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Statistical models to predict color and turbidity after the treatment of raw water with acetylated starch

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Abstract: Statistical models could help to estimate future behavior of a system based on observational data. A statistical analysis was carried out to develop statistical models capable of predicting color and turbidity data after coagulation-flocculation treatment of raw water with acetylated starch obtained from the species topochopelipita plantain clone (*Musa* ABB). For this, the coagulant capacity of low (LAS) and high acetylated starch (HAS)to remove color and turbidity has been evaluated at concentration of 0 mg/L, 50 mg/L, 100 mg/L, 150 mg/L and 200 mg/L. The data were analyzed through STATGRAPHICS Centurion Version 16.1.03 and models which describe regression of color and turbidity values with respect to acetylated starch and its concentration were obtained. It was observed that the higher percentages of acetylating and starch concentrations, the lower the color and turbidity parameters, presenting an increase of these variables in very high concentrations, which was due to a saturation of the system.
Keywords : acetylation, coagulation-flocculation, *Musa* ABB, statistical model.

1. Introduction

The so-called potable water must be aesthetically acceptable, i. e. free of perceptible turbidity, color and taste. Raw water is rarely of satisfactory quality for human consumption use and almost always have to be treated[1]. The processing of raw water involves a physicochemical treatment, known as coagulation-flocculation (CF), and its application includes the removal of dissolved chemical species and water turbidity by the addition of conventional chemical coagulants. Furthermore, CF is a fundamental step in the water treatment process, not only because it removes the particles responsible for the turbidity produced by suspended particles and colloidal material, but also because it removes the particles responsible for the turbidity produced by the suspended particles and colloidal material[2].However, there are disadvantages associated with the use of these coagulants, such as high acquisition costs and production of large volumes of sludge [3]. In addition, there are evidences linking coagulants, based on aluminum, to the development of Alzheimer's disease in humans, due to the presence of residual aluminum in treated water [4]. These situations demonstrate the need to implement new, low cost, innocuous and environmentally friendly coagulant materials for water treatment and purification[2].

Nowadays, CF processes points to the use of natural polymers as coagulants due to their low cost and ecological performance[5]. Furthermore, scientists have been able to say that by using natural materials, the import of chemical coagulants could be reduced or even eliminated [4]. Regarding that, there is an increasing interest to find biodegradable materials based on natural polysaccharides such starch for water treatment[5]. In this way, chemical modification, such as acetylation, arises as an excellent alternative to improve its properties as a coagulant [6].

Currently, in the southern area of the department of Bolívar (Colombia), there are some small river villages that maintain the tradition of purifying raw water with natural materials such as native plantain starch obtained from the species topochopelipita plantain clone (*Musa* ABB). Sometimes, this alternative becomes the only way to obtain safe drinking water for these rural communities, as they are located in hard-to-reach areas [4].

On the other hand, statistical models can be used to characterize observational data to help one to concisely describe the measurements and to help in the development of conceptual models of a system or process; which could help to estimate probabilistic future behavior of a system based on past statistical information[7].Therefore, a statistical analysis was carried out to develop statistical models capable of predicting color and turbidity data after coagulation-flocculation treatment of raw water with acetylated starch obtained from the species topochopelipita plantain clone (*Musa* ABB).

2. Experimental

2.1 Materials

Raw material for starch preparation was obtained from the topochopelipita plantain clone (*Musa* ABB), which was cultivated in the south area of the Department of Bolivar (Colombia). Acetic anhydride (w_B= 98 %), sodium hydroxide (NaOH), hydrochloric acid (HCl)and potassium hydroxide (KOH)were used to prepare acetylated starch. Chemical reagents were purchased from PanreacAppliChem and used as received. Water samples were collected in glass bottles from Canal del Dique in Puerto Badel, Arjona – Bolivar (Colombia).

