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Synthesis and Characterization of a Coagulating Agent from Plantain Peel Starch (*Musa paradisiaca*), as Coadjuvant in Water Treatment

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Abstract Coagulation processes are widely used for water treatment, mainly with chemical coagulants. In this research, starch derived from a waste (unripe plantain peel, *Musa paradisiaca*) was used as a starting point for a chemical modification.

Through acetylation, its chemical structure was modified and characterized by infrared spectrophotometry, for its evaluation as a coadjuvant in coagulation operations to reduce the turbidity of raw water. Two experimental designs were developed to evaluate the incidence of modified starch as the main coagulant, or in conjunction with a conventional coagulant ($Al_2(SO_4)_3$), at different ($Al_2(SO_4)_3$)/acetylated starch ratios, in jar-test experiments.

In the first experimental design, with the acetylated starch as the main coagulant, turbidity removal percentages reached 47.93% (average value, 41.18%). For the ($Al_2(SO_4)_3$)/acetylated starch coagulation process, 98.91% turbidity removal was reached in the second experimental design (average value, 97.16%). The impact of starch chemical substitution degree and the ($Al_2(SO_4)_3$)/acetylated starch ratio on the final turbidity obtained in the jar-tests was determined using ANOVA test. There was a great influence of the chemical substitution degree and the concentration of acetylated starch utilized, when modified starch was used as the main coagulant. For the second experimental design, the ($Al_2(SO_4)_3$)/acetylated starch ratio had a greater incidence on the turbidity removal. Thus, modified starch obtained from plantain peel waste is a promising coadjuvant material for water coagulation processes.

Keywords Plantain peel waste · Plantain starch · Acetylation · Water treatment · Turbidity removal · Coagulation

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1 Introduction

The contamination of water sources is a widespread problematic of international interest in agreement to the sustainable development goals (SDG). The targets proposed for SDG 14 "Life below water" aim to protect water ecosystems from pollution while SDG 6 "Clean water and sanitation" targets aim to protect and restore water ecosystems from untreated wastewater

disposal, and to attack the lack of drinking water problem suffered by about 30% population, due to water stress conditions and lack of treatment and distribution infrastructure (United Nations Development Programme, 2022). Thus, the efforts made for water treatment improvement are of great importance considering that water is one of the most essential substances for life, and it is necessary for both the economic and social development of populations and industries.

Coagulation and flocculation processes are necessary in various fields of human development for the removal or suspended organic or inorganic particles in colloidal forms in water. Coagulant reagents are used to destabilize the colloidal particles that will further add forming flocs and settling. Coagulation and flocculation practices have been applied since ancient times for turbidity reduction in the treatment of drinking water. For example, the Egyptians around 2000 BC used smeared almond fruits to cover their boats external surface as a way to clear the river water. It is also reported that around 77 AD the Romans used to apply aluminum compounds as coagulant for water clarification, while municipal water treatment plants have used aluminum coagulant compounds since the eighteenth century (Bratby, 2016).

Since the demand for innovative and environmentally friendly water treatment technologies is growing, there is currently certain interest in finding alternative and natural compounds, such as starch obtained from organic waste, as a substitute or a coadjuvant for chemical coagulants and flocculants in water treatment, not only for domestic water production, but also for the treatment of greater quantities of water, like industrial and public plants, and as a reagent for processes within the food and beverage industry, biotechnology, and medicine applications. Due to their biodegradability, natural polysaccharides have proved to be useful as coagulation and flocculation reagents, since they are considered to be environmentally friendly when compared to inorganic and organic synthetic coagulants (Bratskaya et al., 2004; Diaz et al., 1999).

Starch is one of the most important commercially available biopolymer sources, since it is used by plants as an energy reserve mechanism, and is abundantly found in plant seeds, roots, fruits, and many vegetable types (Hernández-Carmona et al., 2017; Lopez-Diago et al., 2018; Venegas et al., 2022a, 2022b). Starch is chemically composed of two main structures: Amylose, which is a straight-chain biopolymer with 99% 1–4-alpha bonds and 1% 1–6-alpha bonds, and amylopectin, which is a branched-chain biopolymer with 95% 1–4-alpha bonds and 5% 1–6-alpha bonds (Smith, 2001). Since starch is highly hydrophilic, has a low cost, and is biodegradable, it is considered a naturally renewable biomaterial, which plays an important role in the food industry and is also used as a raw material to prepare different commercial products such as plastics, cosmetics, textiles, paper, and pharmaceutical components (Hernández-Carmona et al., 2017; Masina et al., 2017; Montoya et al., 2015).

