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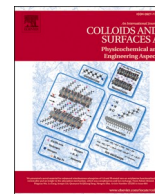
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# Colloids and Surfaces A: Physicochemical and Engineering Aspects

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## Impact of cationic polyacrylamide degradation on flocculation in wastewater treatment

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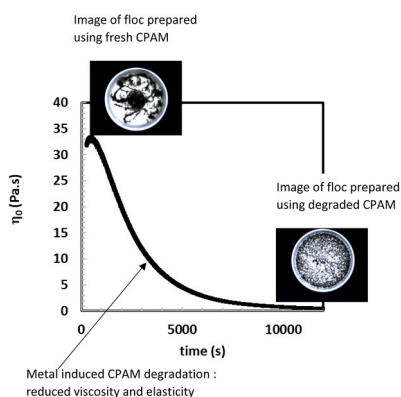
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### HIGHLIGHTS

- Insights into flocculating polymer degradation in wastewater treatment.
- Metal tools exposure degrades CPAM, altering rheology.
- CPAM degradation enhance flocculation efficiency requiring less polymer.
- Faster flocculation dynamics due to CPAM degradation.
- Degraded CPAM alters floc morphology, resulting in smaller, uniform flocs

### GRAPHICAL ABSTRACT



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### ABSTRACT

In wastewater treatment plants, flocculating agents, primarily polymers, are widely employed to cluster sludge particles into larger flocs or aggregates. The flocculation process not only accelerates sedimentation rates of particles but also aids in water release during thickening and dewatering operations. This study explores the effects of cationic polyacrylamide (CPAM) degradation on the flocculation process in wastewater treatment. CPAM undergoes noticeable degradation upon contact with specific metal surfaces, resulting in a substantial alteration in its rheological behavior. These modifications have broad implications for sludge flocculation: 1) accelerating polymer/sludge mixing dynamics, and flocculation kinetics, 2) inducing alterations in the resulting floc morphology, ultimately leading to smaller and less filamentous flocs. Notably, degraded CPAM requires a substantially less polymer quantity to achieve complete sludge flocculation, leading to a reduction in the excessive use of flocculating agents in wastewater treatment.

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## 1. Introduction

Innovating new wastewater treatment strategies or enhancing their efficiency has become essential to address the new challenges induced by environmental concerns, such as pollution and contamination [1], as well as the increased water consumption driven by industrialization and population growth [2,3]. This improvement is vital for managing water resources, utilizing sludge as a renewable energy source [4,5], and reducing the risks of soil and groundwater contamination [6]. Therefore, it is important to develop and implement environmentally sustainable methods that can effectively separate water from sludge with minimal energy use and fewer chemical additives.

Flocculation is a central process in wastewater treatment, facilitating the agglomeration of individual sludge particles into larger, more manageable flocs [3,7–9]. Efficient flocculation requires controlling floc morphology, rheology, permeability, and water retention, all of which depend on choosing the appropriate flocculating agents [3,10,11]. Polymers, particularly high molecular weight cationic polyacrylamide (CPAM), are widely used for their effectiveness in forming robust flocs that enhance separation, thickening, and dewatering [2,3,7,10,12]. CPAM is preferred due to its versatility in molecular weights, architectures, and charge densities, allowing precise customization for specific floc characteristics in various treatment settings [3,13,14]. However, excessive use of CPAM poses significant economic challenges and can become a financial burden for wastewater treatment facilities. Moreover, CPAM presents environmental and health risks due to the potential toxicity of residual polymers and the accumulation of non-biodegradable materials, with its eventual degradation exacerbating these issues. Therefore, optimizing treatment protocols to minimize CPAM use is essential for making wastewater treatment both cost-effective and environmentally sustainable.

The effectiveness of flocculation in wastewater treatment relies on the molecular weight (Mw), architecture, and charge density of the flocculating polymers [10,11,15,16]. Charge density dictates the flocculation mechanisms: charge neutralization, charge patching, and depletion. The architecture of polymers influences the morphology of the flocs [3,14,15,17,18]. For example, high molecular weight linear polymers are particularly effective at forming large flocs through bridging, while smaller polymers typically condense the repulsive double layer, leading to coagulation through van der Waals forces and resulting in smaller aggregates [3,10,19,20]. In contrast, branched and crosslinked polymers tend to form flocs with greater mechanical resistance than their linear counterparts [14,17,21,22].

Polymer rheology influences mixing dynamics and flocculation efficiency in wastewater treatment [15,23–25]. The process begins with the dispersion of polymer chains within the sludge suspension, which is critical for initiating floc formation. This is followed by multiple collision-reaction events that contribute to floc growth and development [25,26]. These collisions are induced by mixing (orthokinetic), which is more effective for larger particles due to velocity gradients, or occur spontaneously (perikinetic) for Brownian particles [25,27–29]. The balance between mixing and the properties of flocculating polymers is crucial; excessive mixing can cause floc breakdown, resulting in smaller, less effective flocs [30,31].

The above-highlighted sensitivity of flocculation to the properties of polymers stresses the importance of understanding how potential polymer degradation might impact the flocculation mechanism. This concern is well-founded, as numerous studies suggest that polyacrylamide-based polymers are prone to degradation [1,32–35]. Chain scission in PAM often occurs during elongational stress in channel flow [36,37]. Additionally, free radicals, such as hydroxyl radicals, can initiate chain scission [35]. Under neutral or basic conditions at temperatures above room temperature, CPAM is prone to hydrolysis of its cationic groups [38]. The degradation of flocculating polymers, especially CPAM, raises significant environmental concerns in wastewater treatment, such as the contamination of local water supplies. This issue

has prompted the implementation of stringent regulations in water treatment processes. Therefore, it is crucial to understand the degradation of CPAM and its impact on the water treatment process. This knowledge allows for better adaptation of treatment protocols to minimize environmental impacts and ensure more efficient and sustainable water resource management.

In the same line, recent results from our laboratory indicate that the rheological properties of several flocculating CPAMs drastically change when in contact with metallic surfaces [39]. This change is particularly evident during rheological measurements using metallic Couette tools, such as those made from dural, stainless steel, or copper. A significant reduction in low shear viscosity by several orders of magnitude and a transition in the polymer's viscoelastic properties from elastic to viscous were observed. Conversely, this effect is notably reduced when thermoplastic materials like PVC are used, suggesting that CPAM undergoes degradation induced by contact with metallic surfaces.

This finding raises critical concerns for the wastewater treatment process regarding how possible CPAM degradation during flocculation affects the mechanism and properties of flocs. This concern is justified, knowing that throughout industrial settings, CPAM polymers come into contact with various metals, including pipe surfaces, mixers, tanks, and dehydration equipment. The interaction between CPAMs and metallic surfaces in these environments could lead to polymer degradation, impacting the flocculation mechanism and floc properties, which could be detrimental to the viability and efficiency of the wastewater treatment process.

To ensure the performance and sustainability of wastewater treatment, it is essential to understand the behavior of flocculating CPAM throughout the process. Investigating how contact with metal surfaces affects CPAM properties and the sludge flocculation mechanism is critical. By identifying and mitigating these interactions, treatment facilities can enhance efficiency and minimize the use of chemical additives.

This study examines how contact with metallic surfaces affects the degradation of CPAM and its subsequent impact on the sludge flocculation process in wastewater treatment facilities. It focuses on the changes in rheological behavior of CPAM during degradation and how these changes influence flocculation efficiency and the morphological properties of the floc.

The study begins by examining the evolution of the viscoelastic properties of two flocculating CPAMs using rheological Couette tools made from dural and stainless steel to assess the reproducibility of degradation behavior observed in previous studies. Following this, the influence of polymer degradation on the flocculation process was investigated using sludge suspensions collected from wastewater treatment facilities. The focus was on three key aspects of flocculation: kinetics, floc morphology, and flocculation efficiency.

