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Tailored cellulose-based flocculants for microplastics removal: Mechanistic insights, pH influence, and efficiency optimization

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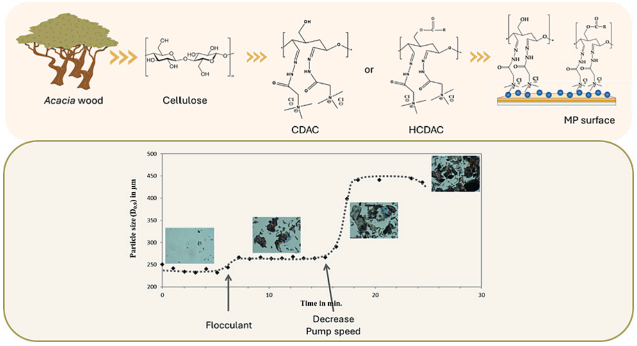
HIGHLIGHTS

- Cellulose derivatives developed were used as flocculants in microplastics removal.
- Bio-flocculants developed included both cationic and hydrophobic moieties.
- MPs flocculation kinetics and evolution of flocs structure with time assessed by LDS.
- It was possible to design the bio-flocculants to remove different types of model MPs.

GRAPHICAL ABSTRACT



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ABSTRACT

This study explores the performance of novel cellulose-derived sustainable flocculants in the flocculation of different model microplastics (MPs), including polyethylene (PE), polyethylene terephthalate (PET) and polyvinyl chloride (PVC). The influence of key parameters, such as pH, flocculant structure and concentration was evaluated by Laser Diffraction Spectroscopy (LDS) and optical microscopy to access their effects on flocculation performance, kinetics and floc structure. The results reveal that a bioflocculant concentration of 0.001 g·mL^{-1} is ideal for effective flocculation, as lower concentrations lead to insufficient floc growth. While electrostatic interactions are a dominant factor in the flocculation process, the study also highlights the role of hydrophobic interactions, its contribution depending on the characteristics of the MPs. Overall, this research highlights the importance of understanding the key interactions governing the flocculation process. It further paves the way for designing and fine-tuning cellulose-based flocculants with improved efficiency and optimized dosages for effective MPs removal strategies.

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1. Introduction

Plastics are unique polymeric materials widely used in industrial and household applications [1]. In the last ca. 20 years, the global plastic production nearly doubled, increasing from 234 million tons to 460 million tons per year [2]. This growth is projected to continue due to plastics' favourale properties, including accessibility, low cost, lightweight nature, and mechanical durability [3]. However, poor human practices combined with the typical low biodegradability of plastics, imply environmental risks, leading to their accumulation in ecosystems, such as aquatic environments [4], soils [5], and surface waters [6]. Annually, an estimated 4 to 12 million tons of plastic material enter the oceans, and by 2050, it is predicted that plastics may outweigh fish in marine ecosystems [7].

Macroplastics can degrade and break down into smaller plastic fibers, particles, or fragments when exposed to external factors, including UV radiation, wave abrasion, high temperatures, and microorganisms. When these smaller plastic materials are smaller than 5 mm, they are known as microplastics (MPs) [8,9]. In addition to plastic degradation, MPs can also be originated from industrial and municipal effluents or added on purpose to different formulations, such as cosmetics [10]. MPs are found in diverse aquatic environments worldwide, including rivers, lakes, and oceans, with concentrations ranging from 13 to over 2000 particles per cubic meter, depending on location [11]. Freshwater systems, such as the Great Lakes in North America [12] and major rivers in China [13], have also been significantly impacted. Additionally, MPs have been detected in drinking water sources, with studies reporting their presence in both tap and bottled water [14].

Removing MPs from the environment, including water sources, is an urgent challenge requiring effective and sustainable treatment methods. Regarding their removal from effluents, many strategies, including filtration and biological treatments, have shown moderate efficiency. These strategies can be improved when combined with processes, such as coagulation, flocculation, and sedimentation. Among these, flocculation is widely applied in industries such as paper making and mineral processing for effluent treatment [15]. Flocculation promotes the aggregation of suspended particles through mechanisms such as charge neutralization and bridging. The flocculation phenomenon strongly depends on the characteristics of the flocculant, the properties of the particles, and the liquid medium conditions [16]. To achieve charge neutralization, electrostatic repulsion between suspended particles may be reduced by using salts or low-molecular-weight polyelectrolytes of opposite charge [17]. Low or medium molecular weight polymers with high charge density often form polymer patches on oppositely charged particle surfaces [18]. Another mechanism occurring during flocculation is bridging, and this occurs when high molecular weight polymers are adsorbed in a stretched conformation on the particle surfaces, creating long loops and tails that form connecting points (bridges) between different particles [19,20].

Most of the studies dealing with MPs removal are focused on coagulation, using salts of aluminum [1,3], or flocculation using polyacrylamides (PAMs) [3]. Recently microbial-derived bioflocculants [21], bacterial [22] or algal biomass [23] have been considered for MPs treatment. However, the use of microbiologically-derived polymers for MPs removal via flocculation remains relatively unexplored. While some studies suggest that microbial bioflocculants have potential for aggregating and removing MPs from aquatic environments [24], gaps remain regarding their efficiency, which can be affected by environmental factors such as pH, temperature, and ionic strength, requiring further optimization for different water conditions [25]. The use of algal biomass for MPs removal may face limitations, including potential secondary pollution from biomass decay and variability in flocculation efficiency, depending on algal species and water conditions [23,26]. Similarly, bacterial bioflocculants also present challenges, including the need for controlled growth conditions, potential pathogenicity of certain strains, and the risk of introducing undesired microbial communities into water systems. Moreover, their flocculation performance may vary depending on nutrient availability and competition with native microbial populations [24].

Prior studies have explored natural polyelectrolytes derived from wood wastes and prepared through modification of cellulose with cationic charges [27] and hydrophobic groups [28,29], with the aim to enhance interactions with negatively charged particles. Several works have demonstrated the efficiency of these bioflocculants in addressing various contaminants removal, including dyes [30] and heavy metals [31], for effluents treatment, but, so far, there is no information about their applicability on MPs removal.

The present work builds on these efforts, focusing on employing cellulose-based polyelectrolytes (PELs), with different architectures, for MPs flocculation and removal. Understanding the interactions involved in flocculation is crucial for designing systems' tailored to MPs removal for water purification. Accordingly, this work evaluates the most promising cellulose derivatives based on their charge density, hydrophobic/hydrophilic balance, as well as the effect of the pH of the media and bioflocculant dosage, to flocculate MPs of different nature. Laser diffraction spectroscopy was used to monitor the flocculation process, enabling a systematic analysis of the efficiency of these biobased derivatives for MPs flocculation applications, including evaluation of the structure of the formed flocs.

The understanding of the bio-based polymer structural features regarding its interaction with MPs and their impact on floc formation kinetics and stability, is clearly lacking in literature. Here, the role of the polymer structure is systematically evaluated regarding the interaction of the novel PELs with three different model MPs (i.e., polyethene -PE, polyethylene terephthalate-PET and polyvinyl chloride-PVC). This work sheds light on which are the most important parameters leading to the formation of large and stable flocs, which can then be easily removed by filtration, sedimentation or flotation.

2. Methods

2.1. Materials

The PE and PET-based MPs used in this study were produced in our laboratory from detergent and water bottles, respectively. To ensure uniformity, these MPs were processed using a knife mill (Thomas Scientific, USA) equipped with a 60-mesh screen. On the other hand, the PVC-based MPs, with a particle size ranging from 20 to 30 μm, were sourced from Cires, Portugal.

