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Polyelectrolyte Biopolymer Based on Modified Barley Straw Cellulose: Synthesis and Potentiometric Properties

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Abstract

This study is based on the concept of sustainable development, focusing on the valorization of plant waste as a renewable resource for cellulose extraction. The extracted cellulose can be used for biomaterial production and in wastewater and soil salinity treatment.

The objective of this work is to synthesize a polyelectrolyte biopolymer by enhancing the hydrophilic character of extracted cellulose (EC) from barley straw. This is achieved by introducing carboxylate groups through the grafting of citric acid (CA). The macromolecular mass of the extracted cellulose was determined by viscometry. Esterification of EC with citric acid results in the formation of cellulose citrates (MBSC), which incorporate a significant number of hydrophilic carboxyl groups. The synthesized copolymers were characterized using thermogravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), viscometry, and potentiometry. Results indicate that MBSC structures vary depending on the extraction method, temperature, treatment duration, and degree of substitution (DS). The influence of esterification temperature and reaction time on DS was also studied, with the highest DS value of 0.36 observed after 20 minutes of treatment at 160 °C.

Keywords: Cellulose, Esterification, Citric Acid, Polyelectrolyte, Copolymer, Degree of Substitution.

1. Introduction

Cellulose is the most abundant renewable polymer on Earth, with an estimated annual production of approximately 100 billion dry tons. It constitutes nearly 50% of terrestrial biomass and is the primary structural component of plant and wood cell walls [1,2]. Additionally, cellulose is present in the cell walls of certain algae [3] and can be biosynthesized by bacteria [4]. This vast vegetal biomass represents a crucial renewable resource, already utilized across multiple industries, with emerging applications in bioenergy production such as bioethanol synthesis [5,6] or in the development of novel materials, including biodegradable plastic films [7] and conductive polymers [8,9].

Many industrial applications require cellulose extraction through chemical or mechanical processes, depending on the intended use. Additionally, various chemical treatments involve cellulose dissolution followed by regeneration [10, 11] to enhance its reactivity [12]. Native cellulose is a homopolymer composed of β-[1,4]D-glucose units [13, 14]. Despite its seemingly simple chemical structure, its high degree of organization results in complex chains with exceptional thermal and mechanical stability. To enable its transformation into functional biopolymers, specific chemical and/or mechanical treatments are required to modify cellulose fibers [15, 16].

The present study aims to develop a polyelectrolyte biopolymer by valorizing agricultural waste and modifying cellulose-based polyesters. The synthesized copolymers are envisioned for potential applications in industrial wastewater treatment and the mitigation of soil salinity in agricultural settings. A key objective of this research is to refine and optimize the hydrophilic and hydrophobic properties of these biopolymers to enhance their functional performance.

The field of modified polysaccharides is rapidly expanding, demonstrating the potential of these materials to meet the evolving demands of various industries [17], including environmental science[18], medicine, agriculture, pharmaceuticals, and biotechnology [19, 20]. A significant number of polyelectrolytes are obtained through the chemical modification of polysaccharides such as cellulose or starch [21, 22].

In this context, the present work focuses on extracting cellulose from barley straw, followed by its purification and chemical modification using citric acid. It has been established that treating agricultural materials with polyfunctional acids at elevated temperatures enhances their physicochemical properties [23]. A detailed investigation of several physicochemical parameters was conducted using potentiometric analysis to improve esterification efficiency and determine the degree of substitution (DS) of citric acid onto the extracted cellulose [24].

2. Materials and methods

2.1. Extraction process of cellulose from barley straw

Barley straw was collected from a local farm. The damaged portions were removed before cutting the biomaterial into 1 cm segments, which were then washed with water to eliminate soil and dust. The cleaned segments were dried in an oven, ground, and sieved. The sieved straw was defatted using a 500 mL mixture of toluene and ethanol (38:62 v/v) for 20 g of substrate under reflux conditions for 1 hour. The mixture was then filtered and treated with 500 mL of boiling water for 2 hours, followed by successive treatments with increasing concentrations of sodium hydroxide solutions. The resulting product was filtered, washed with 20% acetic acid, and subsequently treated multiple times with a 4% hydrogen peroxide solution. Finally, the sample was washed with distilled water and dried to a constant weight [25].