The time evolution of the flocs was monitored for different states of CPAM degradation, encompassing the entire floc growth process from the initial mixing of CPAM and sludge to the completion of flocculation. The kinetics of flocculation were quantified using image analysis techniques based on light absorption. The morphologies of the flocs were examined throughout the flocculation process, with special attention to their final shapes and the role of CPAM degradation in this evolution. Finally, the impact of CPAM degradation on flocculation efficiency was assessed by measuring the amount of CPAM required to fully flocculate the sludge.

The findings of this study could have significant implications for optimizing wastewater treatment processes. A better understanding of how CPAM degradation affects flocculation might lead to improved process efficiency, reduced chemical usage, and enhanced overall performance of wastewater treatment facilities.

## 2. Material and methods

### 2.1. Material

High molecular weight cationic polyacrylamide (CPAM) variants were used as flocculants. These included FLOPAM™ MV 9104 from SNF Floerger (France) and Superfloc XD 5500 from KEMIRA. All polymer preparations and sludge dilutions were conducted using doubly deionized water.

Polymer solutions with a concentration of 5 g/L were prepared in a polyethylene container by dissolving CPAM in doubly deionized water. The mixture was agitated at 250 rpm for 45 min using a custom-made stainless-steel mixing paddle. To counteract the upward motion of the fluid caused by the Weissenberg effect, a polyethylene blade was attached to the paddle shaft to continually scrape and push the fluid downwards. After the mixing process, the solution was left to rest for 1 h before further use.

Primary sludge (issued from primary decantation of pre-treated wastewater) was sampled from Seine Grésillons (SEG) wastewater treatment plant (near Paris, France) managed by SIAAP. SEG has a treatment capacity of 300 000 m<sup>3</sup>/day and the primary sludge is sampled in the feeding tanks of the thickening unit. The selection of primary sludge for this study is motivated by its treatment process. After undergoing physico-chemical decantation, the sludge is chemically treated with cationic polyacrylamides. This conditioning step precedes centrifugal thickening, which is used to enhance the sludge concentration at the digester's inlet. The detailed physico-chemical characterization of the sludge used in this study is summarized in [Table S1](#) in the [supporting information](#). The composition of the sludge varies depending on the lot, as shown in [Table S1](#), and the present study was conducted on several lots that have a pH within the range of 6.8–7.5. The sludge exhibits a broad range of particle sizes, up to few millimeters. Following a drying process at 105°C, the solid content was determined to be 23 g/L. The sludge is stored at 4°C until further processing. Homogenization of the sludge, aimed at producing particles smaller than 100 µm, is achieved using Ultra-Turrax® (IKA) apparatus operating at 20,000 rpm. The homogenization process ceases once large particles are no longer visible, resulting in the production of particles smaller than 100 µm, which was achieved after 10 min.

Conductimetric titration used sodium hydroxide (Cas No. 1310-73-2) and hydrochloric acid (CAS N°:7647-01-0), both from Sigma Aldrich. Additional chemicals for the experiments, like potassium polyvinyl sulfate (KPVS, CAS: 26182-60-5.), orthotoluidine blue (OTB, CAS N°. 95-53-4), and cetyltrimethylammonium bromide (CTAB, (CAS N°. 57-09-0)), were also sourced from Sigma Aldrich and used as supplied.

### 2.2. Characterisation methods

The polymer was analysed using NMR spectroscopy on a Bruker Avance III 400 MHz instrument. Infrared spectroscopy analysis was conducted with a Perkin Elmer Spectrum, compared to the spectrum of cationic polyacrylamide. These analyses confirmed that these polymers are cationic polyacrylamide [40], as detailed in [supporting information S1](#). The zeta potential, indicating a positive charge value of about +50 mV, was measured at 25 °C using the Zetasizer Nano Series.

The polyelectrolyte titration of CPAM followed the method described by [38,41]. Initially, the charge density of the KPVS solution was determined using CTAB as a model for cationic groups. This involved adding three drops of OTB solution to a CTAB solution (0.36 g/L) and titrating with KPVS until the color transitioned from blue to red-violet. A blank sample, containing the same amount of OTB indicator in water, underwent the same titration process. The difference in KPVS volume used for the two titrations provided the charge estimation of KPVS. Following this, KPVS (0.18 g/L) was used to titrate CPAM (0.5 g/L), using the same method to estimate the accessible cationic groups in

CPAM.

### 2.3. Polymer degradation setup

CPAMs can degrade when they come into contact with metallic surfaces [39]. Although the degradation kinetics are significantly influenced by the type of metal, the flocculation process proved similar across all materials tested. While other metals also produced a similar effect on sludge flocculation, the majority of the studies discussed here employed dural.

The degradation procedures involved a custom setup comprising a cylindrical polyvinyl chloride (PVC) tube with a 43 mm internal diameter and a 40 mm cylinder insert made of either PVC, dural, or stainless steel. The polymer solution was introduced into the tube, and the dural or PVC insert was aligned to maintain a 1.5 mm gap. This assembly was kept at room temperature for periods ranging from 0 to 24 h. At every 30-min interval, 0.1 mL of the solution was sampled for flocculation testing, which continued until no further changes in the polymer's rheology were observed. Additionally, for rheometric measurements, 7 mL of the solution was extracted at different time intervals. Another approach involved degrading the polymer within the rheometric measurement geometry of a Couette device, which was constructed from various materials. If not specified otherwise, the dural insert is used in most of the flocculation experiments involving degradation due to its rapid kinetics, allowing the entire experiment to be completed in less than six hours and enhancing reproducibility.

### 2.4. Flocculation process and visualisation procedure

The sludge flocculation experiments were conducted using a custom-built setup consisting of a mixing device, flocculation container, and observation system. The observation setup included a LED light source and a diffuser panel to provide uniformly dispersed light. A transparent sample holder, placed a few centimeters from the panel, held the flocculation container, a transparent cylindrical cup made of plexiglass with a diameter of 35 mm and a height of 1 cm.

The setup was mounted on an orbital shaken reactor (OSR) derived from a modified IKA MS1 minishaker. This modification involved replacing the rubber support with the flocculation setup. The minishaker, with an eccentricity of 4.5 mm, allowed for oscillatory motion in two dimensions, creating a circular movement in the plane of the platform supporting the beaker [42–45]. This mechanism provided mixing or shear stress to the fluid at rotation speeds adjustable between 100 and 2000 rpm. For these experiments, the rotation speed was fixed at 350 rpm, as measured through image analysis.

Visualization was achieved using a Basler camera with 1.3 M pixels resolution, employing a global shutter procedure. Shutter opening times ranged from 100 µs to 1000 µs, allowing visualization of the fluid in motion. Images were captured during agitation at rates varying from 1 to 80 fps, depending on the experiment. In some cases, agitation was intermittently paused every 20 s for about 2 s to capture images of the flocs. This process continued until flocculation was complete. The camera, equipped with a 1.2 mm objective, was positioned approximately 100 mm from the container on a fixed stand to cover the entire surface of the flocculating container.

For each measurement, 1 mL of sludge was introduced into the container, resulting in a shallow film with a thickness of 2 mm. In most measurements, the initial sludge concentration of 23 g/L was diluted using water to achieve an 11.5 g/L sludge suspension. Following this, a 0.1 mL drop of a 5 g/L polymer solution was carefully placed in the center of the cup, and stirring was carried out at a set rotation speed of 350 rpm until the flocculation completed. In different experiments, specifically aimed at studying the influence of polymer quantity, various volumes of the 5 g/L polymer solution, ranging from 0.005 mL to 1 mL, were employed. Unless otherwise specified, flocculation was achieved using CPAM MV9104.

To investigate the effect of agitation setup on flocculation, two other agitation procedures were employed: the SM-30 reciprocating shaker (Edmund Buhler) at 200 rpm and manual agitation. Visualization was carried out intermittently at different time intervals. Since the results are comparable to those obtained using the IKA MS1 minishaker, all results presented below are derived from experiments conducted with the IKA MS1 minishaker.