The cellulose derivatives investigated in this study (Fig. 1) were recently developed by us and were designed through the introduction of cationic and hydrophobic groups (method in Appendix A), thus enabling the novel derivatives to possess tunable hydrophilicity and superior interaction with MPs [28]. These polymers exhibit a range of molecular weights, from 5000 to 7000 Da, varying degrees of cationic substitution, and low levels of hydrophobic substitution (to ensure water solubility). The synthesis was performed following the protocols detailed elsewhere [28].

2.2. Zeta potential determination

The zeta potential of PE, PET, and PVC-based suspensions of MPs was measured using the Zetasizer NanoZS (Malvern Instruments). For each sample, measurements were repeated six times, with each measurement consisting of 15 sub-runs, across a pH range from 2 to 12. In brief, a stock solution was prepared by dispersing 0.1 g of each MP in 30 mL of water. The pH of these suspensions was adjusted to the target value before being transferred to the measuring cell. The zeta potential was determined at 25 °C, following an equilibration period of 60 s.

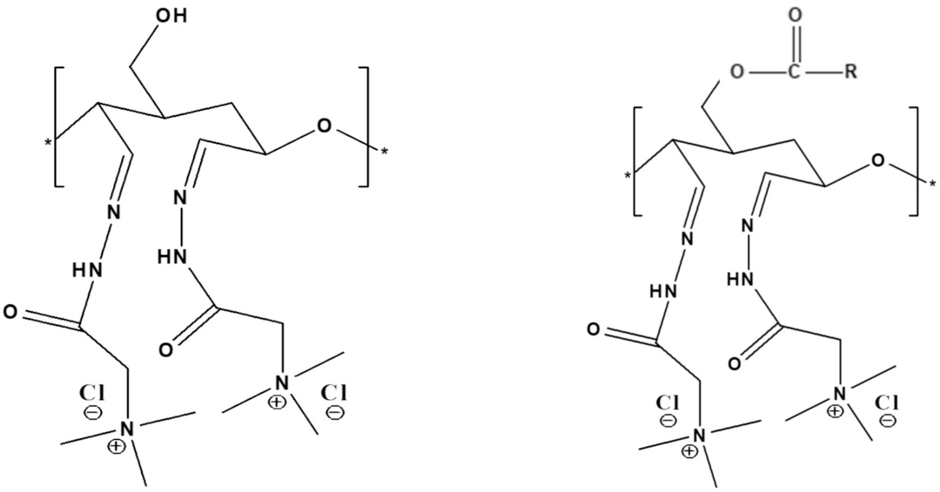


Fig. 1. Molecular structure of cationic dialdehyde cellulose - CDAC (left) and hydrophobic cationic dialdehyde cellulose - HCDAC (right). The 'R' group represents the structure of the hydrophobic moiety, corresponding to an alkyl or alkenyl chain, depending on the fatty acid used.

2.3. *Flocculation studies*

The flocculation effectiveness of the novel cellulose derivatives was assessed using Laser Diffraction Spectroscopy (LDS) with a Mastersizer 2000 device (Malvern Instruments) equipped with a Hydro 2000 module. This procedure follows the method developed by Antunes et al. (2008) and Rasteiro et al. (2011) [32,33] for screening polyelectrolytes for flocculation application. This approach was also previously used by Lourenço et al. (2020) [20,34] to evaluate the flocculation performance of anionic flocculants, and by Pedrosa et al. [35] to infer on the performance of microfibrillated cellulose/nanofibrillated cellulose in the flocculation of PCC (precipitated calcium carbonate).

In a typical LDS assay, 0.01 wt% of MPs were added to the sampling vessel containing 650 mL of distilled water [36]. The pump speed was initially set to 1000 rpm to homogenize the MPs suspension and then reduced to 350 rpm. Once the median particle size of the MPs is stabilized, a certain amount of bioflocculant is introduced in the system. At this stage, the pump speed was increased to 550 rpm to ensure proper dispersion of the flocculant and homogenization of the suspension, thus allowing the initial flocs to form. After 15 min, the pump speed was lowered to 200 rpm to facilitate the flocculation process. These conditions were selected to simulate those typically found in a wastewater treatment plant (WWTP), while minimizing floc breakage. The flocculation process was monitored for an additional 30 min at room temperature (23 ± 2 °C). The evolution of the median size (d_{50}) of the flocs was monitored during the flocculation process. The overall LDS experimental setup is shown in Fig. 2. All tests were conducted in triplicate.

2.4. *Mass fractal dimension of the MPs flocs*

In addition to assessing the average particle size and size distribution, LDS also provides insights into the structure of the formed flocs by determining their mass fractal dimension (d_F) [37,38]. The d_F value reflects how primary particles are distributed within the volume of an aggregate, thus reflecting the flocs' density and structure. From Eq. (1), the mass (m) of a fractal aggregate is found to be directly proportional to its radius (R) raised to the power of the mass fractal dimension (d_F) [35,37].

$$m(R) \propto R^{d_F} \tag{1}$$

A d_F value close to 1 indicates a looser, more string-like floc structure, while a value approaching 3 suggests a denser and more compact floc [38]. According to the Rayleigh-Gans-Debye (RGD) theory, d_F can be determined from the negative slope of the log-log plot of scattered light intensity versus the scattering wave vector (q) given by Eq. (2) [39].

$$q = \frac{4\pi\eta_0}{\lambda_0} sin\frac{\theta}{2} \tag{2}$$

where η_0 is the refractive index of the dispersant medium (1.33 for water), θ is the scattering angle (ranging from 0.01° to 40.6° for the Mastersizer 2000 equipment), and λ_0 is the incident light wavelength in vacuum (630 nm for the LDS equipment used)

The validity of the RGD theory relies on the assumption that the elementary units scatter light independently. This theory is most suitable for sub-micron spherical particles with a low refractive index [40]

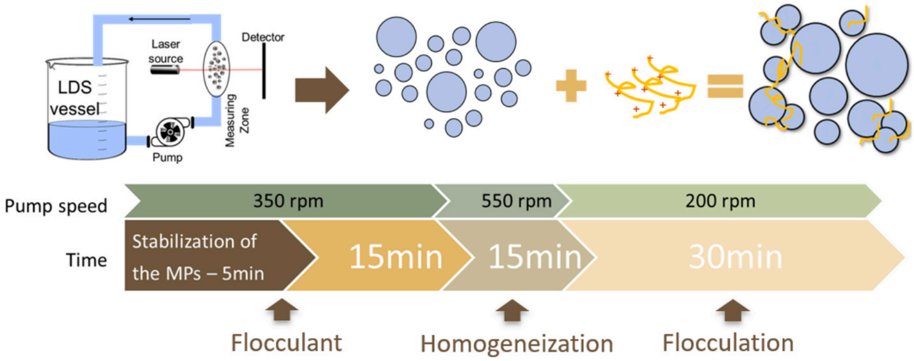


Fig. 2. Schematic representation of the MPs' flocculation process monitored by LDS and using different HCDACs and CDACs.

and it is applicable when q is significantly larger than the primary particles but much smaller than the aggregates, that is for small length scales (Eq. (3)) [41]:

$$\frac{1}{R_{agg}} \ll q \ll \frac{1}{R_{part}} \tag{3}$$

R_{agg} is the radius of the aggregate, and R_{part} is the radius of the primary particle. In systems with extensive flocculation, where the size of the flocs (secondary aggregation resulting from the aggregation of primary flocs) exceeds the applicability range of the RGD theory, large length scales, the floc structure is characterized by the scattering exponent (SE) [32].