2.2. Modification of Extracted Cellulose via Esterification with Citric Acid

Esterification of the extracted cellulose was carried out using citric acid as the esterifying agent. A mixture of 5 g of cellulose, 5 g of citric acid, and 50 mL of distilled water was placed in a flask and refluxed at 120°C under continuous stirring for four hours. The residual water was then evaporated, and the resulting product was dried at 70°C until a constant weight was achieved. The obtained cellulose citrate was purified by washing with cold distilled water and subsequently dried under vacuum.

To investigate the influence of esterification parameters, the thermochemical reaction between citric acid and barley straw was conducted at different temperatures, ranging from 120°C to 180°C, for durations of 5 to 20 minutes. The esterified products were then purified by washing with cold distilled water and dried under vacuum. Since the optimal esterification time for cellulose was determined to be 20 minutes, spectroscopic characterization was performed exclusively on the MBSC product at different temperatures (MBSCX20).

2.3. Preparation of Viscosimetric Solutions

For viscosimetric analysis, 0.1 g of each modified cellulose sample was dissolved in a bi-distilled water/NaOH mixture (V/V = 14/35) in a graduated flask. The solution was stirred magnetically at 25°C for 24 hours to ensure complete dissolution. Various concentrations were prepared by diluting the stock solution, and the final solution was filtered through standard filter paper.

2.4. Sample Preparation for Potentiometric Determination

Solutions of cellulose citrate were prepared in bi-distilled water and stirred magnetically for 24 hours. These solutions were then titrated with NaOH at 25°C to determine their potentiometric properties.

3. Results and discussion

3.1. Characterization of Extracted Cellulose

The extracted cellulose (EC) was characterized using Fourier Transform Infrared (FTIR) spectroscopy, viscosimetry, and thermogravimetric analysis, as detailed below.

3.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were recorded using a Cary 600 FTIR spectrophotometer at the Laboratory of Application of Electrolytes and Polyelectrolytes Organics (LAEPO) at the University of Tlemcen, Algeria. The IR spectrum of EC is shown in Figure 1**.**

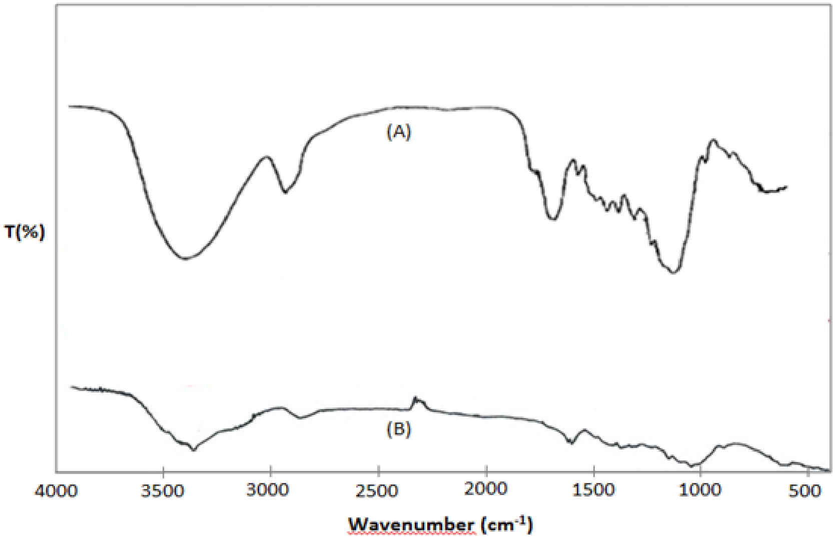


Figure 1: IR spectrum of cellulose extracted from rice straw (A) [26] and cellulose extracted from barley straw (B).

