adding (5, 10, 15, 20, and 25g) respectively of ureido methacrylate UMA from the total amounts of monomer at constant aqueous/oil ratio. The ureido methacrylate is introduced in different amounts, The presence of ureido groups in molecules provides them with hydrogen bonding capabilities, and it is

easy to design a functional molecule containing the ureido group because this group exhibits directional hydrogen bonding patterns. As illustrated in Figure 1, Proposed schemes for the synthesis of the poly acrylamide co-acrylic cross-linked by UMA. By using a rational design of intermolecular hydrogen bonds between ureido groups, The hydrogen atoms of the ureido group efficiently form complexes with electronically negative species [xxix]. The feed composition data as reported above is listed in Table 8.

Table 8 the feed composition data for the (U<sub>1-4</sub>) series

Phase	Material	Amount (g)					
		AA <sub>3</sub>	U <sub>1</sub>	U <sub>2</sub>	U <sub>3</sub>	U <sub>4</sub>	U <sub>5</sub>
Aqueous phase	Acrylamide	190	186	181.5	177	173	169
	Acrylic acid	35	34	33.5	33	32	31
	Distilled water	575	575	575	575	575	575
Oil phase	Ureido Methacrylate	-	5	10	15	20	25
	Liquid paraffin	150	145	140	135	130	125
	Span 80	35	35	35	35	35	35
	Tween 85	15	15	15	15	15	15
Initiator	SBS	0.2	0.2	0.2	0.2	0.2	0.2
	KPS	0.4	0.4	0.4	0.4	0.4	0.4
reaction conditions	Temperature	47	47	47	47	47	47
	Stirring rate (RPM)	400	400	400	400	400	400

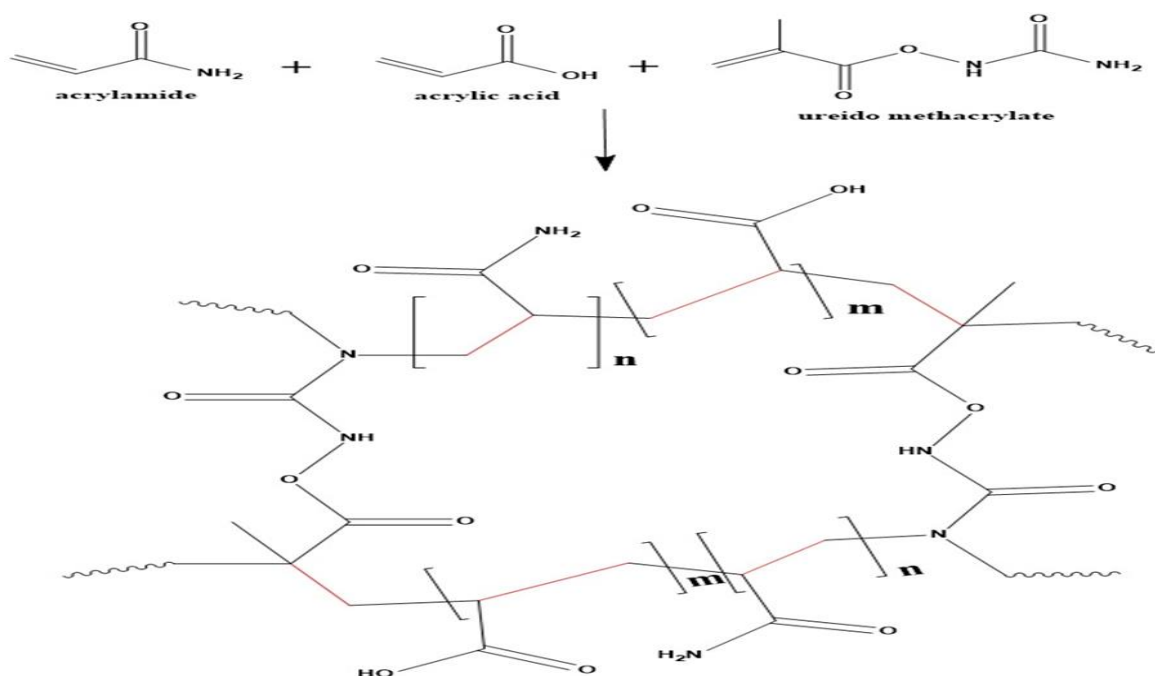


Figure 1 Proposed schemes for the synthesis of the poly acrylamide co acrylic cross-linked by UMA

### 2.3.2. Instrumental characterization

#### 2.3.2.1. Determination of monomer conversion by gravimetric method

The gravimetric method for determining monomer conversion involves measuring the mass of the dried

polymer as compared to the total mass of monomers using oven MEMERT UN 110 (German) and Analytical balance Shimadzu ATY 224 (Japan). The conversion is then calculated using the following equation [xxx].

$$\text{Conversion \%} = \frac{\% \text{ of solids} - (\text{weight fraction of oil} + \text{weight fraction of emulsifiers} + \text{weight fraction of redox system})}{\text{weight fraction of monomers}}$$

It is important to note that the conversion is not always a direct indicator of polymer molecular weight. However, in some systems, the number of average molecular weights increases linearly with the

monomer conversion. Therefore, it is necessary to determine the molecular weight of the polymer using separate techniques [xxx].

### 2.3.2.2. Determination of Intrinsic Viscosity and Molecular Weight of the resultant PAM

In this study, gel permeation chromatography (GPC) analysis is employed to assess the average molecular weight distribution (MWD) of the synthesized polymers. However, it is important to note that GPC may not accurately measure MWD for ultra-high molecular weight flocculants (with molecular weights exceeding approximately  $10^7$  g/mol) due to certain limitations. These limitations arise from the properties of the flocculants being cross-linked polymers or existing in the form of gels, as well as being partially soluble flocculants, such as polyacrylamide-grafted amylopectin. One of the limitations is that the GPC column has a pore size limit, which restricts the fractionation of ultra-high molecular weight flocculants. Consequently, a portion of the polymer chains may be lost in the GPC pre-injection filtration system. Additionally, high molecular weight and bio-flocculants often experience chain scission during the GPC analysis, leading to unreliable MWD results. Furthermore, there may be interactions between the polymer and the column packing materials, further limiting the range of flocculants that can be effectively characterized using GPC [xxxii].

Moreover, the intrinsic viscosity and molecular weight of the resultant PAM were determined using an Ubbelohde viscometer and the Mark-Houwink equation. A portion of each final emulsion was precipitated by an excess amount of acetone (1:6) and washed several times. Precipitates were then dried at 80 °C for 48 h. 200 mg of the purified polymer powder was dissolved in 100 mL of deionized water under gentle stirring. Then the obtained solution was diluted to prepare concentrations of 0.2, 0.4, 0.6, 0.8, and 1 g of the polymer in 1000 mL of deionized water. The viscosity of each solution was measured three times [xxxiii].