The SE is determined from the negative slope of the log-log plot of scattered light intensity versus the scattering vector (q) at large length scales (low diffraction angles). Structural information about the flocs can be derived from the d_F at small length scales (high diffraction angles) and from the SE at large length scales (low diffraction angles), as shown in Fig. 3. These regions correspond to the presence of primary and secondary aggregates, respectively.

The structural information of the formed flocs was extracted by exporting the raw data from the LDS equipment to an external spreadsheet provided by Malvern Instruments. This spreadsheet enables offline analysis based on the information at each detector's angle and the intensity of light scattered to each detector. The data was then processed into log-log plots of scattered light intensity versus the scattering wave vector (q), using Eq. (2) (see Fig. 3 for details). This analysis allowed for the determination of both d_F and SE.

2.5. Optical microscopy

Optical microscopy images were obtained using an Olympus BH-2 KPA microscope (Olympus Optical Co., Ltd) equipped with a high-resolution CCD colour camera (Olympus ColorView III). Samples were analysed qualitatively after placing a few drops of each MPs' suspension, both before and after flocculation, on a glass slide. Images were obtained at various magnifications using the microscope analysis software (Soft Imaging System GmbH).

2.6. MPs filtration and removal

A removal strategy was implemented to simulate a fast and low energy consumption filtration approach in conditions similar to what is applied in wastewater treatment plants, both in domestic and industrial sectors. The method developed consists of using filters with a large mesh (smaller pore size of 212 μm), to provide fast filtration and allowing for the treatment of large volumes of water. The procedure used consisted in dispersing PET-based MPs in water, in the same proportions used in the flocculation studies; after 5 min of dispersion, the selected flocculants were added, and the mixture was stirred at 200 rpm for 15 min before being allowed to settle for 30 min. Finally, the model effluent was filtered through two sieves (850 μm and 212 μm). The filtrate containing the non-retained particles was filtered through a pre-weighed 55 mm glass fibre filter. The filter was dried overnight at 70 °C and subsequently reweighed. The amount of MPs retained in the sieves was calculated and the removal efficiency was estimated by calculating the mass of MPs retained, expressed as a percentage of the initial MPs mass.

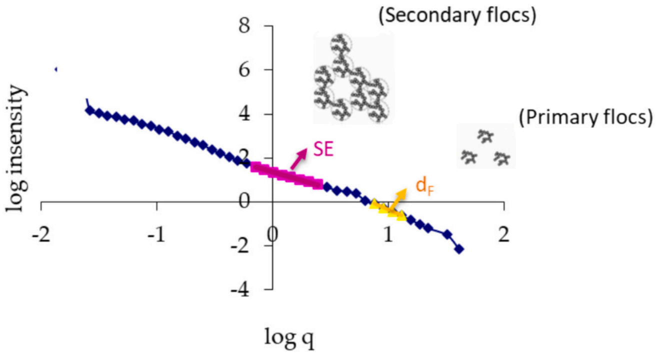


Fig. 3. Example of the log-log plot of the scattering light intensity versus q for the determination of the scattering exponent - SE (first region) and the fractal dimension – d_F (second region).

3. Results

The effectiveness of flocculation largely depends on the flocculant concentration, which should be tailored to the type and concentration of suspended solids in the wastewater. Typically, increasing the flocculant concentration enhances treatment performance. It is noteworthy that exceeding the optimal dosage may actually reduce efficiency due to the stabilization of the primary particles [42]. Mechanical factors, particularly the stirring speed, are also critical to the flocculation process. Stirring enhances the interaction between the flocculant and suspended solids, promoting floc formation. However, excessive stirring can lead to floc breakage [32].

In this study, flocculants were specifically designed to enhance both electrostatic and hydrophobic interactions with MPs, taking into account our previous work [28]. The selection of flocculants was based on their potential electrostatic and hydrophobic interactions, as outlined in Table 1. Cationic polymers with two different degrees of substitution (DS) were selected: one with intermediate and one with high charge density (determined from the theoretical maximum expected DS). Additionally, two derivatives with different cationic charge densities were selected to be further modified with hydrophobic moieties to access the impact of hydrophobicity on the flocculation of MPs: a cationic polymer with a DS of 1.0 and another one with a DS of 1.4.

First, the surface charge of the developed bio-based flocculants and of the different model MPs was determined, for a pH ranging from 2 to 12, Fig. 4.

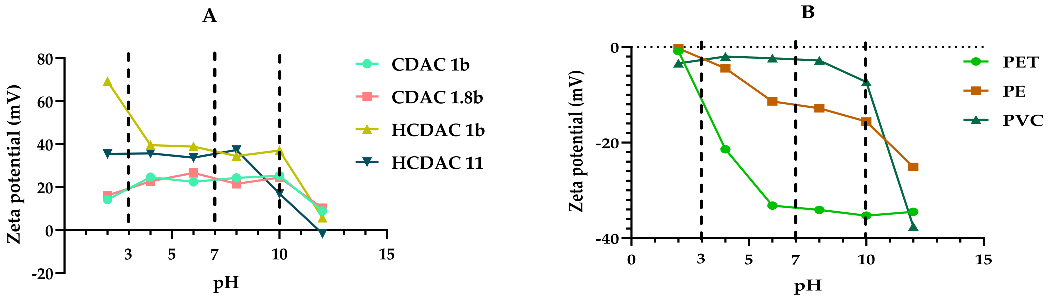
As can be observed in Fig. 4, all model MPs exhibited a predominantly negative surface charge. As the pH increases, the negative charge became more pronounced for all the MPs, enhancing particle suspension stabilization through repulsion effects. This stabilization renders effluent treatment at high pH values more difficult. Nevertheless, it should be noted that all zeta potential values of the MPs remained in the unstable/low stability range, below −30 mV [43].

As mentioned before, LDS was employed to monitor the flocculation process under mild stirring conditions, thus providing insights into flocculation kinetics. Fig. 5 shows the evolution of the d_{50} of the flocs formed when MPs were treated with the developed PELs (i.e., HCDACs and CDACs). The figure displays the effect of the degree of cationization and hydrophobization, at three different pH values, using a concentration of the bioflocculant of 0.001 $g{\cdot}mL^{-1}$. This concentration was selected based on previous results [10] and on the optimization performed (Fig. 6).

At pH 7 and above, all bioflocculants effectively flocculate PET particles. However, at acidic pH levels, the effectiveness of positively charged polymers (i.e., CDAC 1b and CDAC 1.8) decreases significantly. This decrease is due to the reduction in both the PET and the cellulose derivatives charge density at acidic conditions. Therefore, in this case, the presence of hydrophobic moieties becomes crucial. At low pH, the

Table 1
Degree of substitution and Mw of the selected cellulose-based flocculants.

Polymers	Cationic DS	Hydrophobic DS	MW (Da)
CDAC 1b	1.0	0	7169
CDAC 1.8b	1.8	0	5031
HCDAC 1b	1.0	0.12	5328
HCDAC 11	1.4	0.15	5677



pH	Zeta potential (mV) CDAC 1b	 CDAC 1.8b	 HCDAC 1b	 HCDAC 11
3	20.0 (±1.50)	19.9 (±2.95)	52.0 (±2.63)	36.0 (±2.34)
7	22.9 (±1.77)	24.9 (±4.79)	36.2 (±1.37)	36.2 (±0.72)
10	25.3 (±1.05)	24.4 (±1.45)	37.0 (±0.44)	16.9 (±0.16)

pH	Zeta potential (mV) PET Non-polar	 PE Non-polar	 PVC Polar
3	-9.5 (±0.81)	-2.0 (±1.08)	-3.0 (±0.26)
7	-34.2 (±0.69)	-12.5 (±1.12)	-2.5 (±0.78)
10	-35.3 (±1.01)	-15.6 (±0.82)	-7.31 (±1.36)

Fig. 4. Zeta potential of the A) polymers and B) MPs under study, at 25 °C.

