Extraction and Bleaching of Olive Tree Branch Cellulose

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The objective of this work was to extract and bleach cellulose from a low-value agricultural waste, namely, olive tree branches. The extraction procedure began by subjecting finely powdered olive tree branches to alkaline treatment, using different concentrations of sodium hydroxide solution to remove/dissolve the non-cellulosic cementing constituents, such as pectin, hemicelluloses, and natural waxes from the structure of this lignocellulosic network. The second step of the extraction procedure was the oxidation/bleaching treatment, and for this purpose, a powerful oxidizing agent composed of sodium chlorite/triethanolamine salt was used. All factors and conditions affecting the bleaching reaction, including triethanolamine salt concentration, bleaching temperature, and utilization of different triethanolamine salts, were extensively studied. The efficiency of the bleaching/oxidation treatment was evaluated by recording the FTIR spectra of the samples before and after extraction and analyzing the bleached samples to estimate the carboxyl content, loss in weight, and whiteness index.

Keywords: Cellulose; Extraction; Bleaching

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INTRODUCTION

The procedure used for bleaching olive tree cellulose is, to a wide extent, similar to the procedure used for bleaching cotton cellulose. When applying a bleaching process to extract and bleach olive tree cellulose, one must consider two important factors. The first factor to be considered for extracting and bleaching olive tree branches is that the substrate structure contains about 77.17% holocellulose, 62.49% alpha cellulose, and 21.73% lignin (Requejo *et al*. 2012). The structure of this substrate is completely different than the structure of cotton, which contains only about 5% non-cellulosic materials, the rest being pure α-cellulose. The second factor to be considered is the sensitivity of olive tree branch cellulose towards alkali treatment and oxidative bleaching treatment compared to that of cotton fibers. Generally speaking, it is well known that lignocellulosic fibers (wood, bast fibers, and bagasse) contain in their structure various non-cellulosic materials such as lignin, hemicelluloses, pectin, waxes, fats, and naturally occurring coloring materials. The efficient removal of such non-cellulosic impurities through successive preparatory processes applied to these fibers, like scouring and bleaching processes, is needed to perform further successful processes, such as chemical modification (Abdel-Halim *et al*. 2008a, b, 2010; Abdel-Halim and Al-Deyab 2011; Abdel-Halim 2012a; Montazer and Morshedi 2012; Farooq *et al*. 2013; Joshi *et al*. 2013; Al-Hoqbani *et al*. 2014). Due to the important issue of energy conservation, many researchers have placed emphasis on this concept and many research trials have been designed to reduce energy consumption during the successive preparation steps involved in the processing of cellulosic fibers (Ibrahim *et al*. 2008; Palamutcu 2010; Hasanbeigi and Price 2012).

One popular method used to bleach cellulosic fibers includes the activation of oxidative bleaching agents by the use of different chemicals in order to get the highest efficiency of the bleaching agent by raising its oxidation potential to its maximum value without causing any harmful degradation effect on the treated cellulosic substrate (Bösing *et al*. 1999; Tzanov *et al*. 2002; Hou *et al*. 2010; Abdel-Halim 2012b, c, 2013; Abdel-Halim and Al-Deyab 2013; Long *et al*. 2013; Xu *et al*. 2013; Si *et al*. 2014). During the last three decades, many researchers have done extensive research to convert low-value agricultural and industrial by-products or wastes into valuable industrial products at a reasonable cost (Sokker *et al*. 2004; Hashem *et al*. 2005a, b; Abdel-Halim *et al*. 2008c, d, 2015a, b; Sud *et al*. 2008; Abdel-Mohdy *et al*. 2009; Hebeish *et al*. 2010, 2011; Abdel-Halim and Al-Deyab 2012; Anupam *et al*. 2013; Bilal *et al*. 2013; Hegazi 2013; Nguyen *et al*. 2013; Singha and Das 2013; Abdel-Halim 2014; Abdel-Halim and Al-Hoqbani 2015). Agricultural by-products such as jute processing wastes, straws of rice and wheat, bagasse resulting from the sugar industry, and palm tree wastes are available as sustainable and renewable resources. These biomass sources can be subjected to an alkaline pulping process to extract their cellulosic components, and the extracted pulps can be further subjected to functionalization treatments and finally applied as high-value industrial products.

In the present work, extensive experimental work was carried out to find the most suitable procedure to scour and bleach olive tree branches as part of palm tree wastes, taking into account the quality of the resulting olive tree branches from the molecular weight point of view, the cost of the bleaching process, and the environmental impact. The experimental activities include the utilization of sodium chlorite as the bleaching system to clean up olive tree branches and make them accessible for further chemical modification. Factors affecting the bleaching process, like oxidant concentration, bleaching duration, and bleaching medium temperature and pH were analyzed. The bleaching reaction was monitored by measuring the decomposition rate of the oxidant by determining the percent of decomposed oxidant throughout the reaction period. The treated samples were evaluated via determining the physiochemical properties like whiteness index, percent loss in weight, and carboxyl content of the resulting substrate.