Image analysis was conducted using ImageJ and a custom-developed Python program. The Python program converted RGB images to HSV (hue, saturation, value) format, analyzing the three light components separately. In another method, RGB was converted to a 12-bit image, and the light intensity from each pixel was compared to that in a blank image. This technique provided quantitative information about light absorption in different sample zones during flocculation. A histogram of light transmittance and absorption was generated for various pixels in the flocculation container area [46,47].

### 2.5. Rheological characterization

The study of CPAM's rheological characteristics involved using two rheometers: the DHR3 (TA Instruments) and the HAAKE MARS (Thermo Fisher), both utilizing Couette configurations. For the DHR3, the primary Couette setup included a 30 mm dural stator and a 28 mm anodized dural rotor. An alternative Couette variant used a 30 mm stator and a 28 mm rotor, both made from stainless steel 316. Additionally, another variant featured a 43 mm stator lined with PVC and a 40 mm rotor, available in dural, stainless steel, or PVC. The HAAKE MARS rheometer employed a Couette configuration comprising a stainless steel CCB43/SS/SE cup and a Z38 rotor. The Couette geometry allows for the precise measurement of low-viscosity polymer or sludge samples over long periods of time, while effectively preventing solvent evaporation. When adapted with appropriate materials, this geometry is also suitable for investigating degradation.

The flow characteristics of CPAM at various stages of degradation were explored by recording the stress ( $\sigma$ ) over a shear rate range ( $\dot{\gamma}$ ) of 0.001–100 s<sup>-1</sup>. Each measurement stage was allotted sufficient time to reach a pseudo-steady state, and the recorded stress values were used to calculate dynamic viscosity ( $\eta$ ) as  $\eta = \frac{\sigma}{\dot{\gamma}}$ .

Alternatively, the polymer solution, which was degraded using the previously described degradation setup (see polymer degradation setup), was analyzed in rheometry employing the PVC/PVC Couette geometry due to its minimal impact on polymer properties. For this analysis, 7 mL of the solution was sampled every 30 min. The shear flow and viscoelastic properties of these samples were then measured, adhering to the procedure outlined earlier.

### 2.6. Measurement uncertainties

The uncertainty of the measurements is influenced by several factors, including polymer preparation and the precision of the rheometric tools. Due to the high molecular weight of the polymers, which can reach several million kg/mol, and their sensitivity to degradation, the preparation and solubilization of the polymer solution result in a  $\pm 10\%$  variability in low shear viscosity. The DHR3 rheometer's precision varies with the polymer state: freshly prepared polymers give high-precision measurements due to high stress, but as viscosity decreases during degradation to levels near that of water, errors can rise to  $\pm 30\%$ . Degradation effects were assessed by analyzing degradation kinetics and characteristic time. At low temperatures, slow degradation ensures adequate precision, while at higher temperatures (around 30°C), the degradation rate aligns with measurement time, increasing uncertainty. The characteristic degradation time is determined with an uncertainty of less than  $\pm 20\%$ .

The repeatability of flocculation was assessed through more than 20 flocculation tests on the same sludge lot to ensure reliable

reproducibility. These measurements averaged the dispersion of floc shape and size. Additionally, variability in sludge lots contributed to measurement dispersion. Tests were conducted on sludge samples collected at different time intervals, and experiments were repeated for each lot. While overall results from different sludge lots showed slight differences in floc shape, they consistently produced reliable results. The experiments presented here were conducted on a single sludge lot, which is representative of the different experiments.

## 3. Results and discussion

### 3.1. Rheology of the polymer during the degradation process

Fig. 1 left presents the viscosity profile of a 2.5 g/L CPAM (XD5500) solution in a stainless-steel Couette, showing changes over various time intervals as a function of shear rate ( $\dot{\gamma}$ ). The viscosity is measured every 3 h on the same sample. Each measurement reveals a consistent decrease in the solution's overall viscosity across all shear rates and a shift of the Newtonian plateau towards higher  $\dot{\gamma}$  values. Initially, the flow behavior of the freshly prepared solution aligns with the Carreau-Yasuda model (Eq. 1), allowing for the determination of key rheological parameters like zero-shear viscosity ( $\eta_0$ ) in the Newtonian regime, relaxation time ( $\tau_{\text{shear}}$ ) defining the transition to shear-thinning behavior, and the power-law index ( $n$ ) for the shear-thinning regime. As time progresses, the solution's flow behavior continues to fit this model, but with a noticeable reduction in  $\eta_0$  and  $\tau_{\text{shear}}$ , and an increase in 'n' (see [39] for more details)

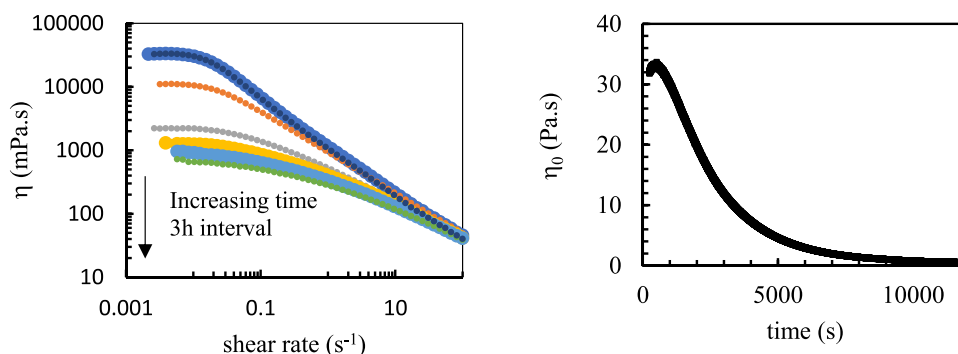
$$\eta = \eta_0 \left( 1 + (\tau_{\text{shear}} \dot{\gamma})^2 \right)^{\frac{n-1}{2}} \quad (1)$$

Using a dural Couette, the viscosity, especially  $\eta_0$ , significantly diminishes within 2–3 h at room temperature (Fig. 1 right). For example, at 30°C,  $\eta_0$  can decrease by several orders of magnitude in just an hour. These results align with those obtained on a similar flocculating CPAM, where both low shear viscosity and viscoelastic properties evolve during rheological measurements within metallic Couette setups. Specifically, low shear viscosity drastically decreases, and the elastic characteristics disappear, transitioning from elastic to viscous [39]. This behavior was attributed to the degradation of CPAM during rheological measurements.

This degradation can be attributed to various factors, including chain scission from mechanical solicitation [36,37], chemical reactions with free radicals [35], or hydrolysis of cationic groups [38]. All CPAM variants investigated in [39] exhibited degradation, with slight differences in the rate and extent, which were notably less pronounced on PVC or thermoplastic surfaces. In contrast, metal surfaces like dural, stainless steel significantly influenced the polymer's rheology. Degradation rates varied from 30 min at room temperature on dural to several hours on stainless steel, and were temperature-dependent, occurring faster at higher temperatures. It's crucial to note that degradation predominantly results from interaction with the metal surface, with shear having a minimal impact within the tested shear rate range [39]. The study henceforth focuses on the dural surface, where most rheological analyses were conducted.

### 3.2. Sludge rheology

The freshly collected sludge is a heterogeneous suspension consisting of particles with varying sizes ranging from a few micrometers to millimeters. To obtain a uniform suspension, an Ultra-Turrax® mixer was used to break the sludge particles into smaller particles to around 100  $\mu\text{m}$  and minimize the dispersion to approximately 40  $\mu\text{m}$ . The resulting sludge suspension displays shear-thinning behavior, where the viscosity reduces with decreasing shear rate from 46 mPa.s at 1 s<sup>-1</sup> to 4.9 mPa.s at 100 s<sup>-1</sup> following a power-law relationship with an exponent of 0.48 (Fig. 2).



**Fig. 1.** Left) Dynamic viscosity vs. shear rate for a 2.5 g/L CPAM (XD 5500) solution measured at different residence times within stainless steel Couette (Rotor Z38S, and stator CCB43/SS/SE) with a time interval between measurements of 3 h. The curves are arranged with the topmost representing the low residence time within the Couette, progressively increasing down the graph. Measurements are conducted in the Mars rheometer at 20 °C. Right) Low shear viscosity ( $\eta_0$ ) plotted against residence time within the Couette geometry made of dural for 5 g/L CPAM solution (MV9104). The solution is measured in the DHR3 in dural Couette at 30 °C at a shear rate of 0.01 s<sup>-1</sup>.