Due to its energy content in the form of carbohydrates, starch-based crops are used as a food basis for people in many countries. Therefore, most industrial starch applications are mainly limited by its need as a food source as well as its physical properties (Zia-ud-Din et al., 2017). In order to avoid using a food supply as an industrial raw material, it has been proposed to use agro-industrial waste as a starch source, thus contributing to the circular economy. An example of starch source are the unripe plantain peels (*Musa paradisiaca*) that contain a significant amount of it and are widely cultivated in Latin American and African countries (Amaya-Pinos, 2018; Chen et al., 2015; Hernández-Carmona et al., 2017; Lopez-Diago et al., 2018). However, the applications of native starch are limited by its solubility properties and its tendency to retrograde. One strategy that shows promising results is the chemical modification of native starch, in order to introduce new functional groups (Ferreira-Villadiego et al., 2018; Masina et al., 2017; Montoya et al., 2015).

In this research, the starch obtained from unripe plantain peels (*Musa paradisiaca*) waste was chemically modified using acetylation in order to evaluate its effectiveness as a coadjuvant in the coagulation and water clarification processes with the aim of reducing the use of synthetic chemical coagulants such as aluminum sulfate ($Al_2(SO_4)_3$).

2 Materials and Methods

2.1 Materials

The raw material selected for starch extraction was unripe plantain peels (*Musa paradisiaca*), obtained from the local food public market in Cartagena

(Colombia). The original sample contained 5-kg unripe plantain peels, which were processed immediately after peeling the fruits and separated in 150-g samples (Hernández-Carmona et al., 2017).

The reagents used to develop the starch chemical modification and water treatment experiments were sodium hypochlorite, hydrochloric acid, and ascorbic acid (AppliChem-Panreac®); sodium hydroxide (Merck®); aluminum sulfate; and acetic anhydride (J.T. Baker®).

2.2 Native Starch Extraction Method

The method used to extract the starch from unripe plantain peels with the best starch yield conditions was optimized and described in detail in a previous work (Hernández-Carmona et al., 2017), where it was evaluated how the extraction parameters, antioxidant concentration, and immersion time affect the starch production yield and purity. The procedure used was a dry extraction process that started with the crushing of the unripe plantain peel wastes in acidic solution (ascorbic acid, 5% w/v) with 5-min contact time, to promote the starch separation from the lignocellulosic fraction. The settled material was smashed to obtain a paste that was then washed and filtered before decanting the starch product. Finally, the starch was dehydrated at 40 °C during at least 10 h obtaining a dry starch powder.

2.3 Starch Chemical Modification

To chemically modify the starch, 40 g of native starch were weighed, adding 100-mL distilled water, and homogenizing the suspension with a magnetic stirrer platform in order to maintain a uniform suspension. The initial pH was adjusted to 8.0–8.5 adding a 3% NaOH solution, which acted as a catalyst. The acetic anhydride was slowly added (dropwise), simultaneously adjusting the pH between 8.0 and 8.5 until the required volume of acetic anhydride was added (volumes of 3.0 and 6.0 mL were used to obtain different degrees of substitution (DS)). Then the system was left to react for 10 min on the magnet stirring platform. Subsequently, the reaction was stopped by adding 0.5 N HCl solution, washing the starch 3 times with water and centrifuging the solution at 2500 rpm for 10 min. The last washing stage was performed with absolute alcohol, centrifuged at 2500 rpm for 10 min, and then dried in a tray oven at 40 °C for 12 h (Guerra-Dellavalle et al., 2009; Mason, 2009).

2.4 Physicochemical characterization

The native starch and the modified starch were analyzed to determine some of their main physicochemical properties including moisture and ash content, starch detection, purity degree, iodine test, Fourier transform infrared (FTIR) spectroscopy, gelatinization temperature, acetylation percentage (acetyl %), and degree of substitution (DS).

Moisture content in plantain peels and starch (native and acetylated) was determined with a MB 45 OHAUS moisture analyzer. Ashes content was measured by incineration at 550 °C during 3.5 h. Both moisture and ash content were expressed as percentage of the sample (AOAC, 2000).