The measurement was conducted at  $25 \pm 0.1$  °C, Using the time of fall of the ball an Ubbelohde viscometer through the polymeric solution ( $t$ ) and the time of fall of the ball through the solvent ( $t_s$ ), as the following equation:

$$\text{Relative viscosity, } \eta_{\text{rel}} = t/t_s$$

$$\text{Specific viscosity } \eta_{\text{sp}} = \eta_{\text{rel}} - 1$$

$$\text{Reduced viscosity } \eta_{\text{red}} = \eta_{\text{sp}}/c$$

Where,  $c$  is the polymer solution concentration (g/L).

Intrinsic viscosity,  $[\eta]$ , was defined from the intercept of a linear regression of the reduced viscosity graph,  $\eta_{\text{red}}$ , versus the aqueous polymer solution concentration, the molecular weights  $\text{g}\cdot\text{mol}^{-1}$   $[M]$  of the final polymers were determined by the below Mark–Houwink equation at 25 °C [xxxiv].

$$[\eta] = 6.31 \times 10^{-3} [M]^{0.8}$$

### 2.3.2.7. Conductivity and dissolution time Measurement for Polyacrylamide:

Conductivity measurement and dissolution time Measurement is a valuable technique used to assess the electrical properties of polymer solutions and exhibits various applications such as flocculation, water treatment, and rheology control. Conductivity measurement provides insights into the ionic characteristics and performance of polyacrylamide solutions, especially in the presence of other electrolytes or additives. The testing is by using ADWA (AD8000, Hungary).

**Conductivity Testing Methods:** Prepare a well-mixed, homogeneous sample of polyacrylamide solution. Rinse the conductivity cell with distilled water; immerse it in the solution, ensuring full electrode coverage. Equilibrate the solution and cell to a consistent temperature, following instrument guidelines for temperature control. Record the stable conductivity reading, typically in micro Siemens per centimeter ( $\mu\text{s}/\text{cm}$ ), and repeat measurements at least three times for each sample to calculate the average conductivity value.

Conductivity measurements can provide indirect information about the dissolution time of polyacrylamide.

**Dissolution Testing Methods:** a solution of 0.04 g of the poly acrylamide and 100 mL of distilled water was added to a beaker at 30 °C. The electrode of the conductivity meter was employed to detect the conductance of the solution; if the conductance did not show any change within 3 min, PAM was considered completely dissolved. The minimum dissolution time required for this experiment was recorded, as the dissolution progresses; the conductivity may eventually reach a saturation point where the concentration of released ions remains constant. This saturation point indicates that most of the PAM has dissolved [xxxv].



### 2.3.2.3. Jar Test

The Jar Test is a laboratory test used to evaluate the effectiveness of chemical coagulation and flocculation in treating water and wastewater. The test is performed by adding increasing doses of a polymer or coagulant to a series of beakers containing a kaolin solution and mixing them at various speeds. The flocculation efficiency is then determined by measuring the turbidity of the supernatant after settling for 30 minutes. The final result is expressed as a percentage of the initial turbidity reduction. The test allows for the evaluation of different coagulants and coagulant aids, as well as the effects of concentration and order of addition [xxxvi]. The test apparatus typically includes a multi-position stirrer, glass beakers, and a turbidity meter [xxxvii].

**Apparatus;** VELP Scientifica™ F105A0109 (Italy) Multiple Stirrers multi-position stirrer with continuous speed variation from about 10 to 300 rpm should be used. Are fitted with a self-locking device with a clutch and the same configuration and size [xxxviii].

Kaolin solution (reagent): 1 g of kaolin was prepared in 1L of distilled water. Kaolin solution is introduced to all jars simultaneously [xxxix]. The test procedure is summarized as follows:

1. Fill the appropriate number of (matched) 1000 mL transparent jars (*or Beakers*) with well-mixed test water, using a 1000 mL graduate.
2. Place the filled jars on the gang stirrer, with the paddles positioned identically in each beaker. Then Mix the beakers at 40 – 50 rpm for 30 seconds. Discontinue mixing until polymer addition is completed.
3. Leave the first beaker as a blank<sup>1</sup>, and add increasing doses of the polymer (or the polymer you want to compare) to subsequent beakers. Inject polymer solutions as quickly as possible, below the liquid level and about halfway between the stirrer shaft and beaker wall.
4. Increase the mixing speed to 200 rpm for 3 min. then reduce the mixing to 100 rpm and continue for 6 min.

5. Turn the mixer off the floc and allow it to settle for 30 min. After settling, the supernatant is quantified using a turbidity meter Lovibond TB 250 WL Fisher Scientific Uk [xl].

The flocculation efficiency (E)

$$E (\%) = [(initial\ turbidity - final\ turbidity) / initial\ turbidity] \times 100$$

### 2.3.2.4. Fourier transform infra-red spectroscopy FT-IR

FT-IR spectroscopy is a powerful analytical technique that can provide information about the functional groups present in a sample. Specifically to identify the presence of ureido methacrylate and its incorporation into the polymer structure, as well as to confirm the formation of the PAm polymer. The spectra were recorded in the range of 4000-400 cm<sup>-1</sup> and the sample was prepared by applying a thin film of the polymer on a glass slide. The sample is tested by BRUKER FTIR INVENIO-S German [xli].

### 2.3.2.5. Differential scanning calorimeter DSC

Differential scanning calorimetry (DSC) is a technique used to study the thermal properties of materials, such as their melting points, glass transition temperatures, and specific heat capacities. DSC works by heating a sample in a controlled manner and measuring the heat flow into or out of the sample [xl<sup>ii</sup>]. DSC curves of the three acrylamide polymers were obtained using a Perkin Elmer thermal analysis (DSC 6000, American) the temperature was raised at a rate of 5 °C per minute under a nitrogen atmosphere.

### 2.3.2.6. SEM-EDX Characterization

Scanning Electron Microscopy (SEM) is an advanced imaging technique widely employed to investigate the surface morphology and microstructural characteristics of various materials. By utilizing electron beams, SEM enables the acquisition of high-resolution, three-dimensional images that provide valuable insights into the surface attributes, particle dimensions, shape, and spatial distribution within polyacrylamide specimens [xl<sup>iii</sup>]. EDX is an energy-dispersive X-ray spectrometer is essential for determining the elemental composition and quantities of materials and can be used for a material characterization. SEM and EDX are often used together as part of an integrated system known as SEM-EDX using Bruker German [xl<sup>iv</sup>].