### 3.3. Flocculation mechanism of sludge during polymer degradation

#### 3.3.1. General trends of the flocculation process using CPAM

Fig. 3 depicts the evolution of the flocculation process in 2 mL homogenized sludge (11.5 g/L) treated with 0.1 mL of a 5 g/L CPAM MV9104 solution (21.7 g Active Matter (AM) / kg Dry matter (DM)), both in its initial state (Fig. 3.a) and after undergoing degradation (Fig. 3.b). The contrast between the transparent polymer domains and the darker sludge areas, due to differential light absorption, enables effective observation of the flocculation process over time, identifying three distinct phases: mixing, flocculation, and clearing.

In the initial mixing phase, polymer droplets experience stretching, erosion, and fragmentation, likely due to hydrodynamic and shear forces near the container's bottom and walls. With continued mixing, the polymer and sludge start intermingling, creating an expanding contact surface. This phase concludes when the polymer is uniformly mixed with the sludge, covering most of the container without visible flocculation. However, in some instances, mixing might be insufficient, leading to large polymer droplets that fail to thoroughly mix with the sludge. The mixing efficiency is influenced by various factors, including the concentrations of polymer and sludge, and the degree of polymer degradation (Fig. 3).

Flocculation initiates with the appearance of darker areas, either as filaments or as sporadic, isolated points. In the case of fresh polymer, flocculation begins around polymer droplets, which stay mostly intact but gradually form filaments through stretching and fibrillation of the polymer (Fig. 3a). Some polymer droplets may remain attached to these blocks, but they contribute minimally to flocculation (Fig. 3a). The

resultant flocs form a network of elongated branches throughout the container, interspersed with clearer, sludge-rich zones that progressively lighten.

Conversely, with fully degraded polymer, flocculation starts with many dark, evenly distributed areas, indicating isolated flocculation zones that slowly expand and darken. The size of these agglomerates typically remains small, only a few millimeters. In the clearing stage, the slightly dark, non-flocculated sludge fluid gradually becomes lighter as the particles join with the existing flocs (Fig. 3b).

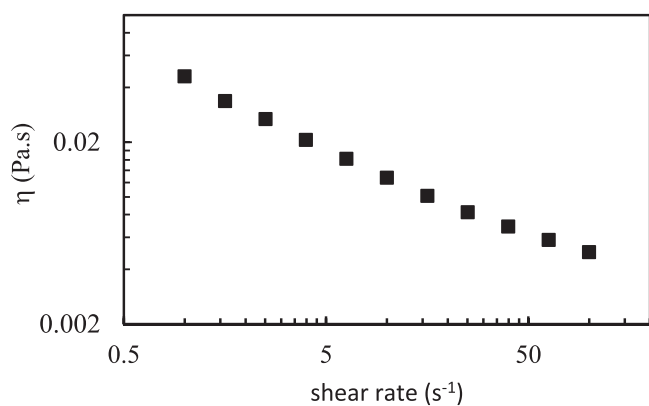
#### 3.3.2. Effect of the polymer degradation on mixing process

The flocculation process in this experiment is largely driven by the mixing step, where a viscous polymer droplet is combined with a less viscous sludge suspension. This critical phase is influenced by several factors, including the viscosity ratio between the sludge and polymer, the viscoelastic properties of the polymer, and the fluid dynamics and stresses produced by the orbital shaker reactor (OSR) mixing system. Fully understanding and quantifying the flows and stresses exerted by the OSR on both the polymer droplet and the sludge suspension is essential to comprehend their interaction during the flocculation process.

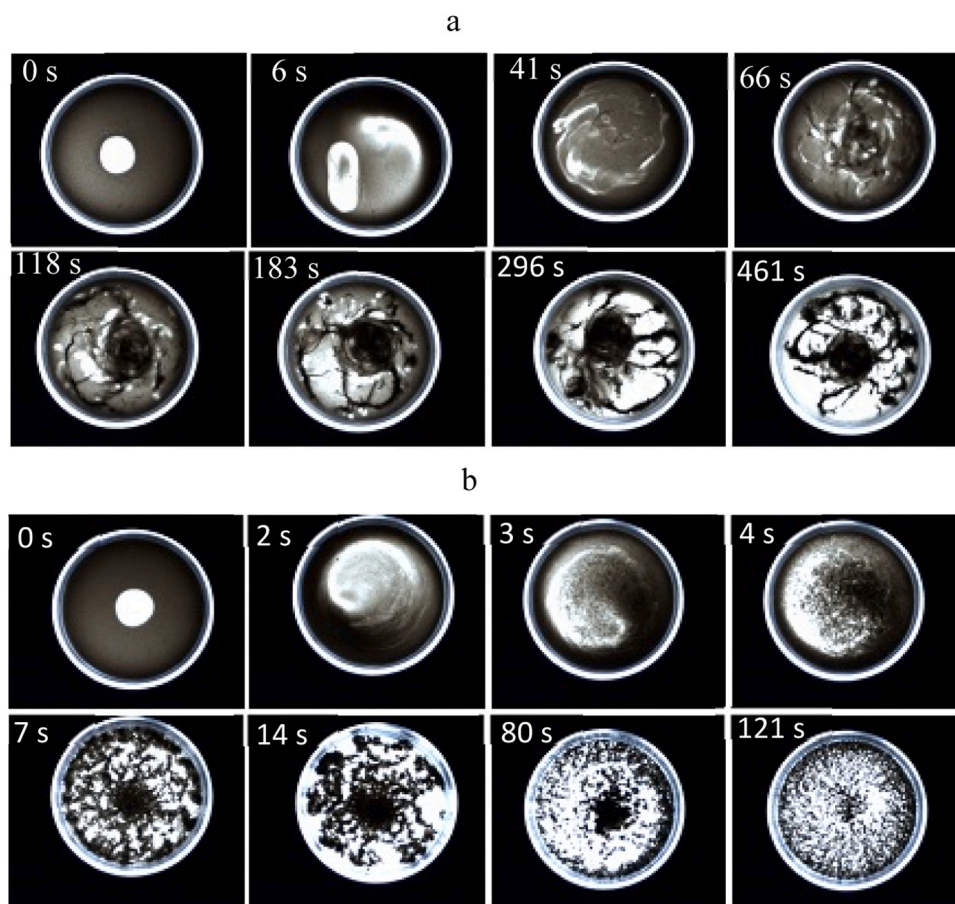
The OSR system, commonly used in biological research, has been the focus of numerous experimental and theoretical studies on fluid mechanics. These studies aim to characterize flow regimes, shear stress, and mixing efficiency [42–45]. In such systems, cylindrical containers moving in an orbital path induce dynamic wave patterns in the fluid along the container walls. As the container moves in one direction, the liquid shifts to the opposite side, forming a wave peak, and when it moves back, a valley forms.

Quantification of flow dynamics is conducted based on physical considerations and using flow control parameters such as container radius (R), eccentricity (a), fluid thickness (h), angular frequency ( $\omega$ ), fluid viscosity ( $\mu$ ), and gravitational acceleration (g). Different regimes can be identified through dimensionless numbers like the Froude number  $Fr = a\omega^2/g$ , eccentricity parameter ( $a/R$ ), shallowness of the fluid layer ( $h/R$ ), and the Reynolds number  $Re = R^2\omega/\mu$ . In the present study, mixing was performed at  $\omega = 36.6$  rad/s leading to  $Fr = 0.62$ , eccentricity = 0.26, and shallowness = 0.12. The Reynolds number varies between 220 and 2200, considering the sludge as the main fluid with a viscosity ranging from 5 to 50 mPa.s. For the degraded polymer, the Reynolds number ranges from 100 to 200, whereas for the fresh polymer, it ranges from 0.26 to 106.