The Lugol test was performed with Lugol iodine, also known as Lugol solution, which was used as a reagent for starch identification in routine laboratory. The Lugol solution was prepared with 5 g of I_2 and 10 g of KI diluted in 100-mL distilled water, giving a brown solution with total iodine concentration of 150 mg mL^{-1} (Lopez-Diago et al., 2018; Valls et al., 2012).

The purity degree of the native starch was identified using the following standards: AOAC 920.44, for starch determination in baking powders by means of acid hydrolysis (AOAC, 1920) method AOAC 906.03, for invert sugar determination in sugars and syrups by Munson–Walker general method (AOAC, 1923). The amylose/amylopectin ratio was then calculated using the colorimetric method described by Morrison and Laignelet (AOAC, 1923; Creed et al., 2002; Morrison & Laignelet, 1983; Prachayawarakorn et al., 2016).

Samples of native and acetylated starch were analyzed in a FTIR SHIMATZU 8400S spectrophotometer, using the KBr pellet method according to the ASTM-E168 and ASTM-E1252 standards, with the objective of obtaining information on the characteristic functional groups. Each spectrum was analyzed in the resolution range from 400 to 4000 cm^{-1} (Sodhi & Singh, 2003).

To determine the gelatinization temperature, 10 g of starch were dissolved in 100 mL of distilled water and the suspension was heated to 85 °C. Then, 50 mL of the suspension were taken and introduced into an

85 °C water bath. The starch mixture was constantly stirred until a paste was formed and the temperature was stable for a few seconds. Finally, the gelatinization temperature was read with a thermocouple (Grace, 1971).

The acetyl % and the DS for both native and acetylated starch were determined titrimetrically following methods described in literature (Rivas-González et al., 2009; Sodhi & Singh, 2005). Initially, 1.0-g sample was placed in a 250-mL flask with 50 mL of distilled water, and the suspension was stirred for 60 min at 25 °C. Phenolphthalein was added as an indicator, the solution was neutralized with NaOH 0.45 N until equilibrium was reached, and stirred for 30 min. Then the samples were titrated with HCl 0.2 N to the end point. A blank sample consisting of native starch was also used for comparison. The acetyl % was determined with Eq. (1).

$$\text{Acetyl \%} = \frac{\left[(\text{mL Blanc} - \text{mL Sample}) \cdot [\text{HCl}] \cdot 0.043 \cdot 100\right]}{\text{Sample weight (g)}} \quad (1)$$

Finally, the DS was defined as the average number of sites per glucose unit that possess a substituent group (Fennema, 2007) and calculated with Eq. (2).

$$\text{DS} = \frac{(162 \cdot \text{Acetyl \%})}{\left[4300 - (42 \cdot \text{Acetyl \%})\right]} \quad (2)$$

2.5 Coagulation-Flocculation Tests

To evaluate the coagulant behavior of the modified starch and the hybrid coagulation agent ($Al_2(SO_4)_3$ + acetylated starch), coagulation-flocculation tests were performed. The raw water samples for the evaluation were taken from Canal del Dique, a 118-km artificial water channel that connects Cartagena's Bay to the Magdalena River (Bolivar Department, northern Colombia), since Canal del Dique is the raw water used by ACUACAR S.A.E.S.P. (drinking water supply company in Cartagena, serving a population over 1 million inhabitants), and several smaller towns and population settlements located along its course.

The turbidity value for the raw water was measured with a VELP® TB1 model turbidimeter, using ASTM method D7315-07a, with an average value of 385.9 NTU. The turbidity removal efficiency of the acetylated starch and the hybrid coagulant agent was calculated with the difference between the initial and final turbidities as a percentage respect to the initial turbidity. The pH values were also measured for each experiment.

The flocculator used to perform the coagulation-flocculation experiments was a 6-jar apparatus from VELP® Scientifica (Fig. 1), following the procedure indicated in ASTM method D2035-13. Initially, 6 raw water samples of 1 L were put into the coagulation flasks and stirred at 200 rpm. Then, the acetylated starch or the hybrid coagulant was added to each flask, and the samples were stirred for 5 min at the same speed to ensure the coagulation process under rapid mixing conditions. After that, the samples were stirred at 45 rpm for the next 15 min to perform the flocculation or slow mixing. Finally, the samples were allowed to settle for 20 min. After sedimentation, the supernatant liquid was collected and analyzed for pH and turbidity. The effect of the acetylated starch was investigated using 100 mg L^{-1} and 350 mg L^{-1} doses and two different DS values (low and high), that correspond to the different acetyl % obtained. Also, the effect of the hybrid coagulant was investigated using a of the hybrid ($Al_2(SO_4)_3$)/acetylated starch coagulant at different ratios with two different DS. All experiments were performed at room temperature (25 ± 1 °C), and each experimental test