### 2.3.2.8. Polyacrylamides reuse efficiency in wastewater treatment

Flocculent can be reused after the removal of contaminants through desorption or regeneration. Desorption involves washing the flocculants with a suitable solvent to remove the adsorbed contaminants, followed by rinsing and drying. The reusability of PAM depends on various factors, such as the type and concentration of contaminants, the nature of the application, and the effectiveness of the regeneration process [xlv]. In some cases, the reusability of PAM can provide economic and environmental benefits by reducing the need for new polymer synthesis and minimizing waste generation. The washing process of PAM from kaolin clay can help to reduce the amount of PAM that is released into the environment. To reuse polyacrylamide that has been used as flocculants in wastewater treatment, the first step is to remove the contaminants that have been adsorbed onto the polymer. This can be done by a process called desorption, which involves washing

the PAM with a suitable water to remove the adsorbed contaminants, followed by rinsing and drying.

## 3. Result and discussion

### 3.1. Influence of initial reaction temperature.

The results of an experiment evaluating the effect of initial temperature on various factors related to polymerization. The experiments show the stability of pre-emulsion, and colloidal polymer emulsion, with no coagulum formation, average molecular weight  $\text{g}\cdot\text{mol}^{-1}$ . The results show that the optimum reaction temperature at  $47\text{ }^{\circ}\text{C}$  in terms of molecular weight rose to  $2.08 \times 10^6\text{ g}\cdot\text{mol}^{-1}$  as shown in Figure 2a, In Figure 2b illustrates the gravimetric conversion increase to 92.68 % and the flocculation efficiency increases to 88.37 %. While at temperatures below  $47\text{ }^{\circ}\text{C}$  there is no reaction observed; this may be due to the low activation energy below  $47\text{ }^{\circ}\text{C}$  which was not able to generate active sites to initiate the polymerization reaction.

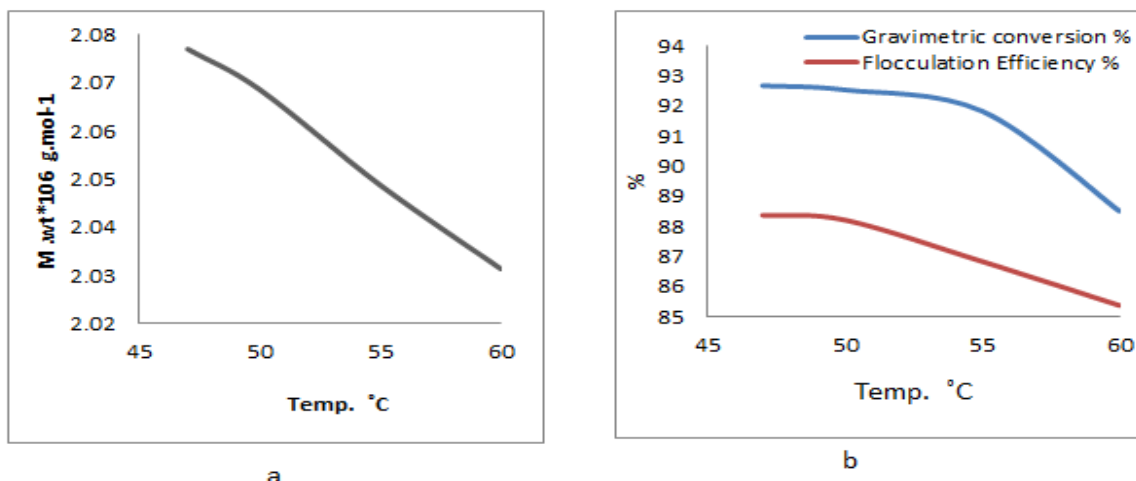


Figure 2 (a) Influence of initial reaction temperature on molecular weight (b) Influence of initial reaction temperature on gravimetric conversion and flocculation efficiency.

### 3.2. The aqueous to oil ratio

Typically, the mass fraction of the aqueous to the oil phase is attempted at the ratio of 70/30; when the aqueous to oil ratio increases, the molecular weight is raised to  $2.2 \times 10^6\text{ g}\cdot\text{mol}^{-1}$  as shown in Figure 3a, and the gravimetric conversion from monomer to polymer also increases to give 97.13 % at the ratio 80/20, as it seems to show more efficient properties as a flocculating agent at the ratio of 75/25 and 80/20 to 89.19 % and 90.49 % respectively as shown in figure 3b. It was reported that the stability of an inverse emulsion and colloidal polymer emulsion refers to

the resistance of the dispersed droplets to coalesce, flocculate, or undergo phase inversion. A stable inverse emulsion will have small, well-dispersed droplets that are evenly distributed throughout the continuous phase. However, when the aqueous phase is too high (85/15), this leads to an unstable pre emulsion and undesirable results. A high aqueous phase can cause phase inversion, where the dispersed phase and continuous phase switch positions, leading to instability of the emulsion [xlvi].

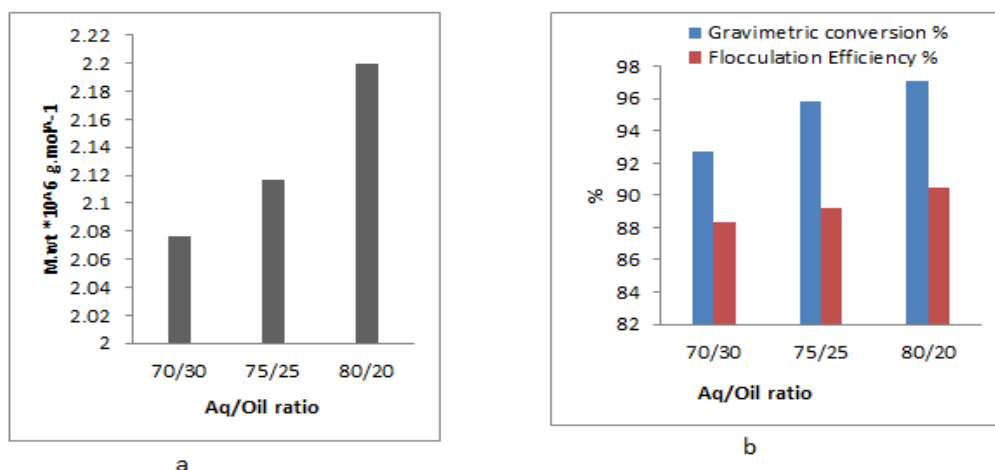


Figure 3 (a) Influence of the aqueous to oil ratio on molecular weight (b) Influence of the aqueous to oil ratio on gravimetric conversion and flocculation efficiency

### 3.3. Influence of the concentration of monomer.

Increasing the concentration of acrylamide from 175 to 200 and 225 g leads to an increase in the molecular weight of the resultant polymer to 2.3, 2.5, and 2.7 \* 10<sup>6</sup> g/mol, respectively, as shown in Figure 4a. Consequently, the flocculation efficiency also increases, reaching 91.57% when using 225 g of acrylamide monomer, as illustrated in Figure 4b.

However, at very high monomer concentrations, coagulation occurs. This behavior can be explained by the fact that as the monomer concentration increases, the rate of polymerization increases, leading to a corresponding increase in the size of the polymer particles. This increase in average particle sizes leads to a decreased stability the colloidal of polymer emulsion.