2.2 Extraction of native starch from plantain

Native starch (NS) was isolated by using the method used by Tirado *et al*.,[4]. For this, 5kg of topochopelipita plantain clone (*Musa* ABB) were weighted, washed, peeled, and chopped into small cylindrical portions with height of about2 cm and diameter of approximately 1.5 cm. These portions were added to 30 L of water at 40ºC for 5min. They were subsequently submitted to a grinding process using an impact resistant blender until a complete disintegration of the material was achieved. The samples were then washed three times with water. A No. 100 mesh was used to eliminate fibbers. This filtered material was stored in a recipient where it settled for 3 h. The supernatant was separated by decantation, while the sediment was kept under refrigeration at nighttime. The same procedure was executed the next day with an additional removal of supernatant. Afterwards, the final sediment was centrifuged at 8011g-force for 15 min to separate water from the pulp. This material was dried in an oven at 40°C for 24 h, pulverized into 5g portions and finally stored in plastic recipients made of polyethylene terephthalate (PET).

2.3 Physicochemical analysis and starch yield extraction

Chemical composition of pelipita plantain pulp was assessed by A.O.A.C. methodology [8]. Furthermore, starch yield extraction was determined.

2.4 Acetylation of starch

Chemical modification through acetylation of starch was performed by following the method described by Tirado *et al*.,[4]. For this, 40g of NS were mixed with100 mL of distilled water and stirred at 250 rpm until obtain a uniform suspension. Then, this mixture wascooledat15 °C, and pH was adjusted at8.5 by using NaOH drops at a concentration of 3 kg $NaOHL^{-1}$water. To obtain a suitable chemical modification, acetic anhydride was added slowly (drop by drop) while keeping a constant value of pH at 8.5. The different levels of acetylation were achieved by adding 5 mL of acetic anhydride for the low acetylated starch (LAS) and 15 mL of acetic anhydride for the high acetylated starch (HAS). Acetylation reaction was carried out for 5 h under constant agitation at 200 rpm and room temperature. Afterwards, the excess of alkali was neutralized with the addition of HCl [0.5 N] up to obtain an acid media ofpH 3.0. The acetylated starches were washed three times with distilled water and once with ethanol using a centrifugeat693 g-force for 10 min. Finally, acetylated starches were dried out in a tray furnace at 40°C for 12 h and stored in Ziploc bags.

To determine the acetylation percentage obtained after the chemical treatment, 1g of acetylated starch (dry basis) was weighted in a 250mL Erlenmeyer flask and 50mL of ethanol at a volume fraction of 75% were added to the recipient. The Erlenmeyer was then covered and submitted to agitation for 30 min. 40mL of KOH [0.5N] was subsequently added to the mixture, with additional agitation for 72 h. The saponified samples were titrated with HCl [0.5N] using phenolphthalein as indicator. After this initial titration, the mixture was left to rest for 2 h, and then the additional alkali that leached with the sample was titrated as well. The same procedure was performed for the NS to obtain the reference value. Percentage of acetyl groups was calculated according to Equation (1), where 0.043 corresponds to the milli-equivalents of the acetyl group.

$$Acetylation\ (\%) = \frac{(mL\ reference - mL\ sample)\ \times\ [HCl, N] \times\ 0.043 \times 100}{Grams\ of\ the\ sample\ (Dry\ basis)} \qquad (1)$$

2.5 Experimental design and statistical analysis

A multilevel general factorial experimental design was used. Modified starch and concentration were the two factors selected for this study. Two levels were chosen for the first factor: low (LAS) and high acetylated starch (HAS). On the other hand, five levels were selected for concentration of coagulant: 0 mg/L, 50 mg/L, 100 mg/L, 150 mg/L and 200 mg/L. Experimental tests were carried out by triplicate for a total of 30experimental runs. The experimental matrix design could be seen in Table 1.

Table 1.Experimental matrix design

Run	Acetylated starch	Concentration mg/L
1	LAS	50
2	HAS	100
3	LAS	200
4	LAS	150
5	LAS	0
6	HAS	0
7	HAS	200
8	HAS	150
9	LAS	100
10	HAS	50
11	LAS	150
12	LAS	200
13	LAS	100
14	LAS	0
15	HAS	150
16	HAS	0
17	LAS	50
18	HAS	50
19	HAS	200
20	HAS	100
21	HAS	100
22	HAS	150
23	LAS	100
24	LAS	200
25	HAS	50
26	HAS	0
27	LAS	50
28	LAS	0
29	HAS	200
30	LAS	150

LAS: low acetylated starch; HAS: high acetylated starch.