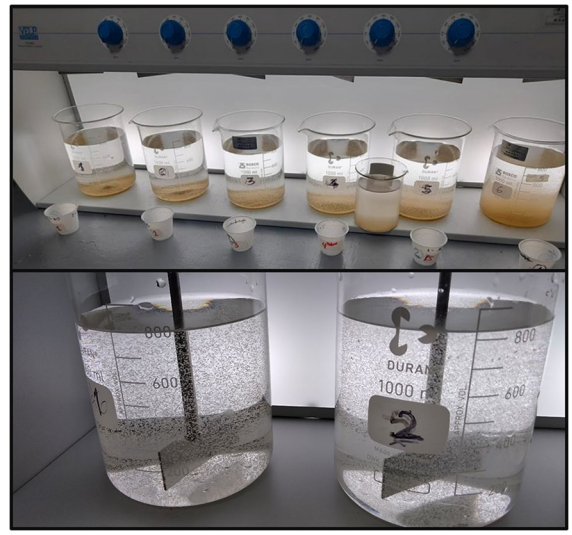

Fig. 1 Coagulation-flocculation 6-jar apparatus

Table 1 Experimental design test 1

Factor	Factor definition	Levels		Symbol
A	Acetylated starch dose	100 mg L^{-1}	Low	-
		350 mg L^{-1}	High	+
B	Degree of Subs. (DS)	0.361	Low	-
		0.562	High	+

was performed three times (Anastasakis et al., 2009; ASTM, 2018, 2019; Diaz et al., 1999).

Experimental design was applied in order to investigate the effects of acetylated starch dose, the DS, and $(Al_2(SO_4)_3)$/acetylated starch ratios. Two different experimental design tests, with two levels and two factors each (2×2), were proposed and 4 independent replications were taken at each of the 2×2 treatment combinations. The first experimental design test was applied to the experiments with acetylated starch as the main coagulant, while the second one was applied to the hybrid $(Al_2(SO_4)_3)$/acetylated starch coagulant. The details of the first and second experimental designs are presented in Table 1 and Table 2, respectively. The design size was $N=2\times2\times4=16$ and was carried out randomly. The response variable for the two designs was the turbidity removal percentage (Montgomery, 2017).

2.6 Statistical Analysis

A significance test for a mean was performed to prove the hypothesis for the means difference. In order to demonstrate whether there was a significant difference in the means of the response values (turbidity) of the experiment, they were divided into two groups characterized by the proportion of acetylated starch as a coadjuvant. Then a test of means difference (two-sample *t* test) was accomplished (Montgomery, 2003).

Table 2 Experimental design test 2

Factor	Factor definition	Levels		Symbol
C	Weight ratio: $(Al_2(SO_4)_3)$/acetylated starch	3:1	Low	-
		1:1	High	+
D	Degree of Subs. (DS)	0.361	Low	-
		0.562	High	+

Based on the data obtained, an analysis of variance (ANOVA) was performed to determine which factors have the greatest influence on the final turbidity degrees. The results were later analyzed with PAST v3.14® and STATGRAPHICS CENTURION XVI ® software for statistical evaluation. A two-way ANOVA test was performed, to evaluate whether the chemical acetylation, the DS, and $(Al_2(SO_4)_3)$/acetylated starch ratios affected the turbidity in raw water, and if there were any interactions between them (Hammer et al., 2001).

3 Results and Discussion

3.1 Native Starch Characterization

The organic unripe plantain peel waste used as a raw material for starch extraction had an average humidity of 86%. From the analysis of the extracted powder, the Lugol test resulted positive for starch, thus confirming the presence of the component in the extracted material. The purity test determined that the extracted dry starch had a purity of 66.87 ± 1.04%, and an ash content of 0.1127 ± 0.001%. The amylose/amylopectin ratio value for the starch extracted using this methodology was 23.62/76.28.