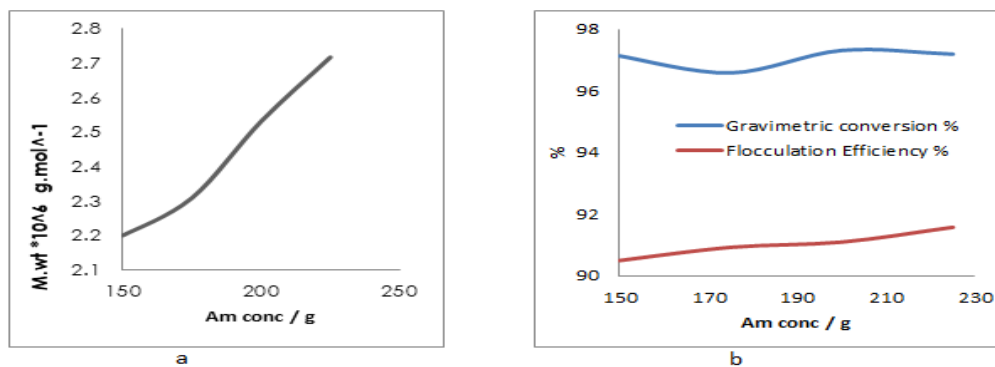


Figure 4 (a) Influence of the concentration of monomer on molecular weight (b) Influence of the concentration of acrylamide on gravimetric conversion and flocculation efficiency

### 3.4. Influence of the type of initiator on the properties of PAm

In this series, different types of initiators namely benzoyl peroxide as oil-soluble, hydrogen peroxide HPO, potassium persulfate (KPS), sodium persulfate (SPS), and ammonium persulfate (APS) as water-soluble initiator. The experiments show the stability of pre-emulsion and colloidal polymer emulsion. However; the oil-soluble initiator benzoyl peroxide BPO and tert butyl hydro peroxide are dissolved in the oil phase, as the indented radicals are formed by

the decomposition of the hydrophobic peroxide; which cannot enter the hydrophilic monomer micelles. This leads to low molecular weights of 1.27 and 1.07 \* 10<sup>6</sup> g.mol<sup>-1</sup> of BPO and TBHP Figure 5a. On the other hand, the use of water-soluble initiators (SPS, KPS, and APS) leads to a faster rate of acrylamide polymerization and higher gravimetric conversion compared to oil-soluble initiators. This impacts Flocculation Efficiency, Where the efficiency reached the highest value with KPS

(92.23%) as in Figure 5b. This may be due to the more hydrophilic radicals formed which can be adsorbed by the hydrophilic monomer micelles to

form polymer molecules by the formation of many active centers.

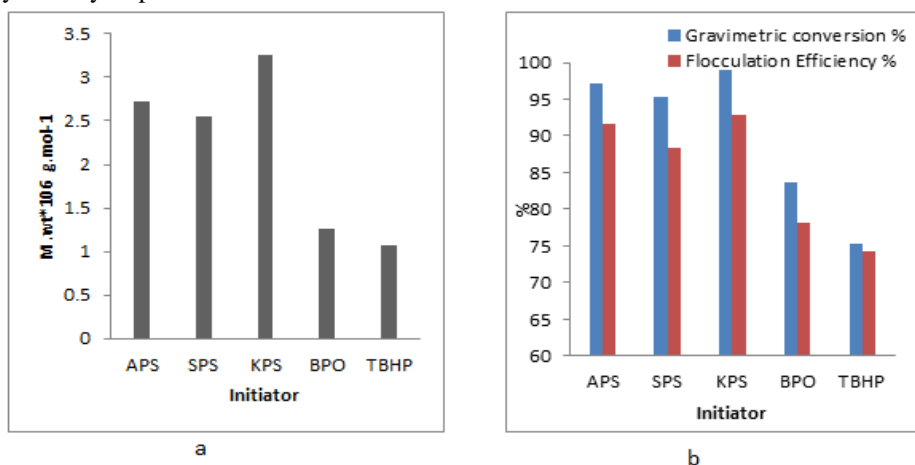
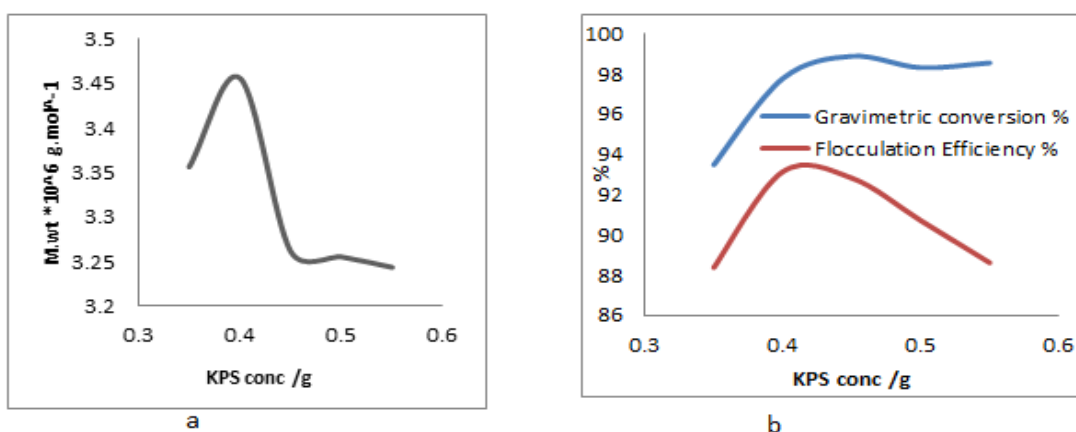


Figure 5 (a) Influence of the type of initiator on molecular weight of PAM (b) Influence of the type of initiator on the on gravimetric conversion and flocculation efficiency of PAM

### 3.5. Optimization of potassium per-sulfate as initiator on the properties of PAM

Based on the free radical polymerization; the rate of polymerization increases with increasing initiator concentration. Figure 6b shows the effect of potassium persulfate concentration on the final conversion and flocculation efficiency of the resulting polymer. The polymerization rate and the degree of final conversion increase with increasing the initiator concentration. On the other hand, as the concentration of the initiator increases, it directly

Moreover, the molecular weight decreased with the increase of the potassium per-sulfate concentration as shown in Figure 6a. The best results were given based on the highest conversion (97.77 %) with the highest number of molecular weight ( $3.46 \times 10^6 \text{ g.mol}^{-1}$ ), which influences the efficiency of the final product as a flocculant with a result of 93.14 %. The rate of polymerization at a lower initiator concentration is slower, and the final conversion only reaches a lower value, and then it remains constant so that the polymerization rate is shown to be longer till



affects the molecular weight of the resultant polymer.

the complete consumption of the KPS initiator.