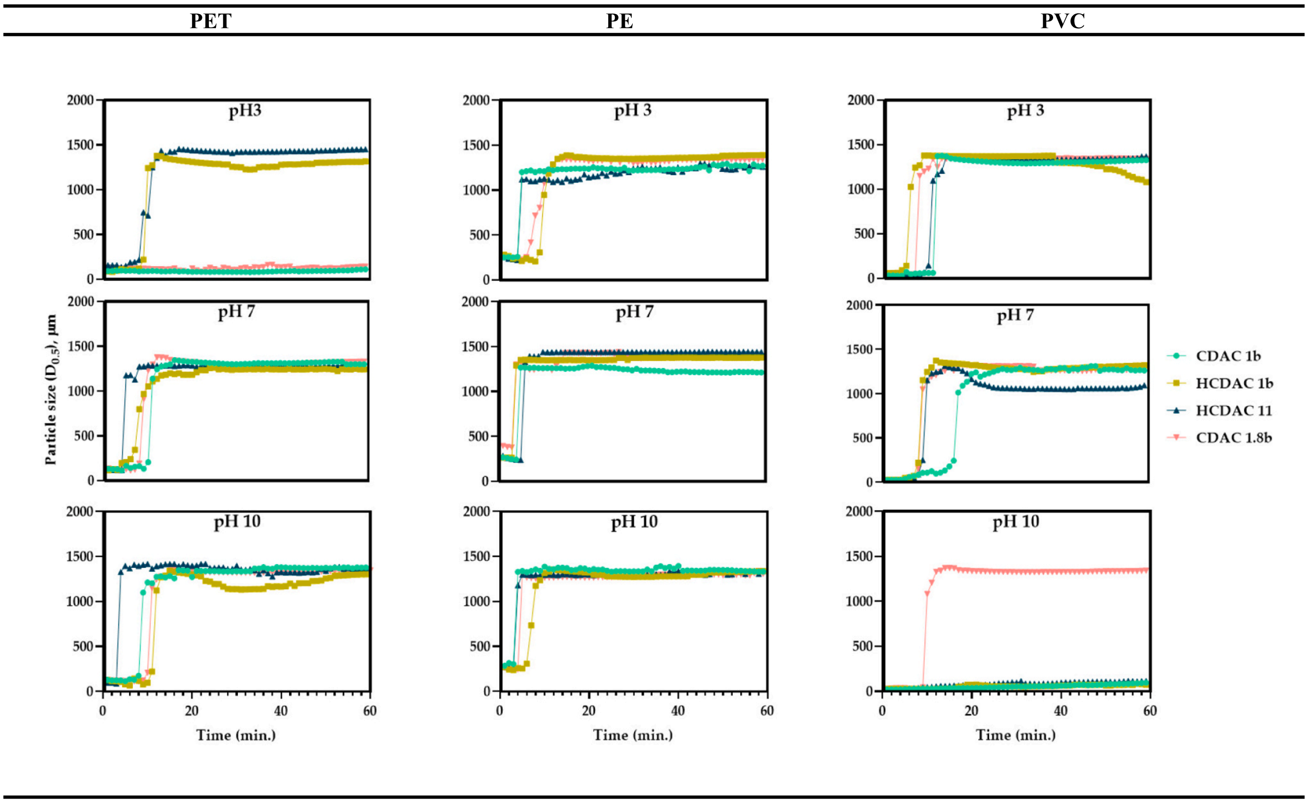


Fig. 5. Median size of the flocs formed with PET, PE and PVC microparticles at 25 °C for the different cellulose-based flocculants (with different degrees of cationization and hydrophobization), at three different pHs and for a constant concentration of bioflocculant of 0.001 g·mL^{-1}. The green symbols represent CDAC 1b, the blue symbols correspond to HCDAC 1b, the yellow symbols indicate the HCDAC 11, and the orange symbols denote CDAC 1.8b. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electrostatic driving for PET-polymer association is low and flocculation is compromised. On the other hand, derivatives containing hydrophobic modifications tend to better interact with the MP particles of low charge density. These hydrophobic interactions enable PET particles to associate with various HCDAC molecules, leading to their aggregation. It is further observed that the aggregates remain stable, as particle size remains constant even with increased stirring during the flocculation process.

For PE microparticles, the developed bioflocculants were effective across all pH levels, with flocs forming more rapidly at pH 7 and above when compared to acidic conditions. Unlike PET, which is derived from aromatic polymers, PE is obtained from aliphatic olefins [44–46]. This

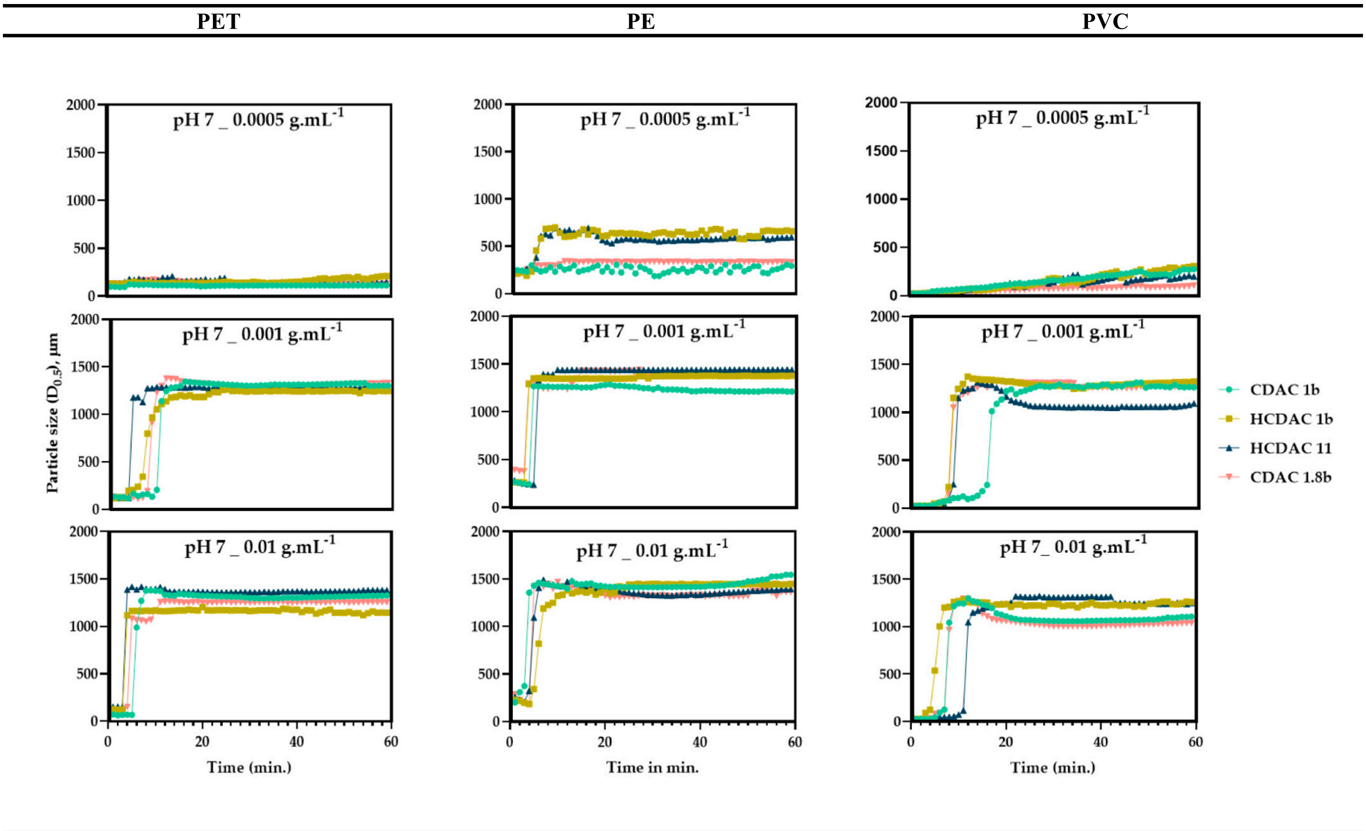


Fig. 6. Optimization of flocculant dosage for PET, PE and PVC microparticles flocculation at pH 7. The green line represents CDAC 1b, the blue line corresponds to HCDAC 1b, the yellow line indicates HCDAC 11, and the orange line denotes CDAC 1.8b. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