A comparison of the infrared spectra of cellulose extracted from rice straw via an acid route (A) [26] and our extracted cellulose from barley straw (B) (EC) reveals a strong similarity. Several characteristic absorption bands of cellulose were identified:

- [897.68–898.90 cm^{-1}]**:** Assigned to β-glycosidic bonds between glucose units and the anomeric C1-H bond.
- [1109.12–1210.81 cm^{-1}]**:** Corresponding to intermolecular hydrogen bonding of cellulose (OH).
- [1319.17–1320.01 cm^{-1}]**:** Attributed to CH_2 deformation in the polysaccharide backbone.
- [1505.40–1505.73 cm^{-1}]**:** Associated with the C-C bonds in the polysaccharide structure.
- [2901.54–2904.31 cm^{-1}]**:** Due to CH and CH_2 stretching vibrations.

Both fibers (A) and (B) exhibit characteristic cellulose signals, including a broad absorption band at 3414.24 cm^{-1}**,** confirming the presence of hydroxyl (OH) groups. These spectral features align with those reported by Pereira et *al*. [27]**.** Additionally, the presence of residual moisture in the extracted cellulose was confirmed by the appearance of vibrational bands between 1617.46 and 1638.09 cm^{-1}**,** characteristic of hydrogen-bonded water.

3.1.2. Determination of Extracted Cellulose (EC) Mass by Viscometry

Viscometric measurements were performed using an Ubbelhode-type capillary viscometer with controlled flow. Temperature was maintained using a thermostatically regulated bath.

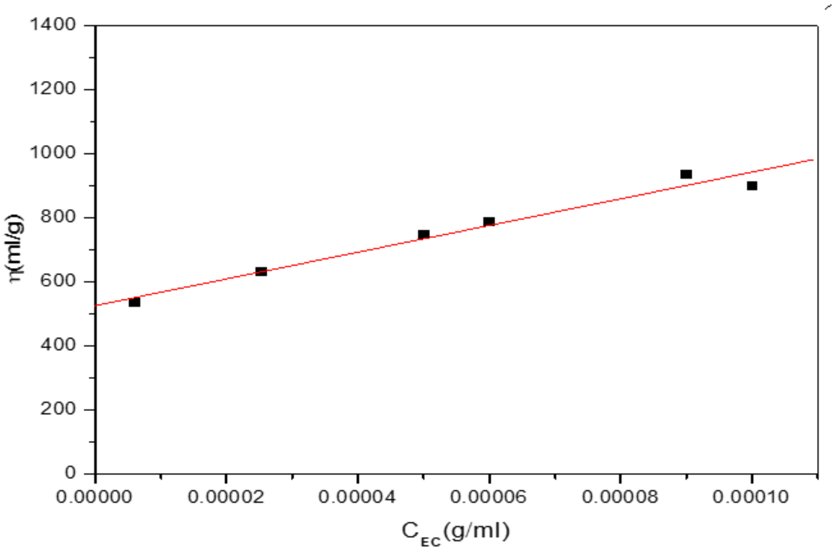


Figure 2 - Variation of the reduced viscosity of EC as a function of its concentration at 25°C.

Figure 2 illustrates the variation of reduced viscosity of EC as a function of concentration. The intrinsic viscosity [η] and the viscometric molecular mass (M̄_V) of EC were determined using the method described in described in the works of Shen et *al.* [28**]** (K (× 102) = 0.43 (mL/g) and a= 1).

The obtained results are:

- [η] = 538 mL/g
- $\overline{M_V}$= 125116.3 g / mol

The average degree of polymerization (DP̄_n) was calculated using the equation:

$\overline{DP_n}$ =M_v / M ", where M' is the molecular mass of an anhydroglucose unit (M' = 162 g/mol).

Thus, $\overline{DP_n}$= 772.32, which is consistent with reported literature values (750 ≤ $\overline{DP_n}$= ≤ 26500) [29**]**.

3.2. Characterization of Cellulose Citrate Copolymers (MBSC)

The cellulose citrate copolymers (MBSC) were characterized by FTIR spectroscopy, thermogravimetric analysis (TGA), viscometric, and potentiometric methods. The modification of EC is schematically represented in Figure 3. This modification involves the reaction between the hydroxyl groups of cellulose and the anhydride of citric acid, resulting in the formation of ester bonds. The successful esterification is confirmed by the IR spectrum.