Figure 6 (a) Optimization of KPS concentrations on molecular weight of PAm (b) Optimization of KPS concentration on gravimetric conversion and flocculation efficiency of PAM

### 3.6. Influence of the type of vinyl co-monomer on the properties of PAm

The type of vinyl co-monomer used in the copolymerization with acrylamide can greatly influence the properties of the resulting PAm copolymer. The use of acrylic acid as a co-monomer results in the higher quantitative conversion of the monomer into a polymer (98.05 %), and also results in higher efficiency as a flocculating agent (96.36 %) in water treatment compared to methacrylic acid and stearyl methacrylate as in Figure 7b. however, stability of pre-emulsion and colloidal polymer

emulsion This can be attributed to the fact that acrylic acid has a higher level of carboxylic acid groups, which give it greater charge density and thus better flocculation properties. Additionally, the average molecular weight of the copolymer also decreases as the co-monomer changes from acrylic acid to methacrylic acid and stearyl methacrylate as shown in Figure 7a. This can also be attributed to the difference in the functional groups of the co-monomers and their ability to participate in the copolymerization reaction.

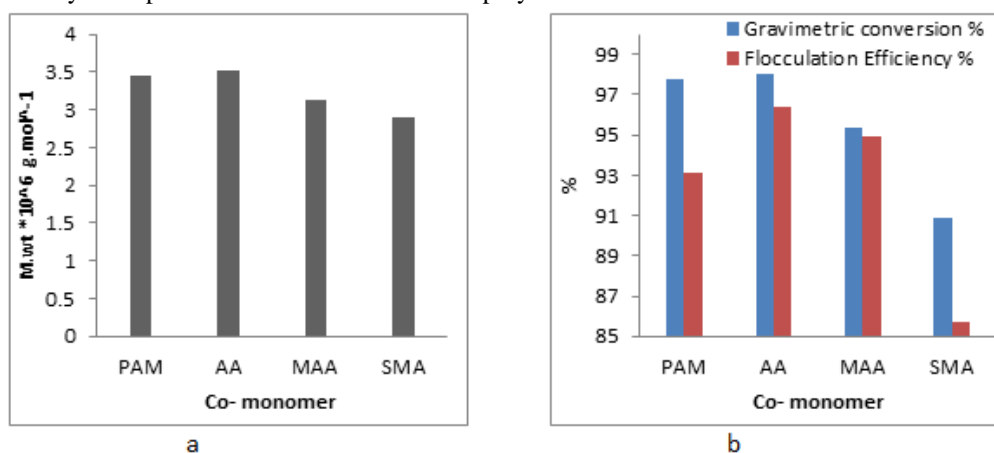


Figure 7 (a) Influence of the type of vinyl co-monomer on molecular weight of PAm (b) Influence of the type of vinyl co-monomer on gravimetric conversion and flocculation efficiency of PAm

### Optimization of acrylic acid as co-monomer on the properties of PAm

The result in Figure 8a shows that the concentration of acrylic acid (AA) increases, the average molecular weight of the resulting polymer increases, and the gravimetric conversion also increases. The pre-emulsion and colloidal polymer emulsion stability is

consistent throughout all experiments.

No coagulum formation is observed, and the flocculation efficiency also increases. Based on these results, it appears that the optimal concentration of acrylic acid for the highest flocculating efficiency is 35 g with 96.67% efficiency, as seen in Figure 8b.

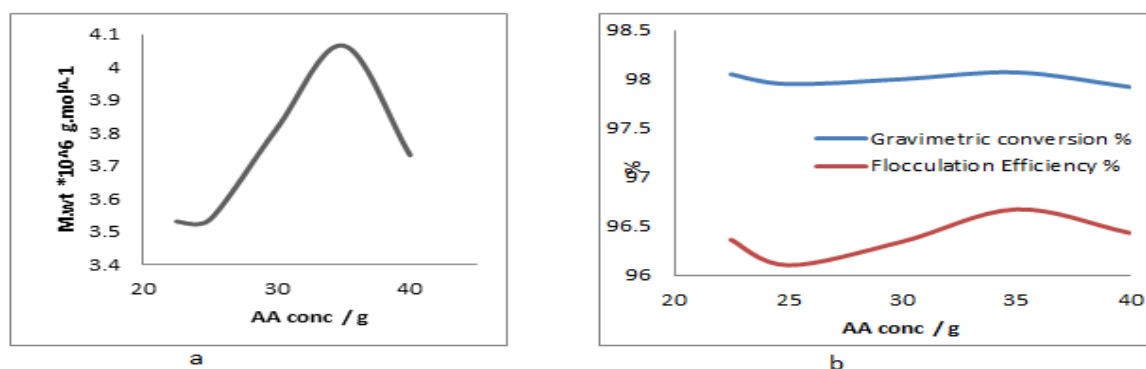


Figure 8 (a) Effect of concentration of acrylic acid on the molecular weight of PAm (b) Effect of concentration of acrylic acid on gravimetric conversion and flocculation efficiency of PAm

### Influence of ureido methacrylate on the properties of PAM

In this preparation series, the UMA monomer was mixed with Am and AA monomers in the polymerization system in different weight ratios to form terpolymers, as the UMA exhibits an ureido group, which is a nitrogen-containing functional group that can form hydrogen bonds with other molecules. This makes UMA useful for creating supramolecular polymers and gels with high molecular weight illustrated in Figure 9a. The UMA seems to improve the performance of the main polymer skeleton by increasing the strength of the interactions between the PAM molecules and the water molecules in the aqueous medium. The results showed improvements in the stability of pre-emulsion and colloidal polymer emulsion. Also, the addition of UMA to PAM leads to an improvement in its flocculation properties which are useful in water treatment. However, there is a slight variation in the gravimetric conversion and flocculation efficiency; where the flocculation efficiency increases as the amount of UMA increases, with the optimum and highest

efficiency achieved at 15g of UMA (98.62%) as shown in Figure 9b. It's worth mentioning that the commercial sample, Magnafloc® LT27AG (a copolymer of acrylamide and acrylic acid), achieved a flocculation efficiency of 97.89%. Moreover, when the UMA was raised to more than 15g, the flocculating efficiency would be decreased. The decrease in flocculation effect can be explained that the flocculation may be decreased with increasing the UMA bulky sites. When the amount of UMA increases, the degree of crosslinking between the polymeric chains also increases. This higher degree of crosslinking impedes the swelling of the resulting gels. The crosslinks act as physical barriers, restricting the movement of solvent molecules into the gel network and reducing its overall swelling capacity. Consequently, the gel becomes more compact and less prone to expansion or absorption of additional solvent. The increased crosslinking density the rigidity of the core of colloids increased contributes to the formation of a more rigid and structurally stable gel with reduced swelling behavior [47].