difference makes PE less reactive, resulting in a lower charge density for the pH range studied and allowing more efficient charge neutralization at acidic pH levels. Due to its inherent hydrophobic nature, PE-based microparticles aggregate more easily after charge neutralization, making all the bio-based flocculants suitable for flocculating PE-based MPs, even without the presence of hydrophobic modifications.

PVC, in contrast to the non-polar and semi-crystalline PE and PET, is polar and amorphous. This distinct chemical structure and physical state affects its interaction with flocculants and its behaviour in suspension. As shown in Fig. 5, PVC flocculates effectively at acidic pH, where its zeta potential is low. At alkaline pH, only CDAC 1.8b, with a higher degree of cationization, effectively flocculates the PVC particles. As the pH increases and the charge on PVC particles rises, electrostatic repulsion may hinder flocculation, requiring a more highly charged polymer to neutralize the particles' charges. The polar nature of PVC does not favour interaction with the hydrophobic moieties of HCDACs, resulting in less effective performance of these derivatives.

The polarity and hydrophobicity of MPs are critical factors affecting their surface adsorption capacity. Cationic cellulose-based flocculants, with positively charged groups, interact with negatively charged suspended MP particles. Additionally, the presence of hydrophobic groups in these flocculants enhances surface activity, leading to stronger interactions with MP surfaces. The relatively long polymer chains with medium charge densities facilitate a bridging mechanism, where adsorbed polymer chains may extend from one particle to another particle. Overall, data suggests that all synthesized cellulose-based flocculants are effective in flocculating the different model MPs at neutral pH, which is usually found in common effluents. Therefore, optimizing the concentration of the bio-based flocculants at neutral pH is important to ensure effective charge neutralization and flocs formation for the conditions usually found in real scenarios.

In this regard, Fig. 6 shows the time evolution of d_{50} for the flocs formed for all four selected flocculants and for different polymer concentrations. As can be observed, increasing the concentration of the flocculant in the suspension enhances flocculation (larger flocs are formed) up to a flocculant concentration of 0.001 $g{\cdot}ml^{-1}$. Additionally, as flocculant concentration increases, the kinetics of flocculation are enhanced and aggregation starts at earlier times. Nevertheless, the equilibrium sizes of the formed flocs remain fairly similar regardless of the concentration of the bioflocculant used, equal or above 0.001 $g{\cdot}ml^{-1}$. At lower concentrations, there is no significant increase in particle size during the flocculation process, especially when using the CDACs. This indicates that at low cellulose-based flocculant concentrations, positively charged flocculants are less effective due to insufficient charge neutralization. Data suggests that a minimum concentration of 0.001 $g{\cdot}mL^{-1}$ is required to ensure sufficient interaction between MPs and the developed flocculants. This trend is similar for all the model plastics tested and for all the selected bio-based flocculants.

Among the bio-based flocculants tested, HCDAC11 proved to be the most promising overall in terms of flocculation efficiency (Fig. 5). Moreover, under most of the tested conditions and for the different types of MPs, HCDAC11 generally exhibited faster kinetics compared to the other polymers studied. As depicted in Fig. 4, its high zeta potential likely facilitates stronger electrostatic interactions with the model MPs tested (i.e., PE, PET, and PVC). In fact, for certain MPs such as PET, electrostatic interactions were expected to drive flocculation given PET's more negative charge density within the pH range studied (Fig. 4) and its lower hydrophobicity.

Apart from the kinetics of flocculation, LDS can provide additional information on the flocs size and structure. In this regard, the flocs compaction can be assessed from the scattering exponent, SE. In Fig. 7, SE is presented, as a function of time, for all bioflocculants at the optimal

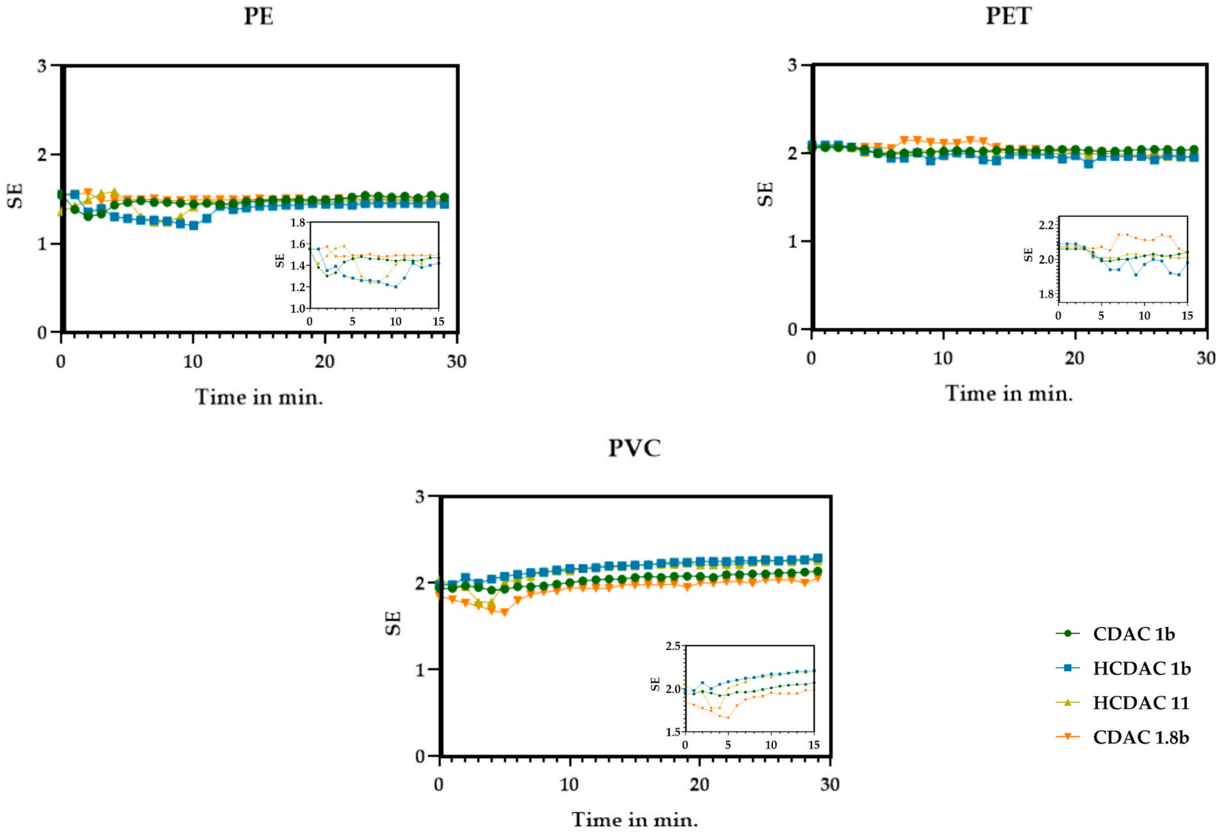


Fig. 7. Time evolution of the scattering exponent (SE) during the flocculation with CDAC 1b (green line), HCDAC 1b (blue line), HCDAC 11 (yellow line) and CDAC 1.8b (orange line) for the optimal flocculant concentration of 0.001 g·mL^{-1}, at pH 7 and 25 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentration of 0.001 g·mL^{-1} and for a pH of 7.