The chemical identification of native starch by FTIR-spectrophotometry can be found in a previous work by Ferreira-Villadiego et al. (2018), who used the same extraction methodology. The FTIR spectrum of native starch produced from the present study corresponded to the characteristic absorption peaks previously reported (Ferreira-Villadiego et al., 2018; Ismail et al., 2016; Mina et al., 2011). The absorption bands belonging to the acetylated sample were detailed in the Table 3. Some variations in the intensity of the peaks may differ from the standards due to the concentration of the polymers constituents (amylose and amylopectin).

The gelatinization temperature values for the native unripe plantain peel (*Musa paradisiaca*) starch used in this research, showed an average value of 72.6 °C, which was similar to the values previously reported for banana species (*Musa cavendischii*) with gelatinization values around 69 °C, which is the average gelatinization temperature in most native starches (Tribess et al., 2009). The unripe plantain peel starch obtained gelatinized in a close temperature range to

Table 3 Typical bands in native starch infrared spectroscopy

Wavenumbers (cm^{-1})	Bond type
3500	Stretching of OH groups
2929.97	Stretching of CH bonds
2150–1370	Modes of atmospheric CO_2 present at the time of analysis
1645	Modes of vibration of H_2O present in the sample (humidity)
1462	Bending CH from CH_3
1167	Stretching and deformation of the C–O–C bond of the molecule

other starches obtained from the Musaceae family, such as that of the Equatorian export banana (*Musa sapietum*) with a range between 77.7 and 80 °C.

3.2 Modified Starch Characterization

The starch chemical modification or acetylation was carried out by varying the volume of acetic anhydride (3.0 mL and 6.0 mL) to obtain different DS, obtaining acetylated starch as a result. From the analysis of the acetyl percentage, we obtained that the modified starches presented acetylation values of $8.77 \pm 0.12\%$ and $13.02 \pm 0.79\%$ (low and high), and the DS calculation results were 0.361 ± 0.013 and 0.562 ± 0.06 (low and high), respectively. The values of the acetylation percentages were in agreement with previous work (Vargas et al., 2016), for the modification of potato-based starch. Additionally, several authors reported values for acetylated starch based also on unripe plantain (*Musa paradisiaca*), regarding the fruit's pulp, which were also in accordance with this study (Rendón-Villalobos et al., 2010; Salcedo-Mendoza, 2016).

The analysis of the modified starch resulted in a gelatinization temperature for the acetylated starch samples with average 67 °C and 60 °C for the low and high DS samples, respectively. If compared to the native starch results, we observed a reduction in the gelatinization temperature when the starch underwent chemical modification, as reported in previous work, while both the native and the modified starch presented gelatinization temperatures in the typical range reported for the starch species (Sandoval et al., 2005).

Finally, the FTIR analysis for the acetylated starch (Fig. 2) confirmed the effectivity of the chemical modification since the bands in the spectrum are in the region between 1580 and 1800 cm^{-1} which is typical for starch that was modified by acetylation (Sánchez-Rivera et al., 2010). These signals correspond to the vibration modes associated to the acetyl groups added to the starch structure. When compared to the native starch FTIR, the main variation in the spectra was caused by the appearance of new bands at 1740 cm^{-1}, 1375 cm^{-1}, and 1240 cm^{-1} that are characteristic to the acetate group which is formed during the acetylation process (Colussi et al., 2014). The decrease in the 1605 cm^{-1} band in the modified starch can be attributed to the lower water affinity in comparison to that of the native sample. The reduction in water affinity due to the introduction of acetyl groups in the starch molecule gives them a hydrophobic characteristic, as has previously been reported (Luo & Shi, 2012).

3.3 Coagulation Test Results

The results of the jar test experiments for turbidity removal performed under the different conditions described in the two experimental designs are shown in Table 4 and Table 5 for the experimental design tests 1 and 2 respectively.