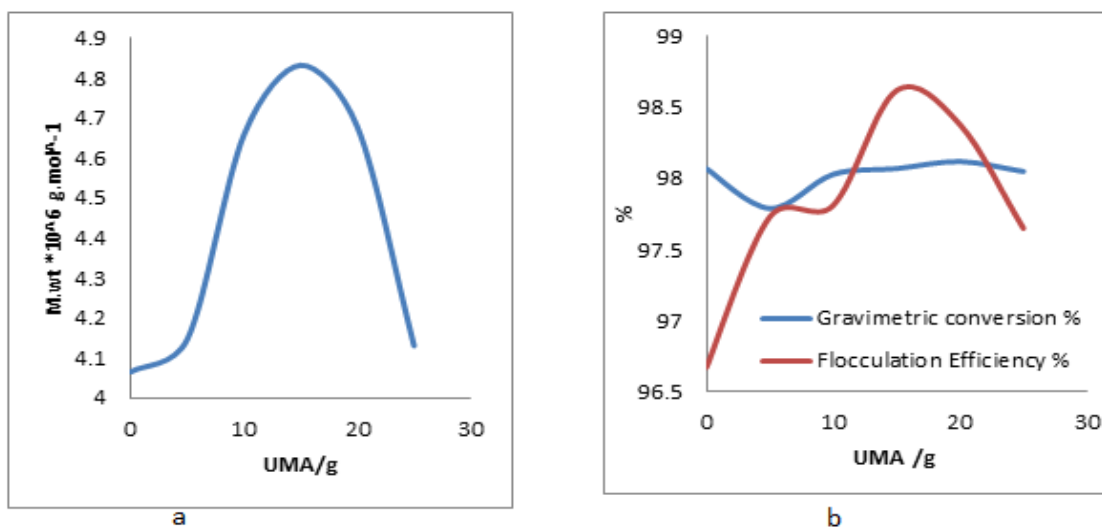


Figure 9 (a) Influence of ureido methacrylate on the molecular weight of PAM (b) Influence of ureido methacrylate on gravimetric conversion and flocculation efficiency of PAM

### Conductivity and dissolution time Measurement for Polyacrylamide

Anionic polyacrylamide contains negatively charged groups that influence its properties and performance. For instance, sample AA<sub>3</sub> exhibits a conductivity 210  $\mu\text{s}/\text{cm}$ , in contrast to the

homopolymer sample P<sub>2</sub>, which records a conductivity 80  $\mu\text{s}/\text{cm}$ . This difference in conductivity providing valuable information about the presence and behavior of charged groups within the solution. Notably, sample AA<sub>3</sub>'s conductivity closely resembles that of

Magnafloc® LT27AG, which measures 203  $\mu\text{s}/\text{cm}$ .

Ureido methacrylate incorporates functional groups that impact the ionic behavior of the resulting polymer  $U_3$ . These functional groups can interact with water molecules and ions in the solution, amplifying the ionization and increasing the polyacrylamide's conductivity 222  $\mu\text{s}/\text{cm}$ .

Furthermore, the dissolution times for samples  $P_2$ ,  $AA_3$ ,  $U_3$ , and Magnafloc® LT27AG are 72, 50, 46, and 54, respectively, demonstrating that the addition of acrylic acid decreases the dissolution time which increases ionization. The conductivity meter can measure the initial increase in conductivity as the polymer chains start to dissolve and release ions. By continuously monitoring the changes in conductivity over time can give you insights into how quickly the polymer chains are dissolving

and releasing ions into the solution.

#### Fourier transform infra-red spectroscopy FT-IR

Figure 10 demonstrates the FTIR spectra of the  $U_3$ ,  $AA_3$ ,  $M_1$ ,  $P_2$ ,  $Am_3$ ,  $A_2$ , and  $T_3$  polymers compared to the PAm polymer. As expected, the spectra of all polymers typically like that of PAm polymer due to no significant differences exist between the structures in terms of peak positions. In all spectra, the absorption bands at about 3330  $\text{cm}^{-1}$  correspond to NH stretching and hydrogen-bonded OH [48]. The broad peak at  $\sim 1560 \text{ cm}^{-1}$  resulted from two peaks related to the C-N and C-O stretching, while the broad bands at  $\sim 2942$  and  $\sim 2849 \text{ cm}^{-1}$  to  $-\text{CH}_2$  stretching vibration. The occurrence of C=O absorption at 1664  $\text{cm}^{-1}$  specify it clearly to carbonyl of acrylamide group. The C=C vibrations were presented around 974  $\text{cm}^{-1}$  may be attributed to free monomer [49].

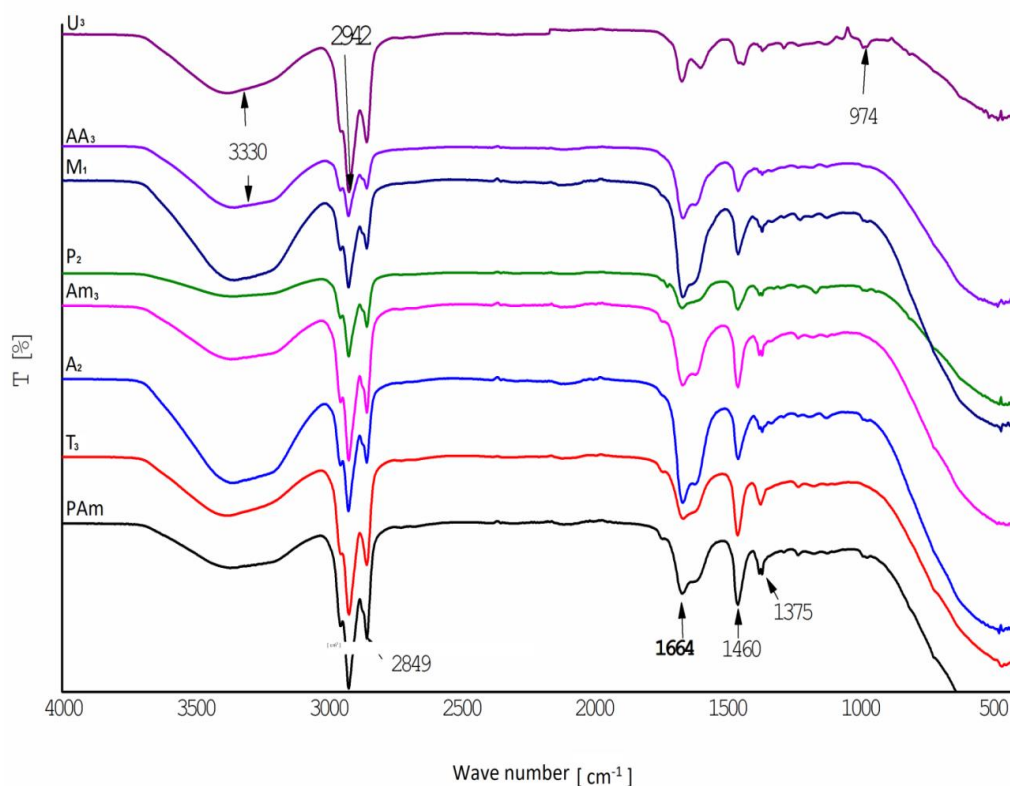


Figure 10 Fourier transform infrared spectroscopy FT-IR

### Differential scanning calorimeter (DSC)

Figure 11 Shows the DSC curve of the  $p_2$  polymer (homo-polymer of acrylamide) would show a single exothermic peak, corresponding to the glass transition temperature of the polymer. The DSC curve of the  $AA_3$  polymer (copolymer of acrylamide and acrylic acid) would show a similar exothermic peak, but it could be shifted slightly to a lower temperature due to the