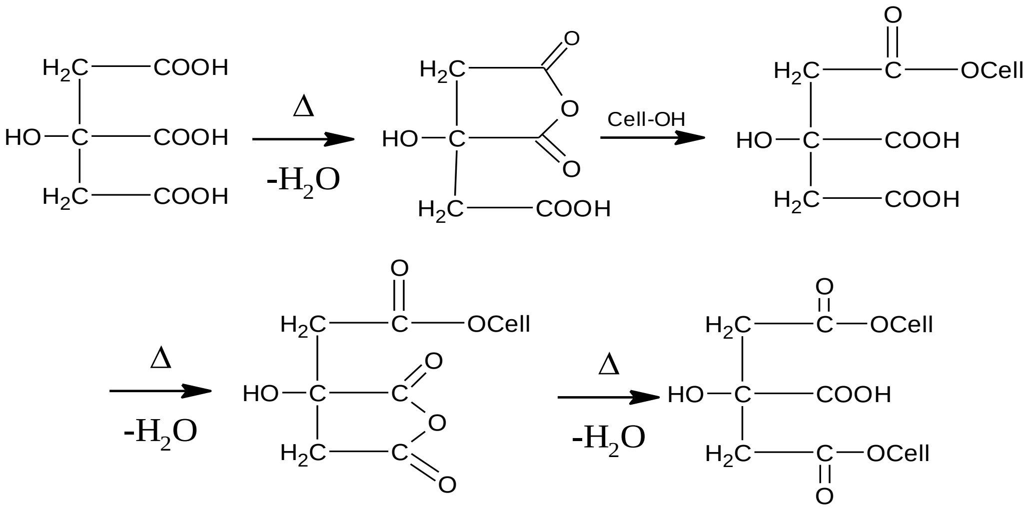


Figure 3: Proposed mechanism for the esterification of barley straw cellulose by citric acid [29]**.**

3.2.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was performed to confirm esterification of the extracted cellulose (EC). The assignments of characteristic cellulose bands and those of various MBSC copolymers obtained at different esterification temperatures (120°C–180°C) are shown in Figure 4**.**

Esterification is evidenced by:

- The appearance of a band around 1733 cm^{-1}, indicative of ester carbonyl stretching vibrations [30].
- A decrease in the signal at 3544 cm^{-1}, corresponding to the progressive disappearance of hydroxyl groups as they are converted into ester functions.

For esterified celluloses (MBSC), characteristic bands are observed at (1733-1756 cm^{-1}) (C=O, ester) and at (1035-1100 cm^{-1}) (C-O-C, ester), however, other bands at (2870 and 2945 cm^{-1}) (CH_2, CH) and at (3000-3600 cm^{-1}) are common to all samples including the structure of cellulose extracted from barley straw (EC).

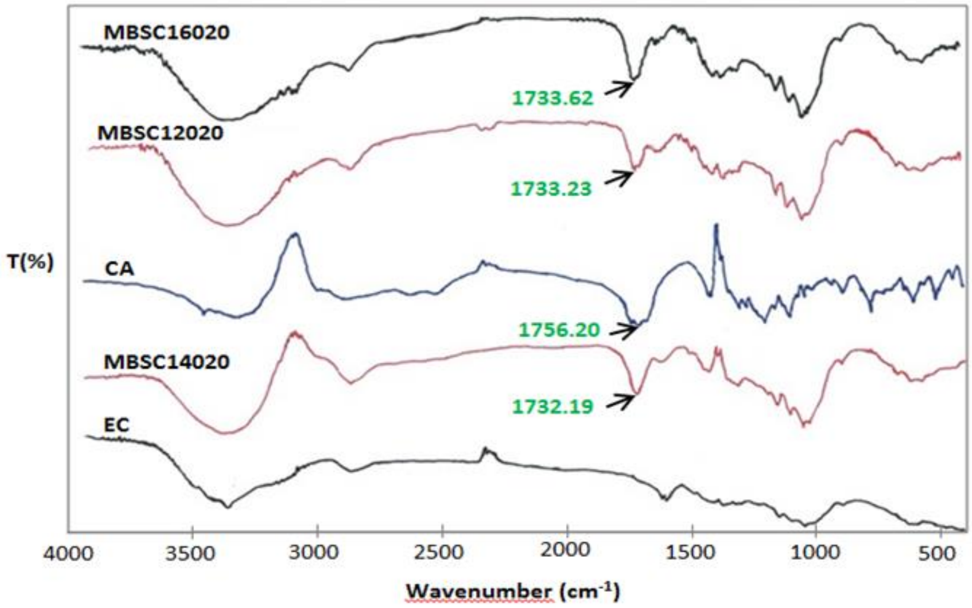


Figure 4: FTIR spectra of extracted cellulose (EC), citric acid (CA) and cellulose citrate (MBSC12020, MBSC14020 and MBSC16020).