When the modified starch was used as the main coagulant reagent (Table 4), the turbidity removal average % increased from 34.2 to 37.5% with the coagulant dose applied, when the low DS starch sample was used. The effect on pH was the opposite with a reduction from 7.4 to 7.2 for the same situation. For the experiments conducted with the high DS starch samples, the turbidity removal % reached 46.5% average while the pH was reduced to 6.9 average, with no significant differences caused by the increase in the coagulant dose. These results indicate that the samples with high DS were more efficient for turbidity removal, with no significant effect caused by the coagulant dose applied. However, the turbidity removal efficiency reached with the modified starch as the main coagulant was not enough to consider it a promising coagulant in this situation, since the final turbidity reached was still too high for a water

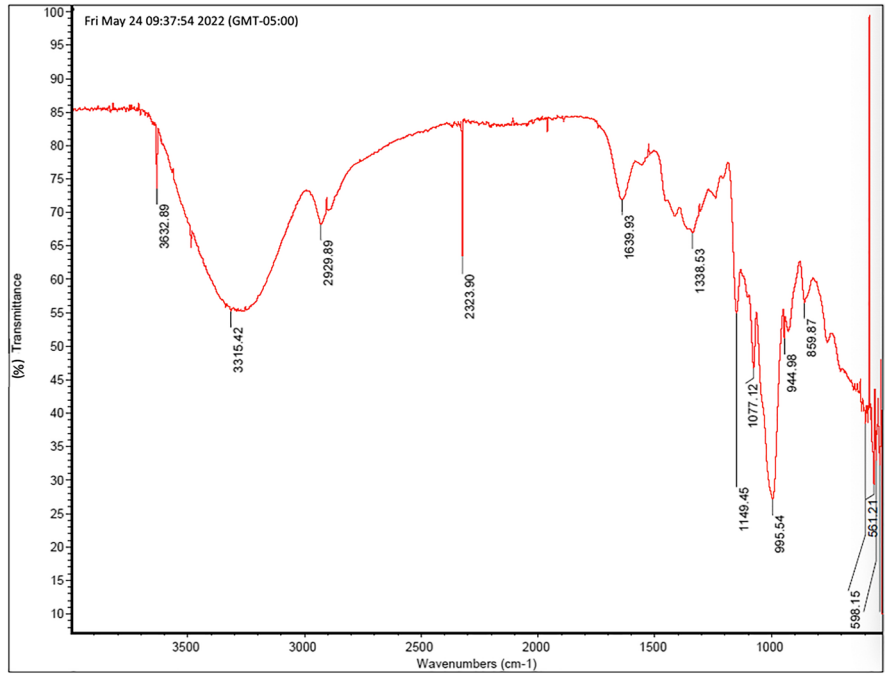

Fig. 2 FTIR spectra from acetylated plantain peel starch

coagulation process to be considered as successful (turbidity should be < 8 NTU if the water continues to a filtration stage as the final clarification step).

In the experiments performed with the hybrid coagulant ($Al_2(SO_4)_3$)/acetylated starch (Table 5), when the modified starch acted as a coadjuvant reagent, promising results were presented, adequate for an industrial process of coagulation, since the turbidity removal rate reached up to 98.91% with a final turbidity of 4.21 NTU, which is enough for water that will later undergo a filtration step. When the low and high DS samples were compared, there was no significant difference in the removal rate, although there was a slight pH reduction for the high DS case. On the other hand, the ($Al_2(SO_4)_3$/acetylated starch ratio showed to affect the removal rate, since there was a significant reduction in the final turbidity for the experiments that were low in starch content (3:1) ratio, when compared to the high starch content (1:1) ratio. These results indicate that the samples with the hybrid coagulant ($Al_2(SO_4)_3$)/acetylated starch were efficient for water treatment processes reaching adequate removal rates and final turbidity values, mainly

Table 4 Coagulation-flocculation test results for the experimental design test 1

Acetylated starch dose (mg L^{-1})	Low DS			High DS		
	pH	NTU	Turb. removal (%)	pH	NTU	Turb. removal (%)
100	7.47	249	35.49	6.87	201	47.93
100	7.34	260	32.64	7.01	208	46.11
100	7.36	259	32.90	7.03	203	47.41
100	7.41	248	35.75	6.97	210	45.60
350	7.22	241	37.56	6.76	206	46.63
350	7.25	242	37.31	6.87	208	46.11
350	7.26	240	37.82	6.93	207	46.37
350	7.21	242	37.31	6.90	209	45.85

Table 5 Coagulation-flocculation test results for the experimental design test 2

$(Al_2(SO_4)_3)$/ acetylated starch ratio	Low DS			High DS		
	pH	NTU	Turb. removal (%)	pH	NTU	Turb. removal (%)
3:1	7.47	6.66	98.27	6.87	4.92	98.73
3:1	7.34	6.33	98.36	7.01	4.21	98.91
3:1	7.36	5.80	98.50	7.03	5.15	98.67
3:1	7.41	5.91	98.47	6.97	5.30	98.63
1:1	7.22	16.07	95.84	6.76	15.79	95.91
1:1	7.25	17.02	95.59	6.87	16.02	95.85
1:1	7.26	18.21	95.28	6.93	16.10	95.83
1:1	7.21	16.34	95.77	6.90	15.80	95.91

for the lower starch ratio, with no significant changes due to the DS.