In the experimental conditions of the present study, the sludge is observed to move away from the center of the container toward the wall, creating rotating wave patterns, as evidenced by an increase in light absorption at the edges and a decrease in the center (Fig. 4). This wave pattern aligns with most models and simulations for similar



**Fig. 2.** Dynamic viscosity vs. shear rate for a sludge suspension (11.5 g/L) in Couette Geometry at 23 °C. The fresh sludge was dispersed for 10 min using an Ultra-Turrax® mixer at 20,000 rpm before measurement.



**Fig. 3.** Images depicting different stages of flocculation of 11.5 g/L sludges with 5 g/L CPAM (MV9104) (21.7 g Active Matter (AM) / kg Dry Matter (DM)) at different times under mixing in an orbitally shaken reactor OSR at 350 rpm. a) Flocculation using non-degraded, freshly prepared polymer; b) Flocculation using degraded polymer within the degradation setup made of PVC/dural. Degradation was carried out for 6 h at room temperature. The cup diameter (35 mm) serves as a scale bar for the image analysis.

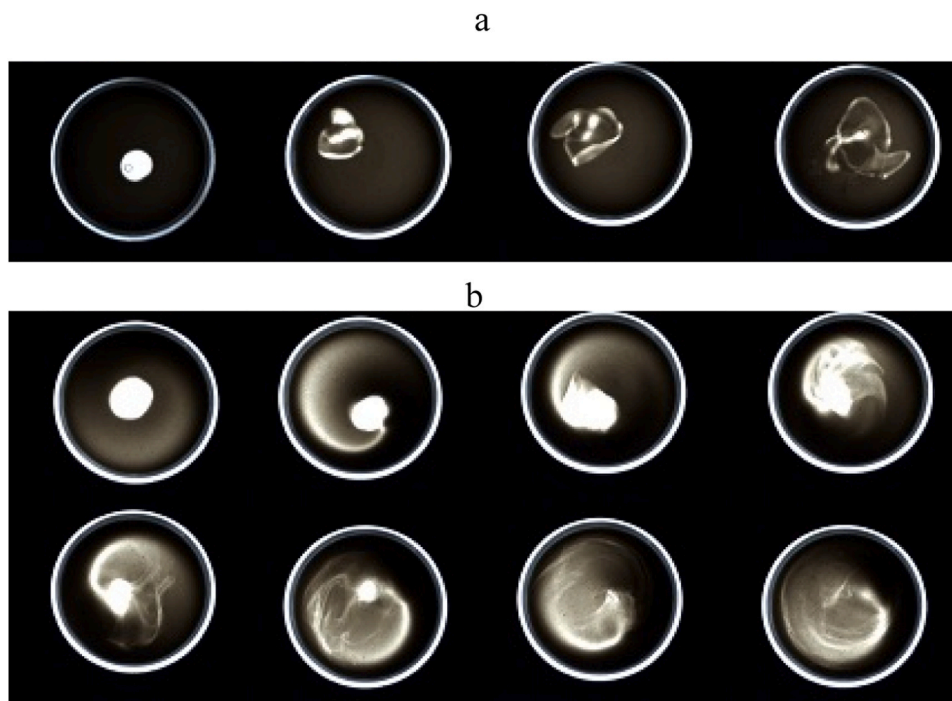
dimensionless numbers [42,43,45]. During the mixing phase, the polymer droplet moves away from the container center toward the wave's edge and positions itself between the center and the wall. As the sludge wave moves alongside the polymer droplet between the wall and the polymer, it can induce erosion, fragmentation, or elongation of the polymer, depending on its viscosity. The polymer droplet also follows the wave path but at a slower speed than the sludge. Throughout the mixing process, the polymer droplet swells, as indicated by changes in transparency at the polymer's edge.

Throughout the mixing process, the fresh polymer remains as a single droplet, elongating and increasing its surface area, resulting in a tortuous surface (Fig. 4a). At the beginning of the mixing stage, the droplet undergoes stretching under the hydrodynamic forces induced by the passage of the sludge wave. It subsequently returns to its initial state within less than 50 ms, primarily due to the elastic behavior of the polymer. However, with each wave passage, the droplet undergoes further deformation, and its ability to return to its initial state diminishes, leading to a continuous increase in the droplet's surface area and overall swelling. Toward the end of this stage, polymer fibers are formed and dispersed throughout the container. This is likely attributed to the elastic behavior of the polymer chain, resulting from entanglement, which limits the polymer dispersion and solubilization within the sludge suspension.

In the case of degraded polymer, fragments of the droplet erode each time the sludge passes through it, facilitating mixing (Fig. 4b). After ten wave passages, the polymer droplet completely disappears and mixes with the sludge. This occurs because the degraded polymer likely

consists of smaller chains with less entanglement than in the fresh polymer, causing it to disperse as small fragments or solubilized individual chains within the sludge. This behavior is consistent across all levels of polymer degradation, and the ability to form small fragments rather than long filaments increases as the polymer degradation progresses.

The above results suggest that the viscosity and elasticity of the polymer, as well as the viscosity ratio between the polymer and sludge, are the primary factors that impede the mixing step and consequently the flocculation. Mixing miscible fluids is directly influenced by their viscoelasticity and particularly their viscosity ratio. When mixing two fluids with similar viscosities, the more viscous fluid tends to spread out more easily, while the less viscous fluid penetrates into the more viscous fluid, resulting in an intermediate viscosity mixture. This is likely the case for the degraded polymer with a viscosity (100 mPa.s) similar to that of the sludge (50 mPa.s). In contrast mixing non-degraded polymer (50,000 mPa.s) with sludge, involves mixing a high viscosity fluid into a low viscosity one. In such a case, the interface between the two fluids exhibits a viscous fingering process [48–50]. This occurs when the fluid with the lower viscosity spreads out rapidly, forming fingers that extend into the slower-spreading, more viscous fluid, leading to the formation of patterns resembling fingers or branches. The clear polymer drops that appear around the flocs are likely the result of the fingering process (Fig. 4a). Furthermore, the elasticity of the non-degraded polymer is a barrier to its deformation under the flow imposed by the sludge flux, which explains the observed resistance to elongation in Fig. 4b.



**Fig. 4.** Images illustrating various stages of mixing drops of 5 g/L CPAM (MV9014) with 11.5 g/L sludges at different time intervals: a) 10 s and b) 50 ms. Agitation is conducted in an orbitally shaken reactor at 350 rpm. a) Flocculation using non-degraded, freshly prepared polymer. b) Flocculation using degraded polymer within the degradation setup made of PVC/dural. Degradation was carried out for 6 h at room temperature. Images taken with time interval of 10 s for the case of fresh polymer (a) and 50 ms for the case of degraded polymer (b). The cup diameter (35 mm) serves as scale bar for the image analysis.

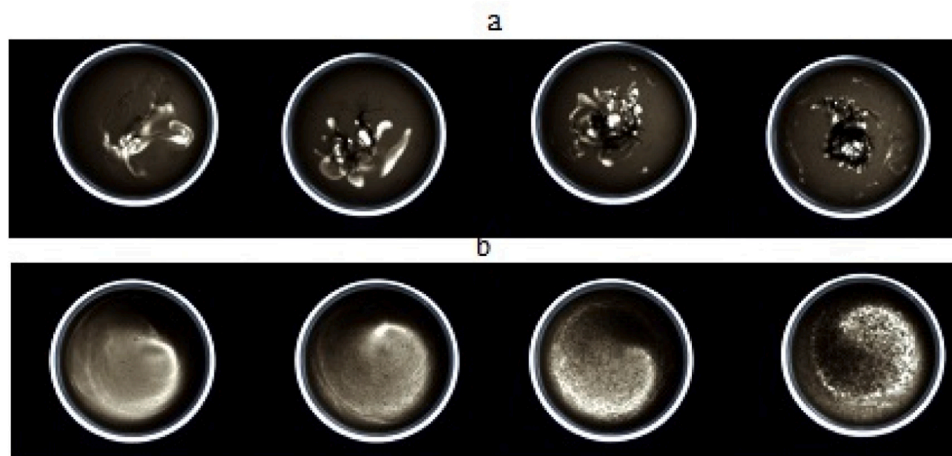
### 3.3.3. Effect of the polymer degradation on the flocculation process

The morphology of flocs during flocculation is significantly influenced by the polymer's degradation state. When using non-degraded polymer, flocs emerge near the polymer drop and form filaments that expand during flocculation, eventually covering the entire container surface as a unified block (Fig. 5a). This process unfolds in two stages: initially, polymer filaments emerge from the polymer drop and stretch under the sludge flow; subsequently, sludge particles aggregate onto the filament surface, resulting in a filamentous floc morphology (Fig. 6).