3.2.2. Thermogravimetric Analysis (TGA)

The thermal stability of extracted and modified cellulose was analyzed over a temperature range of 30 to 900 °C under an air atmosphere. Thermogravimetric analysis (TGA) was conducted using a TA Instruments Q600 (LAEPO Laboratory), and the resulting curves are presented in Figure **5**. The analyzed products were obtained after 20 minutes of heating at various temperatures, ranging from 120 °C to 180 °C. The reference cellulose (Cellref) corresponds to cellulose extracted from rice straw through an acid treatment [31].

The thermogram indicates a 5% weight loss between 30 and 180 °C, attributed to the evaporation of absorbed water and residual solvents such as toluene and ethanol. The weight loss recorded between 182 and 271 °C corresponds to the amount of citric acid incorporated into the MBSCX esters [32]. Based on the curve profiles, the esterification of extracted cellulose (EC) is successfully achieved. The quantity of fixed citric acid varies between 18% and 47%, depending on the modification temperature. A slight pyrolysis of MBSC18020 (resulting in a 7% weight loss) leads to a yellow coloration, likely due to the decarboxylation or dehydration of esterified cellulose [32, 33].

Previous studies have shown that the degradation of cellulose extracted from rice straw (via acid treatment) begins at approximately 300 °C [31, 34]. The degradation and pyrolysis of the main cellulose backbone occur between 430 and 600 °C, corresponding to the depolymerization reaction described by Repllin [35]. Additionally, the thermogravimetric curves of starch-glycerol and starch-Gly-CA films exhibit similar mass loss regions [36].