In this study, SE was used to characterize the compactness of the aggregates, since it describes better the larger aggregates formed during the flocculation process, providing valuable insights into the density of the secondary aggregates produced [33,39]. Since the initial particles are large and rapidly originate secondary aggregates, no data was presented regarding the d$_F$ which can only be used to describe primary aggregates [39]. At the beginning of the flocculation process, the secondary aggregates exhibit an SE of approximately 2 for PET and PVC, and 1.5 for PE. The PE-based system exhibits lower SE, likely due to the presence of larger PE particles that form loose, small aggregates at the onset of the flocculation process. This initial aggregation accelerates the process but prevents higher compaction of the MPs, resulting in less dense structures.

For PVC, secondary aggregates become slightly more compacted over time, as more particles are incorporated, and likely due to particle rearrangement. On the other hand, PE and PET-based flocs maintain a rather constant degree of compactness throughout the flocculation process. Nevertheless, the polymers containing hydrophobic modifications (HCDACs) reach an equilibrium value for SE later than the cationic celluloses (CDAC), which aligns with the aggregates size evolution shown in Fig. 5.

In the case of PVC, an increase in floc compactness is observed with the addition of the various bio-based flocculants. Nevertheless, HCDAC derivatives demonstrate higher compaction efficiency compared to the CDAC ones, most likely due to the lower charge density of PVC MPs, thus demonstrating the existence of relevant hydrophobic interactions in this system.

Overall, the charge density of the flocculant plays a predominant role in the flocculation of MPs, while hydrophobicity does not significantly affect floc density. However, for nonpolar MPs, such as PE, and for MPs with low charge density like PVC, flocculant positive charge density and hydrophobic interactions are relevant to the flocculation process. These results clearly highlight the critical need to account for both electrostatic and hydrophobic properties when designing effective flocculants for MPs removal. Moreover, pH and flocculant concentration are also determinant parameters for the efficiency of the flocculation process. It is worth mentioning that for the optimal concentration determined in this work (0.001 g·mL^{-1}), commercial flocculant systems, such as polyacrylamides, are unable to induce the flocculation of the model MPs tested in this work [10].

The flocs formed were also visualized by optical microscopy for a qualitative assessment of their structure. It is possible to observe that the bio-based flocculants induce particle aggregation as they attract and bind individual MPs together, forming larger clusters of aggregates (Fig. 8 and Appendix B).

This aggregation at the macroscopic level demonstrates the bio-flocculants' effectiveness in promoting flocculation.

After the analysis of the flocculation performance of the novel cellulose-based flocculants when applied to the different plastic materials, MPs removal was also evaluated. To do so, PET was selected as a model MP because it is one of the plastics showing more abundance in contaminated effluents [47], and then the optimal flocculation conditions for this plastic material were applied. The formed flocs were separated by filtering the effluent through a series of sieves as described in the experimental section. Table 2 summarizes the removal efficiencies obtained using the different bio-based flocculants.

The results in Table 2 highlight how the interplay between MW, cationic substitution, and hydrophobization affect the filtration removal efficiency of MP flocs. Without a bioflocculant, this efficiency is observed to be minimal (i.e., 36.01 %), thus emphasizing the need of a bioflocculant for a more effective MPs removal. Among the tested

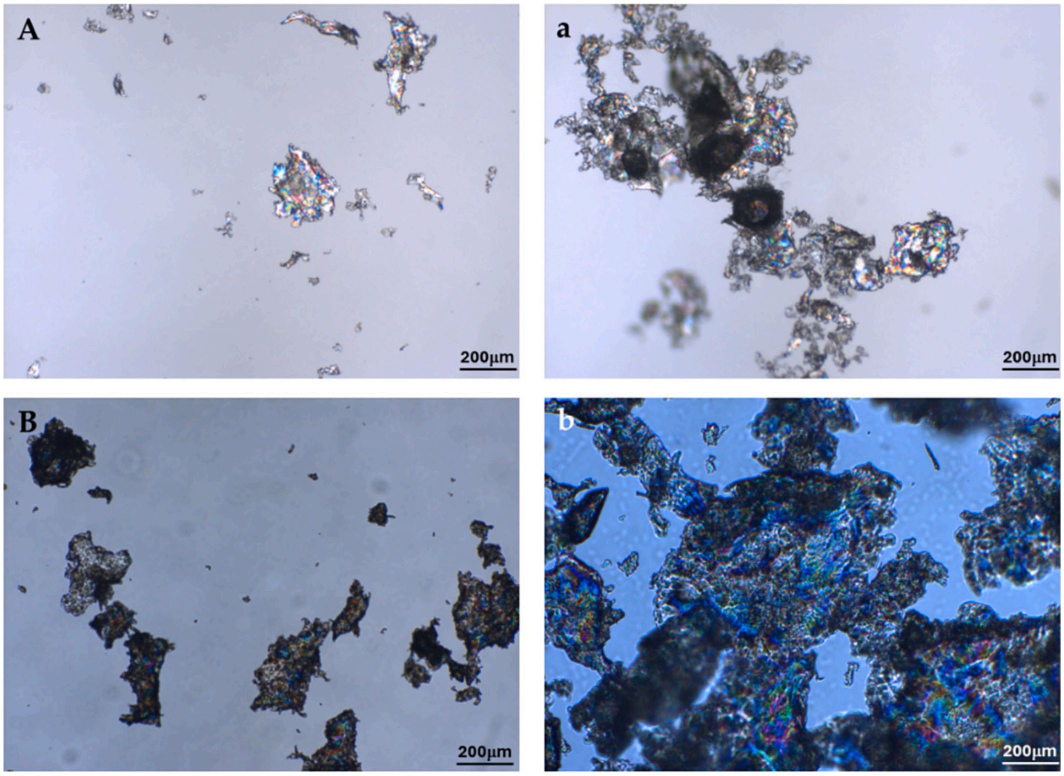


Fig. 8. Optical microscopy images of the original PET-based particles (A, B) and after flocculation with HCDAC 11 (a, b) (concentration of 0.001 g ml^{-1}), at pH 7 and 25 °C.

Table 2
Removal percentage of PET with the different cellulose-based flocculants.

Flocculant	%removal
Without Flocculant	36.01
CDAC 1b	79.53
CDAC 1.8b	52.12
HCDAC 1b	70.40
HCDAC 11	72.12

flocculants, CDAC 1b is observed to achieve the highest removal efficiency (79.53 %), representing an improvement of ca. 120 % compared to the sample without bioflocculant. The performance of CDAC 1.8b (52.12 %), which represents an improvement of ca. 45 % when compared to the system without flocculant, is significantly lower than that of CDAC 1b, despite the former presenting a higher cationic DS. The difference in the performance between CDAC 1b and CDAC 1.8b can be attributed to the lower MW of the later (Table 1), which may hinder the formation of stronger flocs through bridging. On the other hand, the hydrophobized derivatives (HCADC), presented a similar removal performance: 70.40 % for HCDAC 1b and 72.12 % for HCDAC 11, which represents an increase of 96 % and 100 %, respectively, when compared to the system without flocculant. These results further highlight the beneficial effect of hydrophobization in the formation of robust flocs. The hydrophobic modification enhances the interactions with the hydrophobic regions of PET MPs, thus compensating for limitations in molecular weight that can result from the harsher cationic modification needed to obtain a higher charge density. Nevertheless, their performance is slightly lower than CDAC 1b, thus suggesting that MW is the most relevant parameter in the formation of stable flocs.