In contrast, degraded polymer leads to numerous individual zones of flocculation, dispersed randomly within the container and growing darker over time (Fig. 5b). This process occurs in two steps: first, the

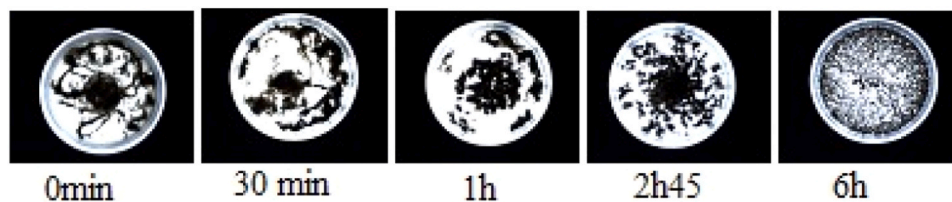
polymer disperses within the sludge as polymer fragments during the mixing phase; second, the sludge particles aggregate around the already dispersed polymer fragments during flocculation. This results in millimetric-sized, non-connected, isotropic, and thoroughly dispersed flocs (refer to Figs. 5–7). As polymer degradation progresses, the size of filament emerging from the polymer drop shortens, ultimately giving way to smaller polymer fragments (Fig. 6). Flocculation around these polymer fragments leads to flocs that progressively transform from branched, filamentous structures to individually dispersed flocs. Consequently, the final flocs become smaller, less connected, and more isotropic (Figs. 6, 7).

The mean floc size is estimated through image analysis with OpenCV

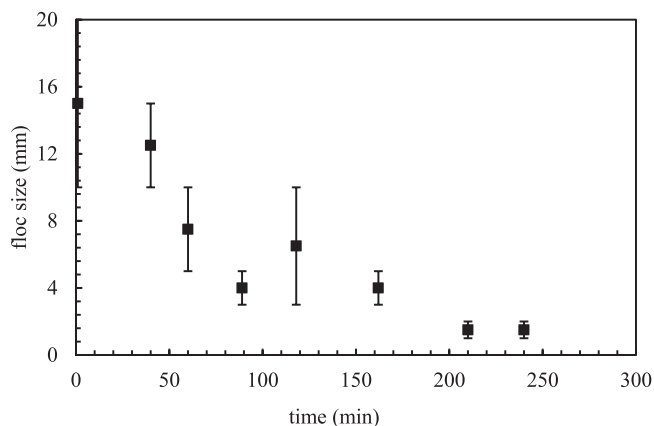


**Fig. 5.** Images illustrating various stages of flocculation of 11.5 g/L sludges using 5 g/L CPAM (MV9014) at different time intervals: a) 10 s and b) 50 ms, following the mixing stage. Agitation is conducted in an orbitally shaken reactor at 350 rpm. A) Flocculation using non-degraded, freshly prepared polymer. Images taken with time interval of 10 s, b) Flocculation using degraded polymer within the degradation setup made of PVC/dural. Degradation was carried out for 6 h at room temperature. Images taken with a time interval of 50 ms. The cup diameter (35 mm) serves as scale bar for the image analysis.





**Fig. 6.** Images depicting the morphology of the floc at the end of sludge flocculation (11.5 g/l) by CPAM (MV9104, 5 g/l) at different states of degradation, sequentially from left as 0 min, 30 min, 1 h, 2h45, and 6 h. The polymer was degraded within the degradation setup made of PVC/dural at room temperature. The cup diameter (35 mm) serves as a scale bar for the image analysis. The final size of the floc is determined when the floc's shape does not evolve with time, typically taken 10 min after flocculation ended.



**Fig. 7.** Estimated arithmetic mean floc size calculated from image analysis of Fig. 6 plotted against degradation time of the CPAM (MV9104).

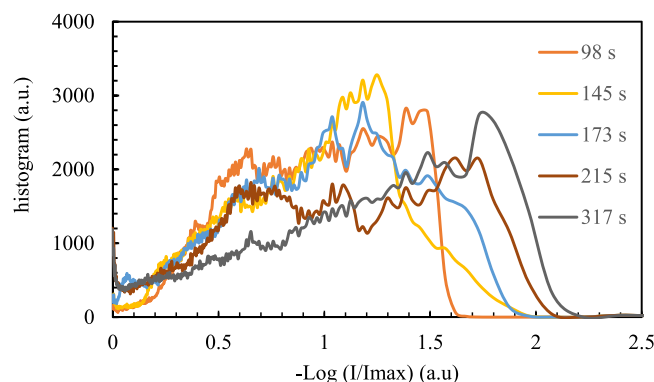
in Python by calculating the average radius of the area encompassing the connected objects, referred to as flocs, within a series of images. For non-degraded polymers, it is commonly observed that the average floc size is comparable to the container's dimensions, reflecting the spatial constraints affecting floc formation. This method yields an approximate size of the flocs, underscoring the spatial factors influencing their development. The estimated average floc size decreases as the polymer degrades (Figs. 6, 7), attributed to an increasing number of polymer fragments, resulting in the formation of multiple flocculation zones. The reduction in polymer viscosity, along with a decrease in its elastic characteristics and elongational viscosity during degradation, likely facilitates the breaking of the polymer into smaller droplets. Across all degradation levels, floc size and number are primarily determined by the efficiency of mechanical sollicitation in increasing the exposed polymer surface, achieved through either polymer fragmentation or stretching and

fibrillation.

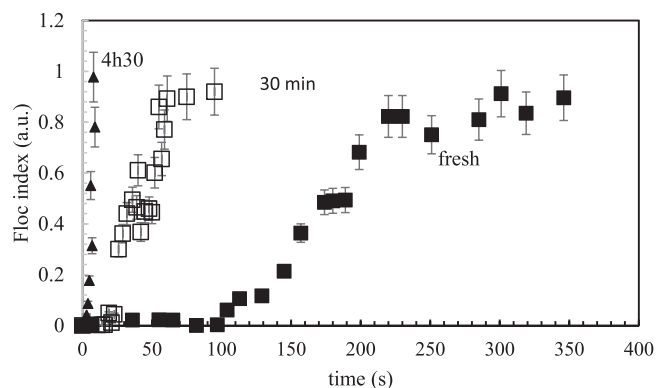
To quantify the flocculation process, the light absorption of both sludge and flocs is measured and converted into a histogram of various grayscale levels, which is then plotted against the logarithm of the intensity. This process is akin to the Beer-Lambert law, which relates absorption to particle concentration and extinction coefficient (Fig. 8). The formation and densification of flocs during flocculation can be monitored by observing the darkest regions in the histogram. To quantify the evolution of flocculation using image analysis, a parameter called 'floc index' was introduced. This index is derived by normalizing the fraction of gray areas to their maximum value, which is attained at the end of the flocculation process. Fig. 9 presents the trend of the flow index over flocculation time for the treatment of sludge with polymer at three varying degrees of degradation: fresh polymer, polymer after 30 min of degradation, and polymer following 4.5 h of degradation. The resulting plot displays two phases: a mixing phase without floc formation and a flocculation phase with increasing Floc index (Fig. 9). For fresh polymers, the mixing phase lasts up to 100 s, while the flocculation phase takes approximately 300 s under the current experimental conditions. A similar mechanism is observed with degraded polymers, but at shorter timescales, as evidenced by the images.