3.4 Statistical Analysis

Finally, to verify if there was a significant difference between the two groups of data derived from the experimental work, they were divided into two groups, experimental design 1 and experimental design 2, and subjected to two statistical tests. First, the *t* test was applied to determine if there was a difference between the means of the two groups of data, obtaining a p value < 0.05. The results were then subjected to the Kolmogorov–Smirnov test to determine if each set of data came from different distributions, obtaining a p value < 0.05. With these results, it could be stated with 95% certainty that the two groups of data reflected phenomena influenced by different factors.

The ANOVA test was performed to determine the statistical significance of each effect by comparing the means square against an estimate of the experimental error. In this way, we analyzed the significant parameters in the turbidity minimization process with the acetylated starch dose and the DS used in the coagulation experiments performed with the modified starch as the main coagulant (experimental design test 1). The results obtained from the ANOVA test are presented in Table 6 which shows that all factors (acetylated starch dose, DS value, and the combination of them) had high relevance (p value < 0.05) in the turbidity removal efficiency.

The estimated response variable as a function of each experimental factor in experimental design test 1 is presented in Fig. 3 where it is clear that the combination of the effects minimized the response variable to some extent; however, the DS values played the most influential and important role for this design. The first section of the graph showed the response variable (turbidity) when the acetylated starch dose went from a low level (100 mg L^{-1}) to a high level (350 mg L^{-1}), while the second showed its response for the DS value going from a low level (0.36) to a higher (0.56) one. The two factors gave negative slope lines which mean that the turbidity response improved if the factor remained at a high level, but,

Table 6 ANOVA test results for the experimental design test 1

Source	Sum of squares	DF	Mean square	*F* value	*p* value
A: acetylated starch	115.563	1	115.563	8.19	0.0187
B: DS	6765.06	1	6765.06	479.18	0.0000
A*B	217.563	1	217.563	15.41	0.0035
Block	55.6875	3	18.5625	1.31	0.3287
Residual	127.063	9	14.1181		
Total (corr.)	7280.94	15			

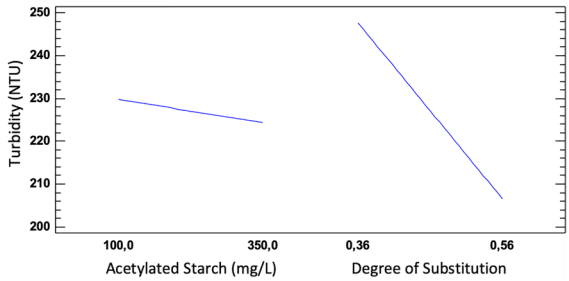

Fig. 3 Main effects for turbidity response (experimental design 1)

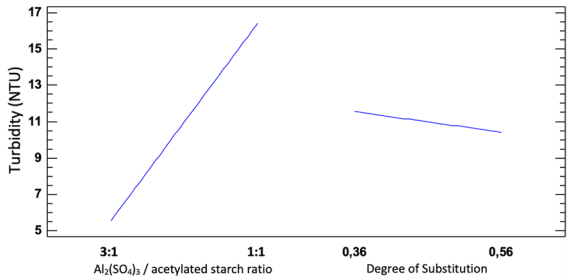

Fig. 4 Main effects for turbidity response (experimental design 2)

with a clear advantage, the DS value showed the highest effect.

Moreover, the results obtained from the ANOVA test in the experimental design test 2 are presented in Table 7 showing that both the $(Al_2(SO_4)_3)$/acetylated starch ratio and the DS value had a high relevance (p value < 0.05) in the turbidity removal efficiency, but there was no influence of the combination of both factors.