presence of the acrylic acid co-monomer [50]. The DSC curve of the  $U_3$  polymer (polymer containing ureido methacrylate) could show intense exothermic peaks higher than those of the other two samples. This is likely because the ureido methacrylate co-monomer may increase the thermal resistance of the polymer, leading to a higher glass transition temperature [51].

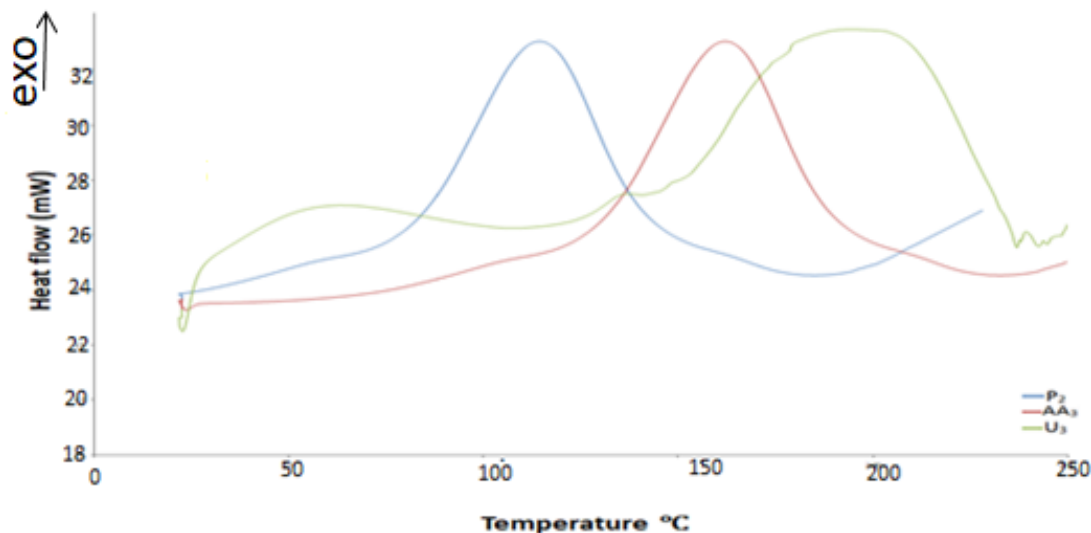


Figure 11 DSC curve of three polymers which  $p_2$ ,  $AA_3$ , and  $U_3$

### SEM-EDX analysis results

In the case of polyacrylamide co-acrylic acid containing ureido methacrylate synthesized through inverse emulsion polymerization, SEM analysis revealed spherical-shaped particles, influenced by the experimental conditions used during synthesis. The SEM images displayed an average particle size distribution ranging from 0.49 to 2.16  $\mu\text{m}$ , providing insight into particle dimensions. Furthermore, SEM observations uncovered porosity within the polymer structure, allowing assessment of polymer chain arrangement. EDX spectra confirmed the presence of carbon, oxygen, and nitrogen, consistent with the expected composition of polyacrylamide, acrylic, and ureido methacrylate. Additionally, sulfur, sodium, and potassium were detected at lower levels, attributed to their use in the initiator system, as illustrate in Figure 12.

### Polyacrylamides reuse efficiency in wastewater treatment

The testing of the recovered Polyacrylamide in the removal of kaolin from wastewater revealed a significant decrease in efficiency. The efficiency was measured to give 93.7 % of the optimal sample.

One potential reason for the decline could be attributed to changes in the polymer's properties due to repeated usage, leading to degradation or alterations in its molecular structure [52]. Moreover, the presence of impurities or contaminants accumulated during previous usage could impact the effectiveness of the reclaimed Polyacrylamide. These impurities and contaminants can interfere with the adsorption and flocculation processes, reducing the overall efficiency of the polymer.