The statistical analysis was developed by STATGRAPHICS Centurion Version 16.1.03 with analysis of variance and correlation between variables within a significance level of $p<0.05$. Color(Pt-Co) and turbidity (NTU) were set as response variables, since those are the main parameters that define water quality[5]. Color and turbidity measurements were performed by using aElich colorimeter AQUATESTER and a Merck Turbiquant® 1100 turbidimeter, respectively. The experimental error was deduced from selected tests that were repeated six times. The maximum standard deviation was 0.55 % and 1.26 % for color and turbidity, respectively.

2.6 Evaluation of the coagulant capacity of modified starches

In order to obtain color and turbidity data, the coagulation capacity of the chemically modified starches was evaluated according to the procedure described by Tirado *et al.*,[4]. For this purpose, the CF process was carried out using a jar test equipment. This device consisted of five beakers with a volume capacity of 1L, which were filled with the untreated water. The evaluated coagulant was then added to the beakers at concentrations of 0 mg/L, 50 mg/L, 100 mg/L, 150 mg/L or 200mg/L. Afterwards, two agitation stages were performed. The first one was at 200rpm (15 s) and the second one at 25 rpm (25 min). Both of them in order to promote floccule formation[4]. Finally, all mixtures were left to rest for 30 min.

2.7 Statistical models

A statistical analysis was carried out to develop statistical models capable of predicting color and turbidity data according to the acetylated starch and its concentration. The statistical model of the complete experimental design with two factors (α, β) and their interaction is shown in Equation (2):

$$Y_{ijk} = \alpha_i + \beta_j + (\alpha\beta)_{ij} + \varepsilon_{ijk} \quad (2)$$

Where Y_{ijk} was the response of the experimental design; α_i was the i-th level effect of the factor A (acetylated starch); β_j was the j-th level effect of the factor B (starch concentration, mg/L); $(\alpha\beta)_{ij}$ was the interaction effect between factors (A*B) and ε_{ijk} was a component of the random experimental error. Taking into account that the factor Acetylated starch was a categorical variable, it was numerically related to its acetylation percentage. Thus, the numerical coding was 18.35 and 23.74 for LAS and HAS respectively.

3. Results and Discussion

3.1 Chemical composition

Table 2 shows the average values of the chemical composition obtained by A.O.A.C. methodology [8]of the plantain pulp. Similar results were reported by Granados *et al.*,[9] with the same banana variety. Comparing the compositional results of this study with those obtained by other authors in plantain hartón[10], [11], pelipita presents lower moisture content and higher ash content, which was there as on why the plantain of this study presented higher hardness (Bugaud *et al.*, 2013; Granados *et al.*, 2014). In Table 2, the sum of amylose and amylopectin corresponds to 100% of the starch.

Table 2.Chemical composition of pelipita plantain pulp

Component	**Composition %**
Moisture	53.54 ± 1.23
Ash	1.83 ± 0.05
Starch	26.64 ± 0.65
Amylose	16.76 ± 0.06
Amylopectin	83.33 ± 0.97

Table 3.Average extraction yield

Material	Weight kg	Composition %
Raw material (plantain)	5.00	100.00
Peel	2.14	42.80
Wet pulp	2.86	57.20
Initial pulp moisture content	1.58	55.48
Starch in wet pulp	0.76	26.64
Recovered starch	0.66	87.15

3.2 Starch yield extraction

From an initial weight of 5 kg of the plantain sample selected for this study, 42.80 % corresponded to peel and 57.20 % to wet pulp, from which 664 g of dry starch was obtained, representing 87.15 % of the total starch(See Table 3). The extraction yields of this study (87.15%) was higher than those reported by other authors in the extraction of plantain starch [12], [13]. This indicated good extraction efficiency through the procedure used in this work. This could be explained by the method of milling and drying used, variety or the degree of ripeness, since starch was the main component of green plantain and undergoes important changes during ripening.