The estimated response variable as a function of each experimental factor in experimental design test 2 is presented in Fig. 4 where it is clear that the combination of the effects minimized the response variable; however, the DS values did not have a high influence on the $(Al_2(SO_4)_3)$/acetylated starch ratio. The first part of the graph shows the response variable (turbidity) when the starch content in the $(Al_2(SO_4)_3)$/acetylated starch coagulant went from a low starch ratio (3:1) to a high starch ratio (1:1), while the second part shows its response for the DS value going from low ratio (0.36) to high (0.56). The DS factors resulted on negative slope lines which mean that the turbidity response improves if the factor remains at a high level but, since the slope is low, the influence can be considered minimum. On the other hand, the $(Al_2(SO_4)_3)$/acetylated starch ratio presented a positive and high slope confirming that this factor has the most important influence in the turbidity results with the best removal efficiency when the starch content in the hybrid coagulant is low.

4 Conclusions

Unripe plantain peel (*Musa paradisiaca*) starch was extracted from the residual biomass confirming that the product obtained was rich in starch (66.87% purity) and presented a FTIR response that corresponds to the values previously reported. After modifying the starch by means of an acetylation reaction, the FTIR spectra confirmed the effect of the acetylation procedure due to the changes in the spectra and the analysis in the degrees of substitution.

The coagulation-flocculation experiments performed with the acetylated starch as the main coagulant under the conditions of the experimental design test 1 indicate that the highest turbidity removal rates were obtained from the starch with the highest degrees of substitution with no significant influence from the coagulant dose. However, the turbidity

Table 7 ANOVA test results for the experimental design test 2

Source	Sum of squares	DF	Mean square	F value	p value
C: $(Al_2(SO_4)_3)$/acetylated starch ratio	473.824	1	473.824	1269.70	0.0000
D: DS	5.11891	1	5.11891	13.72	0.0049
C*D	0.0885063	1	0.0885063	0.24	0.6379
Block	0.616469	3	0.20549	0.55	0.6603
Residual	3.35861	9	0.373178		
Total (corr.)	483.007	15			

removal efficiency reached for these experiments was low for a coagulation-flocculation process to be considered successful for a water treatment plant, since the minimum turbidity value reached was 201 NTU, which is far from the recommended 8 NTU required for a plant with filtration stage as the final clarification step. On the other hand, the experiments conducted using the modified starch in a hybrid coagulant with ($Al_2(SO_4)_3$), that correspond to the experimental design test 2, confirm that the modified starch is a promising coadjuvant reagent for the coagulation-flocculation water treatment, since the turbidity removal was considerably higher, reaching final turbidity values as low as 4.21 NTU.

The statistical analysis helped to identify the dependence of the turbidity response with the coagulant dose, the degrees of substitution obtained from the starch modification and the starch ratio in the hybrid coagulant. All the factors presented an impact on the turbidity removal rate; however, there were some differences in their intensity. When the modified starch was used as the main coagulant, the most important factor was the degree of substitution, meaning that the chemical modification process had a significant effect on the behavior of the coagulant, resulting in higher efficiency for the higher acetylation effect. On the other hand, when the modified starch acted as a coadjuvant in a ($Al_2(SO4)_3$)/acetylated starch hybrid coagulant, the turbidity responses were not dependent on the degrees of substitution, but were mainly affected by the modified starch proportion in the hybrid coagulant.

Finally, it was concluded that the best experimental conditions for the use of unripe plantain peel (*Musa paradisiaca*) modified starch as a reagent for coagulation-flocculation processes were found for a hybrid ($Al_2(SO4)_3$)/acetylated starch coagulant reagent with high degrees of substitution levels, reaching a turbidity removal efficiency adequate for water treatment plants.

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Author Contribution All authors contributed to the study conception and design. Mr. Cortés-Pérez and Mr. Pérez-Montalvo performed the experiments. Mr. Puello-Silva provided technical support, participated in the design and interpretation of the data, supervised the research, and revised the manuscript. Dr. Pasqualino provided technical support, participated in the design and interpretation of the data, wrote the paper, and participated in the revisions of it. Mr. Lambis-Miranda conceived this research, designed and performed the experiments, participated in the design and interpretation of the data, supervised the research, wrote the paper, and participated in the revisions of it. All authors read and approved the final manuscript.

Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Statement of Novelty The food industry worldwide produces a large amount of waste from agro-industrial raw materials. This work presents a route for the reuse of agroindustrial waste (*Musa paradisiaca*) to generate a boost to the circular economy. Their chemical modification for use as coadjuvant agents in water treatment is a novel alternative to progressively reduce conventional coagulating agents' use.

Ethical Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication Not applicable.

Conflict of Interest The authors declare no competing interests.

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