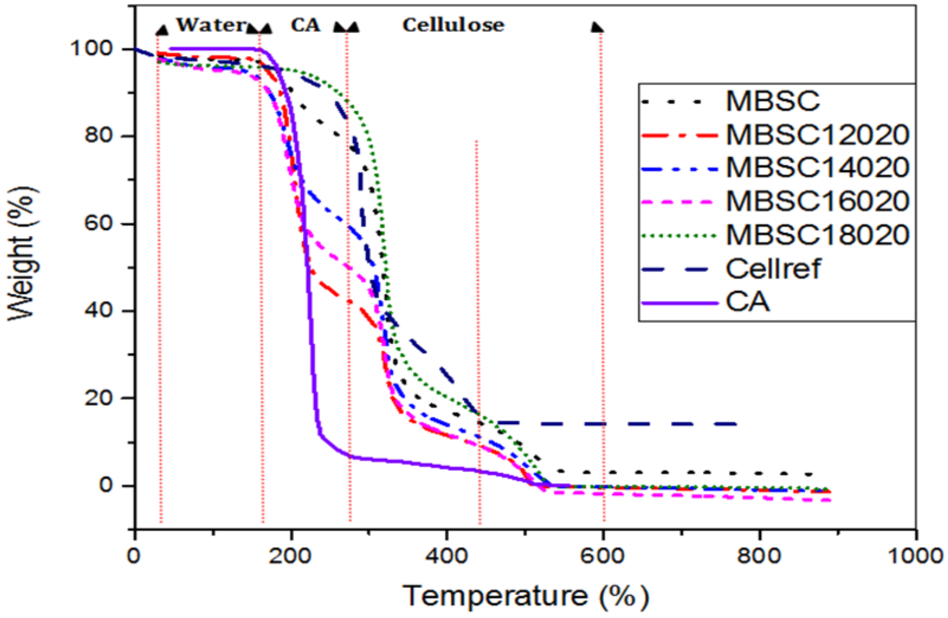
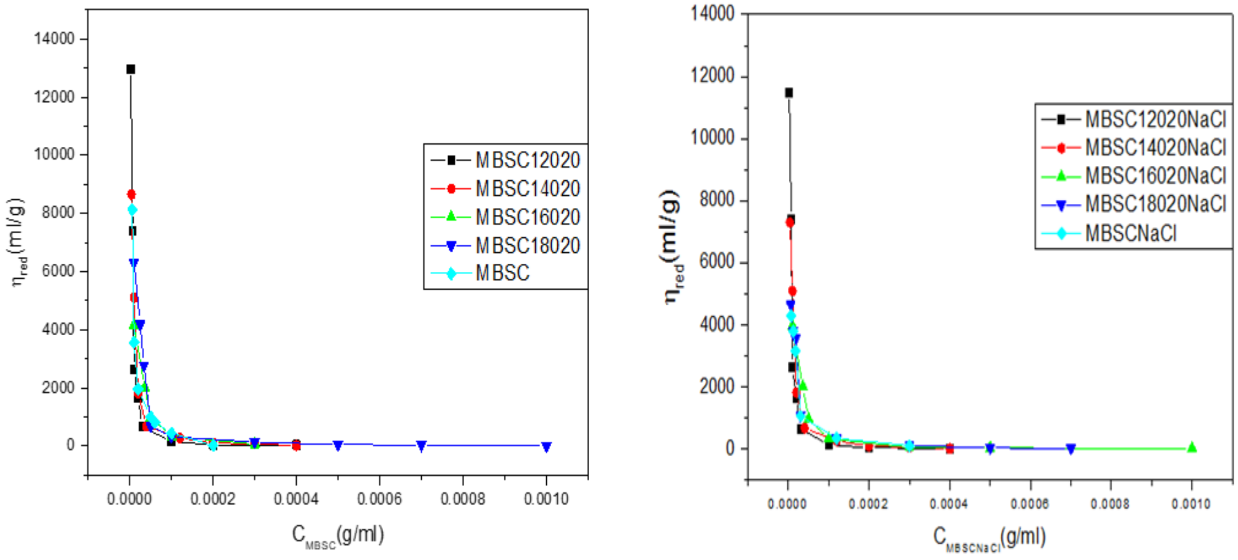


Figure 5:TGA curves of extracted cellulose (EC), modified celluloses (MBSC), cellulose reference (Cellref) [31] and citric acid (CA).

3.2.3. Viscometric Measurement

The chemical modification of cellulose introduces charged groups, imparting a polyelectrolyte behavior to the material. First, we analyze the evolution of the reduced viscosity of MBSC, obtained after 20 minutes at different temperatures (120°C, 140°C, 160°C, and 180°C), as a function of concentration at 25°C. The results are then compared with those of the unmodified cellulose (EC).

To evaluate the influence of temperature on viscosity, we compare the reduced viscosities (η_red) of the cellulose esters. Figure 6a illustrates the variation in reduced viscosity of the synthesized esters at different temperatures after 20 minutes, plotted against concentration in the absence of salt. The cellulose citrates (MBSC) exhibit polyelectrolyte behavior. At low concentrations in the dilute regime, the polymer initially shows an increase in reduced viscosity, reaching a maximum before decreasing as the polymer concentration further increases.



(a) **(b)**

Figure 6: Variation of the reduced viscosity of the various MBSC as a function of their concentration.

This behavior is characteristic of polyelectrolytes with high molecular weight [37]. The observed trend is attributed to the presence of carboxylate groups along the polymer chains. Additionally, a decrease in reduced viscosity is noted with increasing temperature, likely due to partial degradation of the polymer chains at elevated temperatures.

However, in the presence of NaCl (Figure 6b), a reduction in reduced viscosity is observed across all polymers. This can be explained by charge screening effects of the carboxylate groups within the polymer chains. Such behavior further confirms the polyelectrolyte nature of the modified cellulose.

3.2.4. Potentiometric Determination

The potentiometric determination of cellulose esters involves neutralizing the acidic functions attached to the anhydro glucopyranose unit. Potentiometric titrations were performed using a HANNA 209 pH meter equipped with a combined glass electrode.