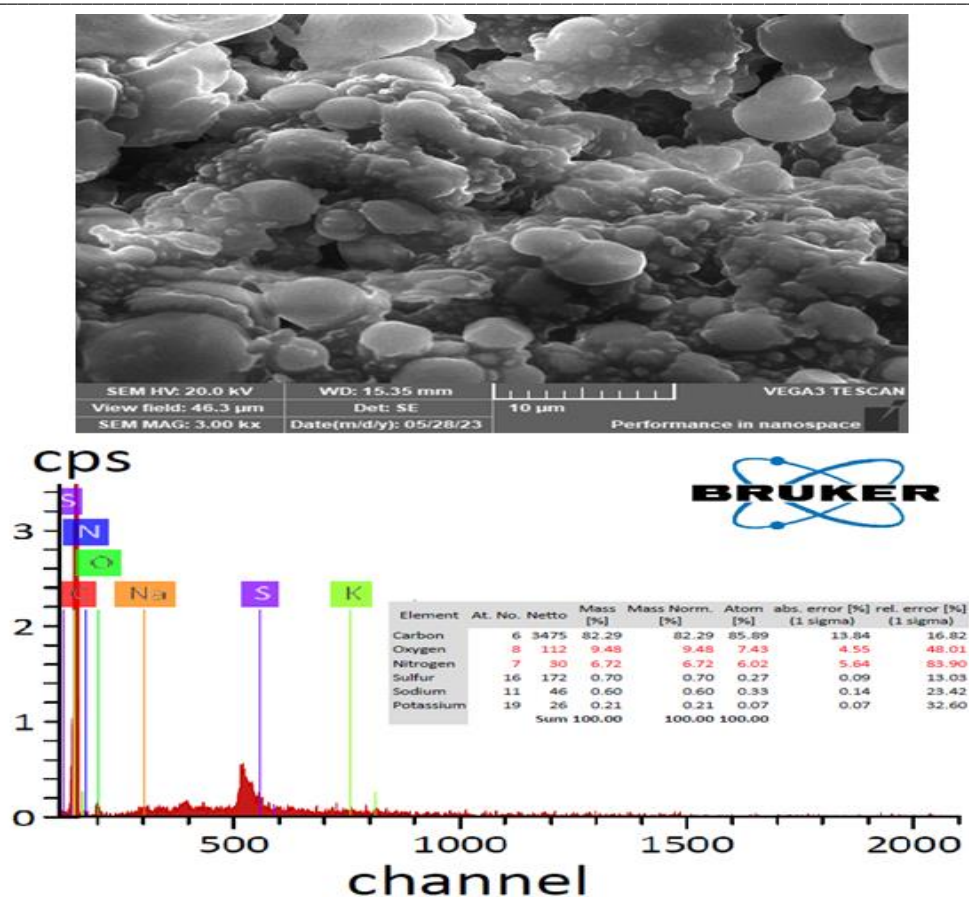


Figure 12 SEM-EDX analysis for polyacrylamide co-acrylic acid incorporating UMA

**Kinetic investigation**

In this study, the kinetics of the interaction between polyacrylamide of optimum sample U3 and kaolin were investigated at varying concentrations of polyacrylamide (0.2 g, 0.4 g, and 0.6 g) and over different time intervals (20, 30, 40, 50, 60, 70, and 80 minutes). The efficiency of kaolin removal was monitored during the experiment. The results, as illustrated in Figure 13a, revealed a notable increase in efficiency with increasing polyacrylamide concentration and time. Specifically, at 0.2 g of polyacrylamide, the efficiency ranged from 8.7% to 28.096%, while at 0.4 g and 0.6 g, the efficiency exhibited a more substantial improvement, reaching values as high as 52.78% and 98.62%, respectively. The flocculation process was mostly considered as a bimolecular reaction, which was expressed as [53].

$$Eq \quad (N_0/N_t)^{1/2} = 1 + 0.5 kN_0t$$

where

$N_0$  is the initial content of the kaolin particle (measured by using initial turbidity in this work),  $N_t$  is the content of kaolin particles with respect to  $t$  (min) (measured by using residual turbidity), and  $k$  ( $s^{-1}$ ) is the kinetic constant of particle collision and aggregation. The experimental data demonstrate that the functional relationship between  $(N_0/N_t)^{1/2}$  and  $t$  can be linearly fitted, and the fitting results are shown in Figure 13b.

The  $kN_0$  value is 0.0404, 0.0488, and 0.0675  $s^{-1}$  for dose the 0.2, 0.4 and 0.6 g respectively it appears that the rate constant  $k$  increases with increasing concentration as in Figure 13c this suggests a first-order reaction [54].

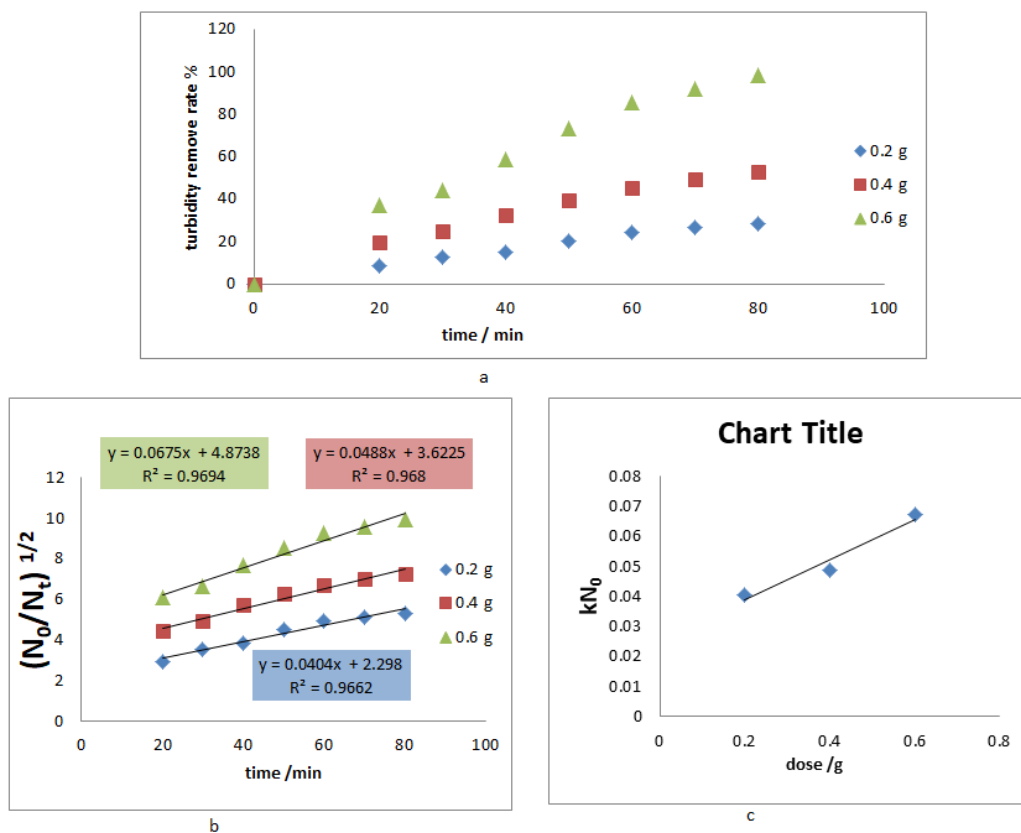


Figure 10 (a) Turbidity removal rate with different  $U_3$  dosage changes with flocculation time, (b)  $(N_0/N_t)^{1/2}$  changes with flocculation time, and (c)  $kN_0$  changes with flocculant dose

## Conclusion

The comprehensive investigation into the synthesis and characterization of polyacrylamide (PAM) and its derivatives through inverse emulsion polymerization has yielded valuable insights into the factors affecting their properties and performance. Here are the key findings:

The optimal reaction temperature was found to be 47°C, resulting in a high molecular weight of  $2.08 \times 10^6$  g/mol, the mass fraction of the aqueous to oil phase significantly impacted PAM properties. An increase in the aqueous phase led to higher molecular weights (up to  $2.2 \times 10^6$  g/mol), Increasing acrylamide concentration from 175 to 225 g resulted in higher molecular weights (up to  $2.7 \times 10^6$  g/mol) and improved flocculation efficiency (up to 91.57%). The choice of vinyl co-monomer significantly impacted PAM properties. Acrylic acid as a co-monomer showed the highest flocculation efficiency (96.67%) compared to methacrylic

acid and stearyl methacrylate. The addition of ureido methacrylate (UMA) improved the stability of pre-emulsion and colloidal polymer emulsion. the highest efficiency (98.62%) was achieved at 15g of UMA.

Conductivity measurements and Dissolution time provided insights into the presence and behavior of charged groups in the polymer solution. DSC analysis highlighted differences in thermal behavior among polymer samples, with the presence of acrylic acid and ureido methacrylate affecting the glass transition temperature. SEM images showed spherical-shaped particles with average sizes ranging from 0.49 to 2.16  $\mu\text{m}$ . It's essential to consider the economic benefits of reusing the polymer and its performance compared to commercial products like Magnafloc® LT27AG from BASF.

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