### 3.3.4. Effect of the polymer structure on the kinetic of mixing and flocculation

The characteristic mixing time ( $t_{mix}$ ) is evaluated during flocculation by analyzing image sequences to identify the moment when the sludge and polymer are fully mixed prior to flocculation. In other cases, this time is evaluated as the onset time for the rapid increase of the Floc index. Similarly, the characteristic flocculation time ( $t_{floc}$ ) is evaluated by examining the sequences of images to identify the moment when the shape of the flocs stops evolving or by using the Floc index to identify the moment when the Floc index approaches 90%. Fig. 10a depicts the relationship between  $t_{mix}$  and  $t_{floc}$  as a function of the time taken for polymer degradation. This finding indicates that  $t_{mix}$  and  $t_{floc}$  decrease



**Fig. 8.** Histogram illustrating the gray level as a function of the logarithm of transmitted light intensity for various flocculation times using non-degraded CPAM. The histogram is generated by analyzing images during flocculation at different time intervals (Figs. 4 and 5) using home-built program. The operating conditions corresponds to the non-degraded polymer (MV9104) at a concentration of 5 g/L and mixed with 11.5 g/L sludge in an OSR at 350 rpm.



**Fig. 9.** Floc index estimated from histogram of the gray level of Fig. 8, taken from the peak absorption between 2 and 2.2 plotted against flocculation time for the CPAM (MV9104) at 5 g/l at different stages of degradation: (■) fresh polymer, (□) degraded 30 min and (▲) degraded 4h30. The flocculation is carried out on homogenized sludge at 11.5 g/L.

by over 40 times during degradation, following a comparable trend with  $t_{floc}/t_{mix}$  to be almost constant and equal to  $4.74 \pm 0.36$ . One plausible explanation for the constancy of the  $t_{floc}/t_{mix}$  ratio, irrespective of the degradation state, is that the flocculation process is primarily governed by the mixing step. Indeed, flocculation is a synergistic process involving collisions and reactions, with the flocculation rate being the product of these two rates. In the context of non-Brownian particles discussed in this study, mechanical mixing is the dominant factor affecting the collision process, thereby making the mixing rate a significant indicator of the collision rate. Therefore, the constancy of the  $t_{floc}/t_{mix}$  ratio suggests that the reaction rate does not change significantly during degradation, and that most observed variations in the flocculation rate are attributed to changes in the mixing rate, which in turn may be hindered by various factors such as the viscosity and viscoelasticity of the polymer, as well as the sludge's viscosity and the mechanical stresses exerted by the OSR.

The rate of flocculation of particles of size  $l$  and  $k$  ( $K_{lk}$ ) can be mathematically expressed as the product of the collision efficiency ( $\epsilon_{lk}$ ), the collision frequency ' $\beta_{lk}$ ', and their particle concentrations  $C_l$  and  $C_k$ :

$$K_{lk} = \epsilon_{lk} \cdot \beta_{lk} \cdot C_l \cdot C_k \quad (2)$$

The parameter  $\epsilon_{lk}$  denotes the fraction of collision events resulting in flocculation, akin to the reaction rate previously described. It spans from 0, indicating no flocculation, to 1, signifying complete flocculation in every collision... For the non-Brownian particles under investigation, the collision diffusion rate component of  $\beta_{lk}$  can be ignored, leaving only the mechanical mixing component. In the case of laminar flow  $\beta_{lk}$  can be

written as function of shear rate ( $G$ ) and the particles diameters  $d_l$ ,  $d_k$  [27–29,51].

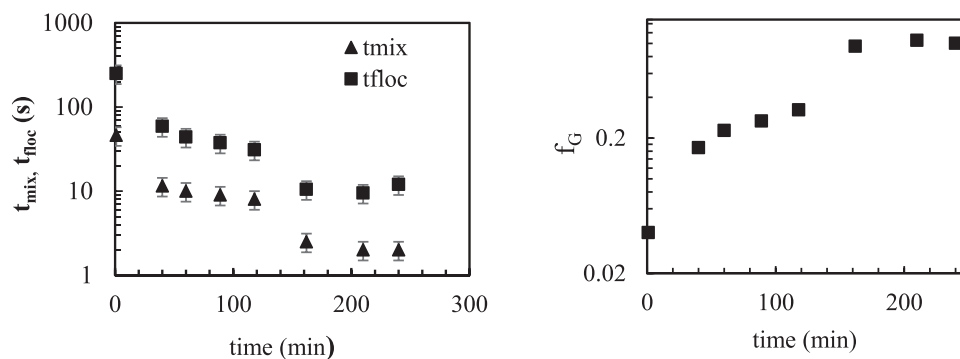
$$\beta_{lk} = 1/6 \cdot G \cdot (d_l + d_k)^3 \quad (3)$$

The present study suggests that flocculation occurs due to the reaction between sludge particles and active sites of the polymer. This leads to  $K_{lk}$  being proportional to the collision probability between sludge and polymer, which is enhanced by the shear rate as indicated by the  $\beta_{lk}$  term. In this context,  $k$  represents the exposed active CPAM sites, and  $C_k$  represents their concentration, while  $l$  denotes the sludge particles and  $C_l$  their concentration. This model can explain the case of sludge flocculation using degraded polymer, where the oligomers are fully mixed with sludge, and  $C_k$  being the concentration of oligomer fragments. However, it is unable to account for the case of non-degraded polymer, where the number of active polymer sites  $C_k$  is likely to increase during flocculation through stretching the polymer filaments, exposing further active sites. This suggests that flocculation using degraded polymer is limited by the collision between polymer and sludge due to the shear, whereas flocculation using non-degraded polymer is limited by the fibrillation kinetic of the polymer.

To take into account the fibrillation process during flocculation, it is possible to modify Eq. 2 by adding a parameter  $f_G$  that describes the efficiency of polymer fragmentation during mixing. The parameter  $f_G$  ranges from 0 when no active site is accessible to 1 when all active sites are accessible. The  $f_G$  value can be estimated by assuming that during degradation, the number of active sites  $C_k$  remains unchanged, and only a fraction  $f_G$  of these active sites are accessible during flocculation. Moreover, the fully degraded state corresponds to the case where all active sites are accessible ( $f_G=1$ ), and  $K_{lk}$  is proportional to  $1/t_{floc}$  ( $t_{floc}$  being the flocculation time). Fig. 10. right displays the evolution of  $f_G$  during polymer degradation as calculated by dividing  $t_{floc}$  with that obtained after complete degradation. These results suggest that during degradation, the flocculation mechanism shifts from being limited by polymer fibrillation to being limited by sludge-polymer collision.

### 3.3.5. Effect of the polymer degradation on the flocculation efficiency

The effectiveness of sludge flocculation using MV9104 under specific mixing conditions was assessed by monitoring the fraction of CPAM per sludge ( $\phi_{CPAM/sludge}$ ) necessary to flocculate all the sludge into compact flocs and clarify the solution. Different volumes of CPAM, varying from 5  $\mu$ L to 1000  $\mu$ L and exhibiting varying degrees of degradation, were introduced into 2 mL of sludge. This mixture was then subjected to agitation. Analysis of the images after complete flocculation (after 10 min of agitation) involved quantifying the colorimetry of the aqueous phase or using gray levels in Fig. 8, determining the fraction of CPAM at which a totally clear zone appeared. Fig. 11 illustrates the appearance of a clear aqueous phase for different mass fractions of CPAM per sludge



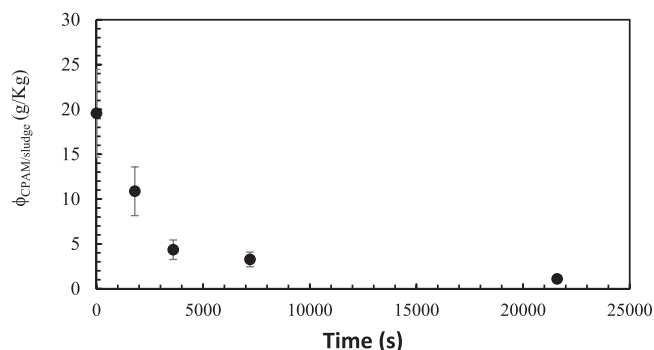
**Fig. 10.** Left) Mixing time ( $t_{mix}$ ) and flocculation time ( $t_{floc}$ ) estimated from image analysis during flocculation and plotted against degradation time.  $t_{mix}$  is roughly estimated as the time at which the sludge and polymer are fully mixed prior to flocculation or estimated as the time corresponding to the onset of increase in the floc index.  $t_{floc}$  is estimated as the time for which the shape of the flocs stops evolving or identified as the moment when the floc index approaches 90 %. Right) Parameter  $f_G$  plotted against the degradation time.  $f_G$  describes the efficiency of polymer fragmentation during mixing.