To determine the degree of substitution (DS), the amount of acid functions was quantified by potentiometry, measuring the pH variation as a function of the volume of sodium hydroxide solution (NaOH, 10^{-2} M) added. The results are presented in Figure 7 and summarized in Table 1.

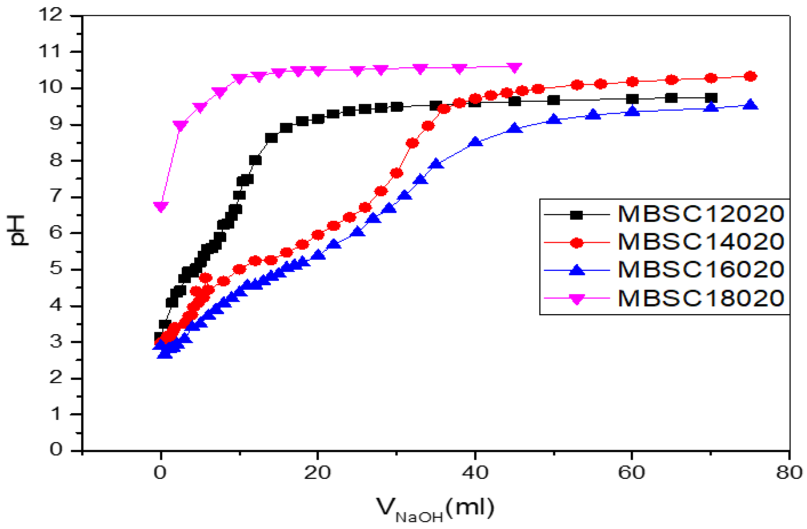


Figure 7: Variation of pH of MBSC esters as a function of the added volume of NaOH (10^{-2} M).

Table 1: Potentiometric titration results of cellulose citrates with sodium hydroxide (NaOH, 10^{-2} M).

Sample	m_{CA} (g)^1	m_{EC} (g)^2	T (°C)	t (min)	V_e (mL)^3
MBSC12020	5	5	120	20	10.5
MBSC14020	5	5	140	20	31
MBSC16020	5	5	160	20	32
MBSC18020	5	5	180	20	-

[1] *m_{CA}: mass of citric acid*

[2] *m_{EC}: mass of extracted cellulose (EC)*

[3] *V_e: equivalent volume*

3.2.5. Calculation of the Degree of Substitution (DS)

The degree of substitution (DS) of citric acid grafted onto the extracted cellulose (EC) is calculated using the following equation [38]:

$$DS = \frac{162\,Q}{2-174\,Q}$$

Where, **Q** represents the capacity or the number of equivalents of OH^{-} required to neutralize one gram of cellulose ester.

3.2.6. Evaluation of Reaction Time and Temperature

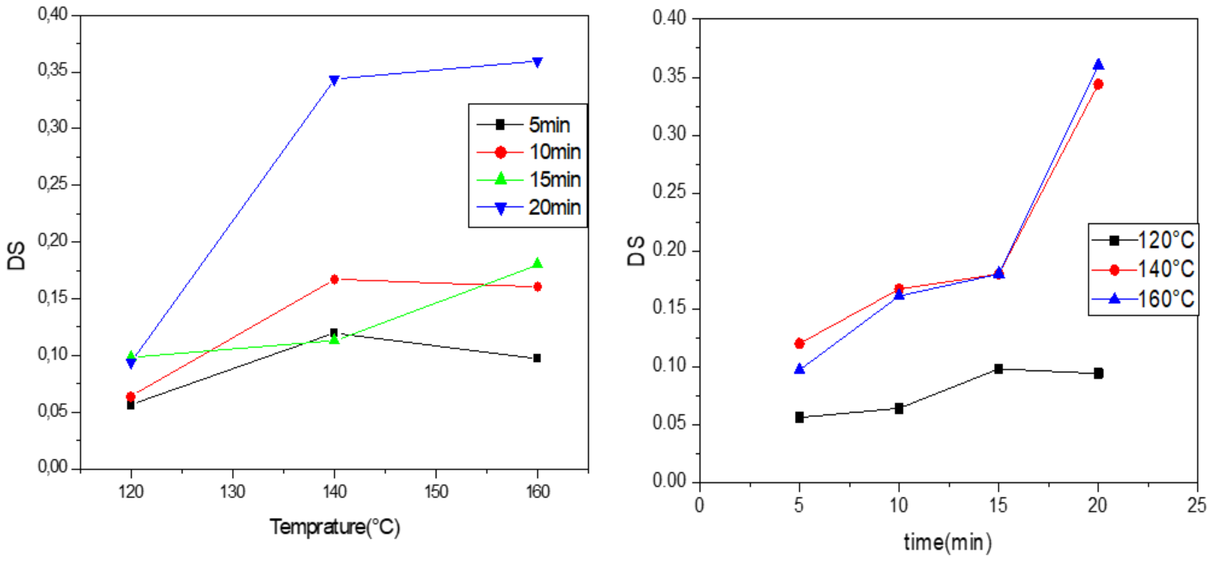
To determine the optimal esterification conditions, we investigated the influence of reaction temperature and duration. The obtained results are summarized in Table 2.