3.3 Percentage of acetyl groups of acetylated starch

Percentage of substitution achieved after chemical modification of the starch are reported in Table 4. There, a significant increase could be seen as a function of the volume of acetic anhydride used for modification. LAS and HAS presented significant differences ($p<0.05$) regarding content of acetyl groups (Table 4). The difference found between LAS and HAS was caused by the volume of acetic anhydride that was added during the modification process, which led to a higher number of acetyl groups to be introduced into the starch molecule.

Table 4. Percentage of acetylation and degree of substitution

Starch sample	Acetylation %
LAS	18.35±0.87
HAS	23.74±0.92

LAS: low acetylated starch, HAS: high acetylated starch.

Rendón-Villalobos *et al.*, [14] reported the acetylation of *Musa paradisiaca* L. In that work, authors achieved acetylation percentages of 12.90 % and 21.93 % at low and high levels of acetylation, respectively. In a different study using the same plantain species, Rivas-González *et al.*,[15] reported a maximum acetylation percentage of 22.58 %, lower than in this study, showing the versatility of the implemented method in this work. Even though all the compared results were below those obtained in the current research, it must always be taken into consideration that the acetylation percentage depends on the vegetal source and granular structure of the NS [4], [6], [16].

3.4 Color and turbidity assessment

Analysis of variance evidenced that concentration was the only factor with statistically significant effects on the response variables (color and turbidity data) at a confidence level of 95%. After this evaluation, it was determined by using the Platinum-Cobalt (Pt-Co) method that water with the lower coloration was the one treated with LAS. Regarding that, Table 5 shows color and turbidity values obtained for the analyzed samples.

By Table 5, it could be observed the great coagulant power of LAS and HAS, almost compared to those obtained by a conventional treatment such as by using aluminium sulphate [4].However, LAS had the lowest values, for both color and turbidity, between the two modified starches. It was possible that HAS had a more electronegative surface than LAS, as more acetyl groups were incorporated in its structure [16]. These

electronegative groups could repeal molecules with negative charge, such as organic acids that are present in naturally colored waters such as has been reported by Tirado *et al.*,[4].

Table 5. Color and turbidity data obtained

Coagulant	Concentration mg/L	Color Co-Pt	Turbidity NTU
LAS	0	493	172.67
	50	55	11.82
	100	50	9.53
	150	40	8.74
	200	35	7.52
HAS	0	493	170.33
	50	65	16.21
	100	65	12.32
	150	60	9.97
	200	55	8.51

LAS: low acetylated starch, HAS: high acetylated starch.

High concentrations of starch could hinder the effectiveness of flocculation. This could be due to the fact that starch covers completely the surface of the particles, which prevents the creation of bridges between them [4].However, these results present a e economical and environmentally friendly alternative.

3.5 Statistical model

The model obtained was a second-order polynomial as shown in the adjusted Equation (3).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \qquad (3)$$

Replacing terms in Equation (3), the models which describe regression of color and turbidity values with respect to acetylated starch and concentration factors was obtained. In Equation (3), X_i, and X_i are the factors acetylated starch and concentration of starch respectively. Equations (4) and (5) are the ones that have been adjusted to the color and turbidity data respectively, where the values of the variables are specified in their original units.

$Color = (431.87) + (0.60\ x\ \text{Acetylated starch}) - (7.09\ \text{x Concentration}) + (0.02\ x\ \text{Acetylated starch x Concentration}) + (0{,}02\ \text{x Concentration}^2)$	(4)
$\text{Turbidity} = (15097.70) + (14.35\ \text{x Acetylated starch}) - (248.51\ \text{x Concentration}) + (0.14\ \text{x Acetylated starch x Concentration}) + (0.90\ \text{x Concentration}^2)$	(5)

Figures 1 and 2 represent color and turbidity variations respectively, as function of acetylated starch and concentration of starch obtained by the adjusted regression model of Equations (4) and (5). It wasobserved that the higher percentages of acetylation and starch concentrations, the lower the color and turbidity parameters, presenting an increase of these variables in very high concentrations, which was due to a saturation of the system [17].