( $\phi_{\text{CPAM/sludge}}$ ). At low  $\phi_{\text{CPAM/sludge}}$ , the final solution contained dispersed flocs within a gray solution. As  $\phi_{\text{CPAM/sludge}}$  increased, the flocs became denser, and the aqueous phase cleared. The transition from gray to clear indicated the critical fraction of CPAM necessary to flocculate all dispersed sludges. The gray color resulted from small sludge particles ranging from colloidal to micron-sized objects. Notably, these small particles were the last to flocculate within the sludge solution, with larger particles flocculating first, inhibiting further flocculation and reducing efficiency. At higher CPAM fractions, these small particles flocculated, leading to a clear aqueous phase.

The critical  $\phi_{\text{CPAM/sludge}}$  was found to be significantly influenced by CPAM degradation. For freshly prepared CPAM under the experimental conditions, with the applied mixing by the OSR setup,  $\phi_{\text{CPAM/sludge}}$  exceeded 20 g AM/kg DM (Fig. 12). However, after complete CPAM degradation,  $\phi_{\text{CPAM/sludge}}$  decreased by more than 20 times. These results suggest that during polymer dispersion in the mixing procedure, flocculation of sludge particles occurs around the polymer droplet, creating an aggregate that inhibits further polymer dispersion and, consequently, flocculation. In contrast, during polymer degradation, mixing generates small polymer droplets, increasing the polymer surface area and creating more flocculation zones, thereby accelerating the flocculation process.

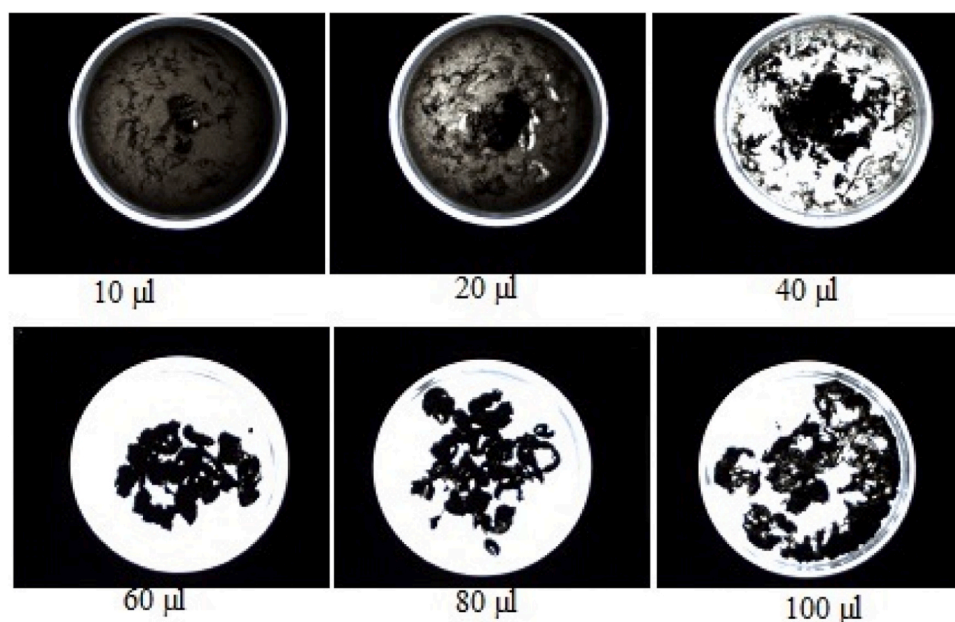
#### 4. Conclusion

This study underscores the critical impact of cationic polyacrylamide (CPAM) degradation on sludge flocculation within wastewater treatment systems. The investigation confirmed previous results that CPAM degrades significantly when exposed to metal surfaces, altering its viscosity and elastic properties, and demonstrated that this process is general for other CPAMs. These findings demonstrated that changes in viscoelastic properties profoundly affect the flocculation behavior of sludge, highlighting a significant phenomenon that must be considered in wastewater treatment processes. The research focused on the role of CPAM degradation in three key aspects: flocculation kinetics, floc morphology, and flocculation efficiency. It was observed that the time required for CPAM to disperse in sludge decreased from several minutes to just seconds as degradation progressed. Similarly, the characteristic



**Fig. 12.**  $\phi_{\text{CPAM/sludge}}$  as a function of degradation time.  $\phi_{\text{CPAM/sludge}}$  represents the fraction of CPAM per sludge required for complete flocculation of the sludge (sludge volume = 2 mL, solid concentration = 11.5 g/L). The calculation is based on the volume of MV9104 required to generate a clear aqueous phase after flocculation. MV9104 (5 g/L) was degraded within a dural Couette at room temperature for varying durations. Flocculation was carried out under agitation using the OSR system at 350 rpm.

time for flocculation reduced significantly throughout CPAM degradation, decreasing by up to an order of magnitude for the highest degree of degradation. Degradation led to changes in floc structure, transitioning from interconnected, branched flocs to smaller, individual particles. The efficiency improved with degradation, as indicated by a substantial reduction (approximately 2000 %) in the amount of CPAM required to achieve complete flocculation. These findings highlight the importance of understanding the effects of CPAM degradation on flocculation to optimize wastewater treatment processes. Reduced polymer usage due to improved flocculation efficiency can lead to significant environmental benefits by minimizing chemical consumption. However, further research is needed to fully understand the impact of CPAM degradation on other critical physical properties of flocs, such as sedimentation, permeability, and dewatering. These aspects are essential for the overall viability and efficiency of the treatment process. In conclusion, the degradation of CPAM in contact with metallic surfaces has a substantial effect on the rheology and flocculation process in wastewater treatment.



**Fig. 11.** Images depicting the morphology of flocs generated by the flocculation of sludge (2 mL, 11.5 g/L) using MV9104 at a concentration of 5 g/L. The images were obtained after 10 min of flocculation under agitation using the OSR system at 350 rpm. The cationic polyacrylamide (CPAM) was degraded for 30 min within a Dural Couette at room temperature. The images are arranged in a sequence from top left to bottom right, corresponding to different volumes of MV9104 (10  $\mu\text{L}$ , 20  $\mu\text{L}$ , 40  $\mu\text{L}$ , 60  $\mu\text{L}$ , 80  $\mu\text{L}$ , and 100  $\mu\text{L}$ ).

This insight should guide the design and operation of wastewater treatment facilities, either by selecting appropriate installation materials to avoid degradation or by exploiting CPAM degradation beneficially to accelerate flocculation and reduce the amount of polymer needed. Reducing the quantity of CPAM needed for effective flocculation is a key environmental objective, and this study provides a crucial step towards achieving it.

#### CRedit authorship contribution statement

**N. Elkissi:** Resources. **P. Ginisty:** Resources. **Y. Fayolle:** Resources. **M. Oliveira:** Resources. **D. Blésés:** Resources. **L. Jossic:** Resources. **N. Loukili:** Investigation. **Y. Rharbi:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **A. Magnin:** Supervision, Resources.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.colsurfa.2024.134975](https://doi.org/10.1016/j.colsurfa.2024.134975).

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