In summary, these results reinforce the conclusion that while cationic substitution is necessary for flocculation, increasing it beyond an optimal level can be counterproductive, particularly under aggressive modification methods, which can lead to a reduction in molecular weight. Hydrophobization improves removal efficiency, but molecular weight remains a key factor in determining flocculant performance and flocs stability, mainly under more aggressive removal conditions, such as the use of high shear rates. Thus, CDAC 1b's superior performance highlights the importance of a balanced flocculant design to maximize removal efficiency under harsher conditions.

4. Conclusions

This study provides a comprehensive analysis of the flocculation dynamics of the most prevalent MPs—PE, PET, and PVC—using newly designed cellulose-based flocculants. By focusing on flocculation kinetics and floc structure evolution, an optimal flocculant concentration of 0.001 g·mL^{-1} has been found with the aid of Laser Diffraction Spectroscopy, which provides valuable insights into the flocculation mechanisms, helping on the optimization of the bioflocculants. Such concentration was found to ensure effective aggregation across all tested systems. Concentrations below this threshold led to insufficient floc growth, underscoring the critical role of precise dosing. Our findings highlight the influence of pH, hydrophobicity, and electrostatic interactions on flocculant adsorption to MPs. Notably, cationic cellulose-based flocculants with hydrophobic modifications exhibited superior interactions, promoting enhanced aggregation. Moreover, the kinetics of the flocculation process is also further enhanced when using the derivatives containing hydrophobic moieties. Optical microscopy provided visual insights revealing that MPs treated with these bio-based flocculants formed smoother and more compact aggregates, further validating their efficiency. Beyond demonstrating the efficacy of bio-based flocculants, this study emphasizes the interplay between MPs charge density, polymer characteristics, and environmental conditions in optimizing treatment strategies. Integrating advanced analytical techniques, such as LDS, facilitates the pre-screening of flocculants and guides their refinement for improved environmental remediation.

Future research should explore flocculant performance under real wastewater conditions, which may contain other materials besides MPs, for instance organic material; assess biodegradability for long-term stability; and fine-tune formulations for lower MPs concentrations. Initial ecotoxicity studies performed confirm environmental safety of the developed cellulose-derivatives, reinforcing their potential suitability as sustainable biofloculant agents. This work serves as a platform for future advancements in sustainable MPs mitigation strategies. Given the novelty of this approach, further research is needed to optimize its implementation and scalability.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

CRediT authorship contribution statement

Solange Magalhães: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Magnus Norgren:** Writing – review & editing, Visualization, Validation, Formal analysis. **Luís Alves:** Writing – review & editing, Validation, Supervision, Methodology, Formal analysis. **Bruno Medronho:** Writing – review & editing, Validation, Supervision, Methodology, Formal analysis. **Maria da Graça Rasteiro:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

All authors declared that there are no conflicts of interest.

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Appendix A. Synthesis of the cellulose derivatives

A.1. Cationization

The modification of cellulose was performed using a dual step cationization, in which the biopolymer was first oxidized to DAC followed by cationization with GT.

The procedure used was adapted from the work developed by Kinga et al. (2018) [48]. The first step focuses on the oxidation of the cellulose material, which avoids the use of alkali treatments. Briefly, 4 g of cellulose are dispersed in 250 mL of distilled water and stirred overnight using a magnetic stirrer. Then, the suspension was placed in a round flask and diluted with 200 mL of distilled water. The reaction vessel was covered with an aluminum foil to prevent the photo-induced decomposition of periodate and then placed in an oil bath. Precise quantities of NaIO4 (7.2 g) and LiCl (8.2 g) were added to the aqueous dispersion to initiate the reaction. According to Sirviö et al. (2011) [49], LiCl can act as a catalyst and improve the oxidation efficiency [50]. The improvement obtained is attributed to the ability of the lithium ions to disrupt the hydrogen bonds between the cellulose chains and facilitate the interaction between the chemical reagents and the cellulose chains [50]. After the reaction end (3 h), the product was filtered and washed several times with distilled water to remove iodine compounds from the obtained DAC.

The cationization of DAC is finally achieved by redispersing it in distilled water (0.8 g on a dry basis in 80 mL of water) and adding the GT reagent. The selected GT/aldehyde ratios are 1.8 and 2 (*w*/w). The pH of the mixture was adjusted to 4.5 with HCl, and the reaction was allowed to continue at 70 °C for 1 h. After the reaction ended, the obtained mixture was diluted with isopropanol to precipitate the insoluble products (CDAC). The precipitated material was centrifuged and washed with a water/isopropanol mixture (1/9, *v*/v) to remove the unreacted GT reagent. The schematic reaction steps and mechanisms are summarized in Fig. A.1.

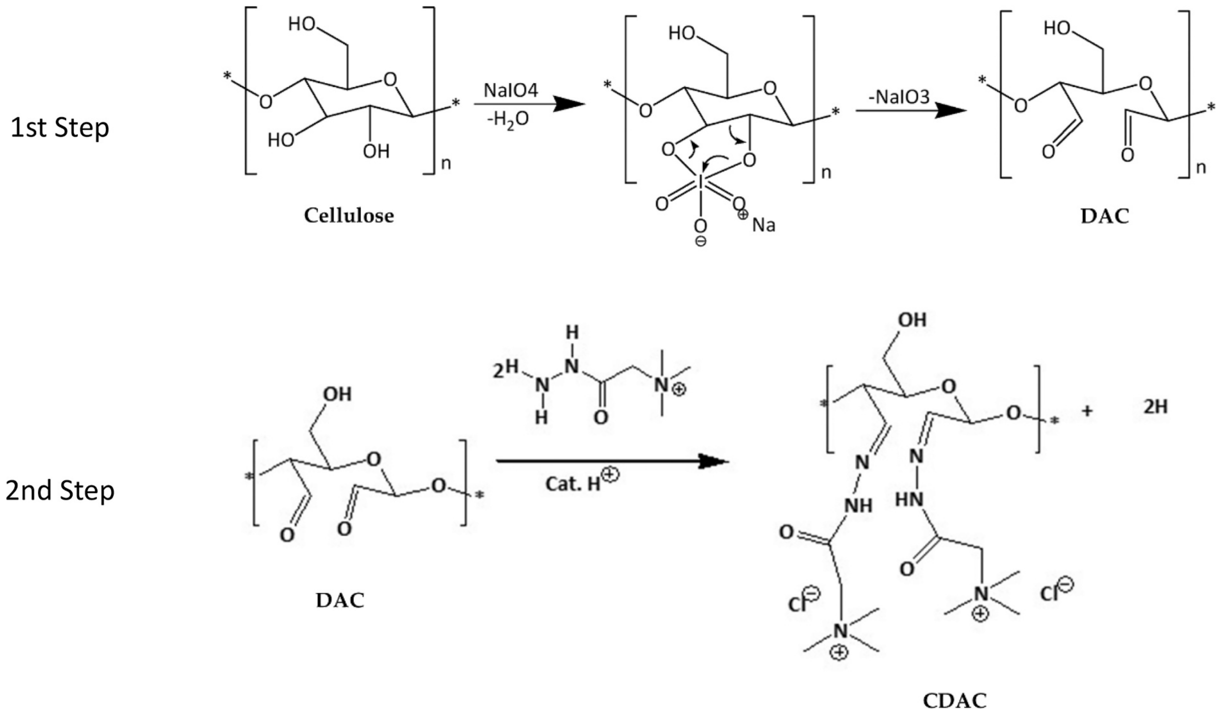


Fig. A.1. Dual step cationization of cellulose with GT via periodate oxidation of cellulose to create DAC (1st step), followed by the synthesis of cationic cellulose using Girard's reagent (2nd step).