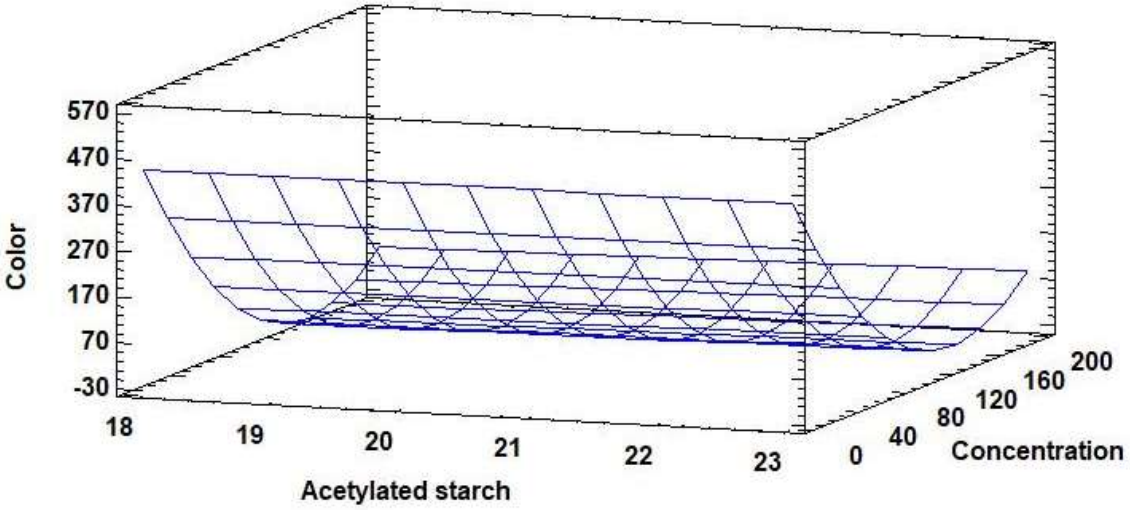

Figure 1.Color as function of type and starch concentration

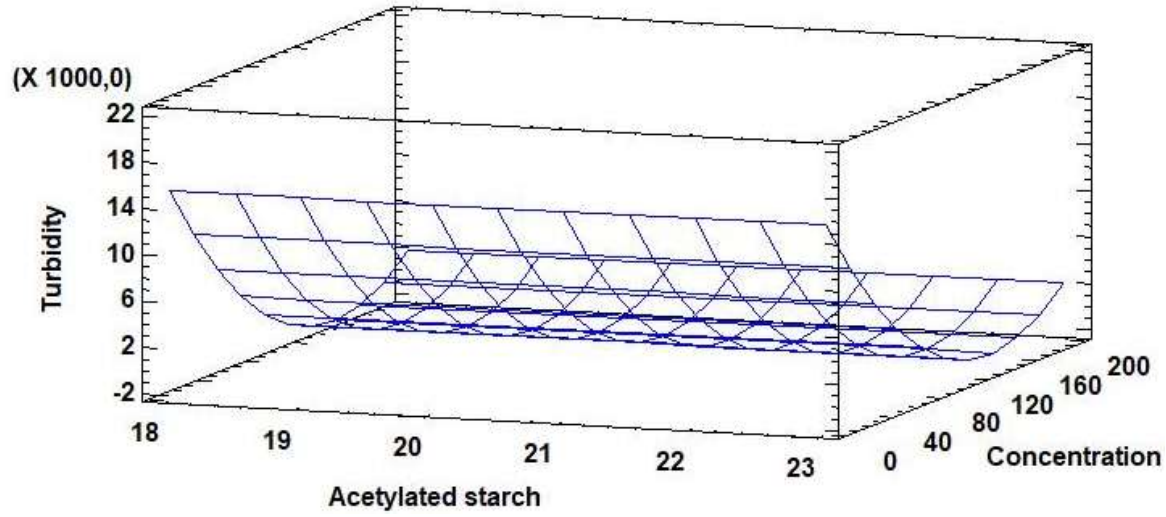

Figure 2.Turbidity as function of type and starch concentration

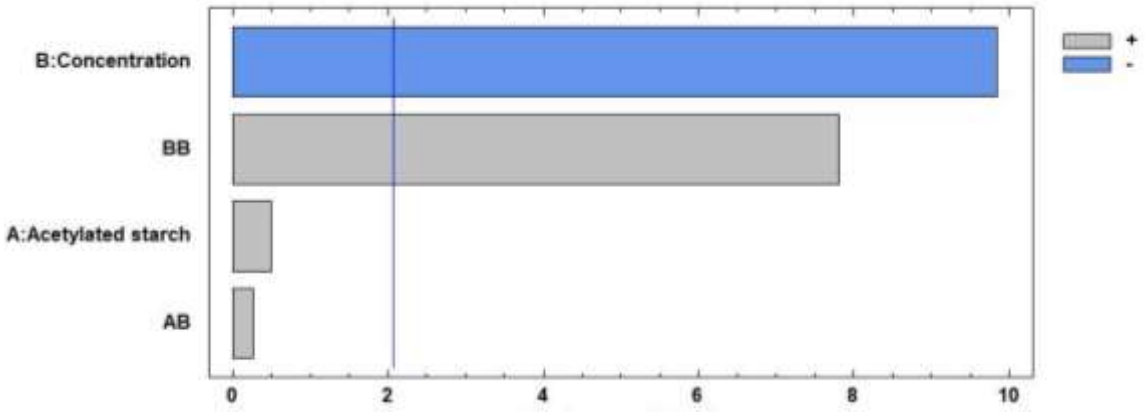

Figure 3.Pareto diagram for standardized color effects

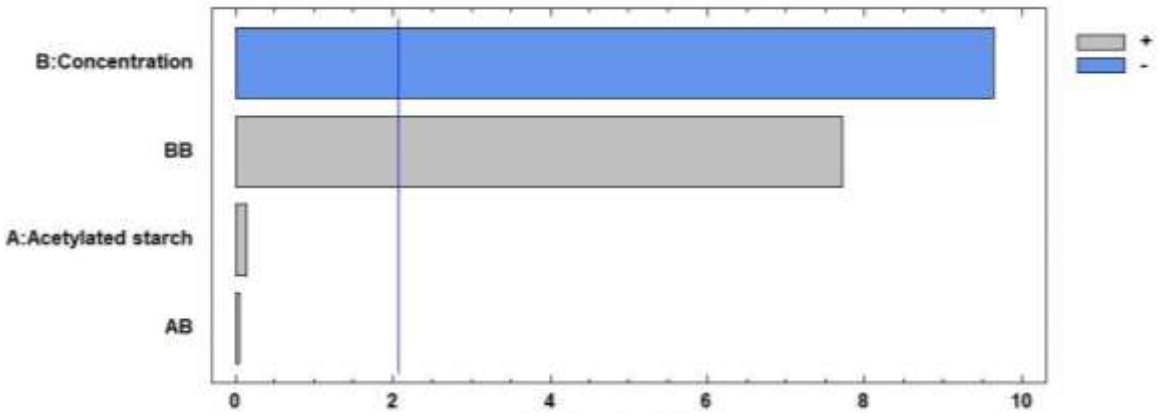

Figure 4.Pareto diagram for standardized effects for turbidity

In Equations (4) and (5) the low values of the coefficients accompanying the interaction Acetylated starch*Concentration in color and turbidity equations can be observed, which could be an indication of the lack of interactions effect. Pareto diagrams are shown in Figures 3 and 4, which verify the lack of interactions effect Acetylated starch*Concentration.

4. Conclusions

The possibility of obtaining starch from the topochopelipita plantain clone (*Musa* ABB) was reported, obtaining 87 % yield extraction from an easy and inexpensive route. On the other hand, modified starch obtained with a low degree of acetylation was able to reach percentages of color and turbidity removal comparable to those obtained by conventional methods, which are more expensive and harmful to the environment. Statistical models capable of predicting color and turbidity values according to the acetylated starch and its concentration in coagulation-flocculation systems could be developed successfully.

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