Table 2: Potentiometric parameters obtained from the titration of cellulose citrates with NaOH (10^{-2} M)

Ester	T (°C)	t (min)	R [a]	R_{dt} [b] (%)	V_e [c] (mL)	n_{COOH} [d] (mol/g)	DS [e] (%)
MBSC1205	120	5	1	98	6.66	0.0027	5.6
MBSC12010	120	10	1	98	7.41	0.003	6.4
MBSC12015	120	15	1	96	11.00	0.0044	9.8
MBSC12020	120	20	1	94	10.50	0.0042	9.4
MBSC1405	140	5	1	97	13.00	0.0052	12.0
MBSC14010	140	10	1	96	17.50	0.0070	16.7
MBSC14015	140	15	1	92	12.50	0.0050	11.3
MBSC14020	140	20	1	90	31.00	0.0124	34.4
MBSC1605	160	5	1	98	10.90	0.0040	9.7
MBSC16010	160	10	1	94	17.00	0.0068	16.1
MBSC16015	160	15	1	88	19.00	0.0076	18.0
MBSC16020	160	20	1	86	32.00	0.0130	36.0

(a)R: relative quantity (m_{CA} / m_{EC}), (b)R_{dt}: weight yield, (c)V_e: equivalent volume, (d)n_{COOH}: number of fixed acid groups, (e)DS: degree of substitution.

The variation in the degree of substitution as a function of temperature and reaction time is illustrated in Figure 8a and Figure 8b, respectively.



(a) **(b)**

Figure 8: Variation of the degree of substitution of cellulosic citrates according to **(a)** the reaction temperature; (**b)** the reaction time.

An increase in the degree of substitution (DS) is observed as the reaction temperature rises to 160°C, with an optimal reaction time of 20 minutes. This can be attributed to the increased mobility of citric acid molecules and hydroxyl clusters within the cellulose chain, facilitating esterification. However, beyond this temperature, DS decreases due to partial degradation of the modified cellulose.

4. CONCLUSIONS

A 53 % of cellulose was successfully extracted from barley straw through alkali treatment. The extracted cellulose (EC) was modified by citric acid by esterification which led to cellulose citrate (MBSC) containing a substantial amount of carboxyl groups. It's shown that the structure of various polyesters synthesized varies with the method of extraction and the degree of substitution (DS).Esterification has been proven by the appearance in FTIR spectroscopy of new vibration bands at 1732 cm^{-1} and by thermogravimetric analysis showing the appearance of new thermal landing in the corresponding thermograms and which do not appear in that of native cellulose. A mass yield of 90 % of modification was carried out. The copolymers obtained are biodegradable and present a polyelectrolyte and hydrophilic character verified by viscosimetric study. It’s meets industrial, agricultural, and pharmaceutical requirements. This esterification allowed us to obtain a series of MBSC with different DS determined by the potentiometry method. The highest DS = 0.36 was obtained at 160 °C after 20 min of reaction, which is the optimal temperature and time. Finally, in addition to the various characterizations carried out, much remains to be done, with perspectives of expanding our work by quantitative and kinetic studies of the using MBSC in dye treatment of industrials wastewater and treatment of agricultural soils salinity.

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