A.2. Hydrophobization

The hydrophobic modification of CDAC begins by dissolving 0.11 to 0.18 g of catalyst (K_2CO_3) in 10 mL of MeOH with constant stirring for 30 min. Then, CDAC and fatty acids were added to the reaction mixture in different ratios: 1:1, 1:2 (w/w). The reaction was left to proceed for 3 to 24 h at 50 °C, according to the experimental design developed. After the reaction was completed, the mixtures were heated to 90 °C until all MeOH has evaporated. Once the MeOH was fully evaporated, hexane was added to the resulting pellet to remove unreacted fatty acids, and the HCDAC was recovered by filtration. The overall hydrophobic modification reaction scheme is depicted in Fig. A.2.

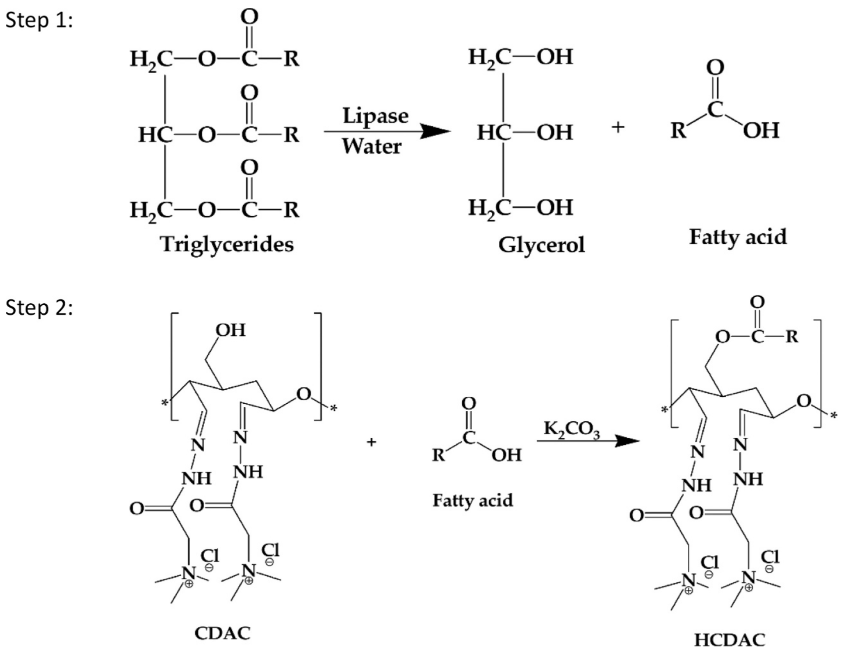
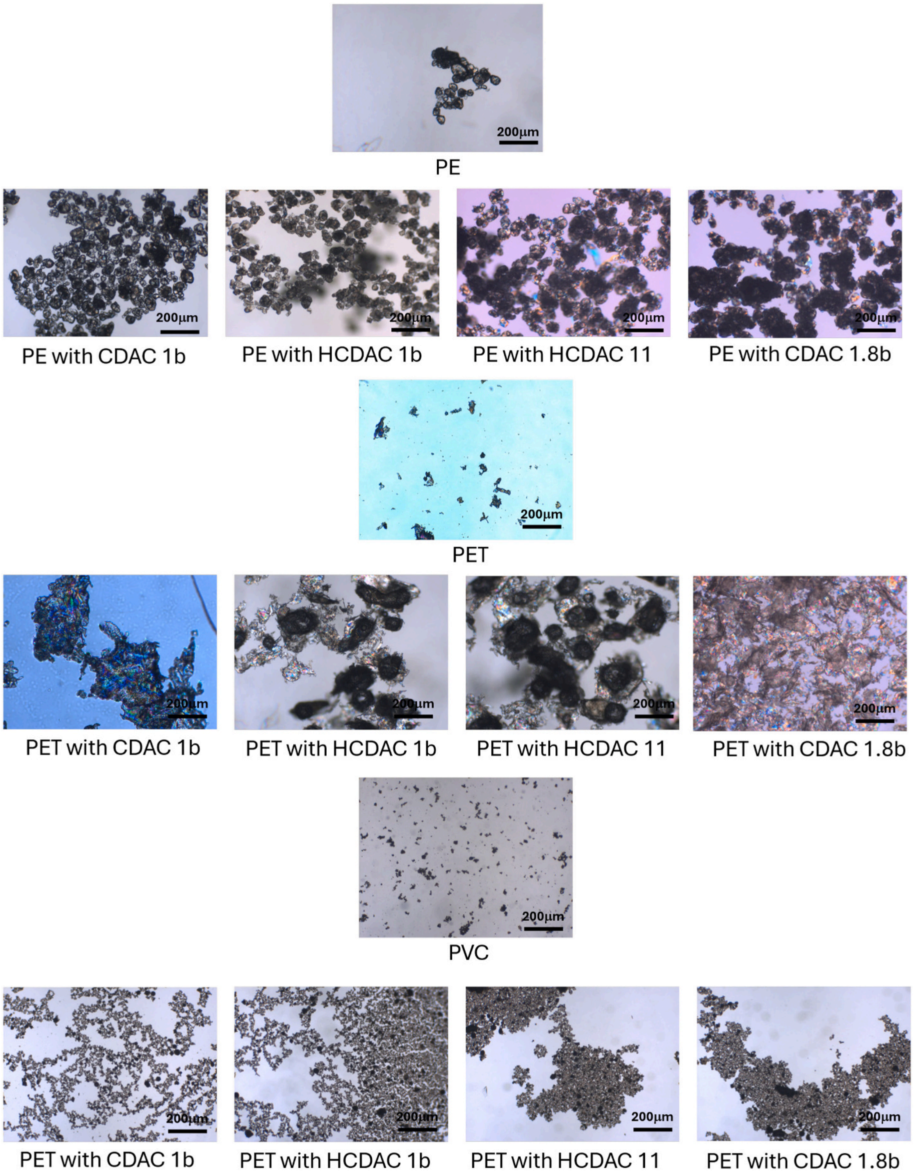


Fig. A.2. Fatty acids extraction (step 1) and CDAC hydrophobization (step 2).

Appendix B. Optical microscopy of the original PE, PET and PVC MPs and corresponding flocs obtained with all BIOPELS studied (CDAC 1b, HCDAC 1b, HCDAC 11, CDAC 1.8b)



PE

PE with CDAC 1b

PE with HCDAC 1b

PE with HCDAC 11

PE with CDAC 1.8b

PET

PET with CDAC 1b

PET with HCDAC 1b

PET with HCDAC 11

PET with CDAC 1.8b

PVC

PET with CDAC 1b

PET with HCDAC 1b

PET with HCDAC 11

PET with CDAC 1.8b

Optical microscopy images of the original MPs and corresponding flocs obtained with the different bioflocculants

Data availability

Not applicable.

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