EXPERIMENTAL

Materials

Olive tree branches were collected from an olive tree farm. Sodium hydroxide, potassium permanganate, sodium carbonate, potassium bromide, potassium iodide, and sodium thiosulfate were all laboratory grade chemicals. The auxiliaries Texazym T (non-ionic wetting agent) and Texamyl BL (bacterial alpha-amylase) were supplied by Inotex Company, Czech Republic. Triethanolamine (99.0%) was supplied by Sigma-Aldrich, through Bayouni Trading Co. Ltd. Al-Khobar, Saudi Arabia.

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Methods

Alkali treatment of olive tree branch wastes

Olive tree branch wastes were left to dry in an open sunny area to a moisture content of 5.2%. The dry olive tree branch wastes were ground into fine particles using a mill. The alkali treatment procedure involved different concentrations of sodium hydroxide solution to dissolve the non-cellulosic cementing materials and facilitate the extraction of the cellulosic fibers from the structure of the olive tree branches. In this procedure, samples of olive tree branch wastes were treated with different concentrations of sodium hydroxide ranging from 0.5% to 10% (W/V) together with a (2 g/L) nonionic wetting agent with a material-to-liquor ratio of 1:20 at the boiling temperature under reflux for a period of 60 min. At the end of the treatment duration, the scoured samples were removed from the alkaline liquor by filtration, washed well several times with hot distilled water, rinsed twice with cold distilled water, and finally dried in open air.

Formation of different salts for triethanolamine

For salt preparation, equivalent amounts of hydrochloric, sulphuric, phosphoric, acetic, and formic acid were separately reacted with a known amount of the alkali triethanolamine (Abdel-Halim 2013). The resulting hydrochloride, sulphate, phosphate, acetate, and formate salts of triethanolamine were respectively noted as: (TEA-HCl), (TEA-H_2SO_4), (TEA-H_3PO_4), (TEA-CH_3COOH), and (TEA-HCOOH). This step was just a salt formation reaction to produce the corresponding triethanolamine salts, which were used later to activate sodium chlorite decomposition during the bleaching of the olive tree branches.

Bleaching procedure

Unless otherwise reported, the olive tree branch samples (5 g of each sample) were introduced to a reaction bottle containing sodium chlorite (3 g/L) and the (TEA) salts (0 to 10 mmol/L). To this bleaching bath, a nonionic wetting agent (2 g/L) was added and the material-to-liquor ratio was finally adjusted to 1:20 (Abdel-Halim 2013). The bleaching treatments were performed at different temperatures ranging from 50 °C to 95 °C and the reaction continued for different durations ranging from 30 min to 240 min. Samples from the reaction medium were withdrawn regularly in order to estimate the residual sodium chlorite concentration, from which the extent of sodium chlorite decomposition could be determined. At the end of the bleaching duration the olive tree branch samples were separated from the bleaching medium, washed well with hot water followed by cold water, and then left to dry in open air.

Testing and Analysis

The percent loss in weight of the olive tree branch samples due to either scouring or bleaching treatment was calculated according to the following equation (Eq. 1),

$$\text{Percent weight loss} = (W_1 - W_2) \times 100/ W_1 \qquad (1)$$

where W_1 is the weight of the olive tree branch sample before the treatment and W_2 is the weight of the olive tree branch sample after the treatment. The percent decomposition of the sodium chlorite was calculated via a quantitative estimation according to a reported method from Vogel (1961). The W_1 of the bleached olive tree branch samples was measured by use of a Hunterlab Reflectometer (Model D25 M/L-2). The whiteness index was calculated in terms of CIE Y (green) and (blue) reflectance components using the following equation (Eq. 2) (ASTM Method E31373).

$$\text{Whiteness index} = (4Z/1.18) - 3Y \qquad (2)$$

where Y is the relative luminance (brightness) of green color and Z is a value quasi-equal to blue color stimulation. The method reported by Mattisson was used for carboxyl content determination (Mattisson and Legendre 1952).

RESULTS AND DISCUSSION

Alkali Treatment of Olive Branch Wastes

The data in Table 1 demonstrate the relation between the sodium hydroxide concentration and the amount of impurities removed from the olive tree branches during the alkaline scouring process. The concentration of sodium hydroxide solution during the alkali treatment ranged from 0.5% to 10% and the treatment was carried out for one hour. Table 1 reveals a sharp increase in the percent loss in weight with each increase in sodium hydroxide concentration, and this is true only up to a sodium hydroxide concentration of 7%. It is also observed that any increase in sodium hydroxide concentration beyond 7% is accompanied by a further slower increase in weight loss. The increase in impurities removal, expressed as percent loss in weight, upon increasing the sodium hydroxide concentration up to 7% is obviously understandable in terms of improvement in the fiber swell ability, which leads to enhancement in the penetration of sodium hydroxide into the fiber phase giving rise to impurities dissolution. The decreased impurities removal beyond a sodium hydroxide concentration of 7% indicates that there was a lack of impurities to be dissolved and removed and that the role of sodium hydroxide in this stage was to dissolve and remove the cellulosic fragments having low molecular weights.

Table 1. Effect of Alkali Concentration on Weight Loss of Olive Tree Branches

[NaOH], (W/V)	0.5	1	2	3	4	5	6	7	8	9	10
Loss in olive tree branch weight (%)	4.5	5.3	7.1	8.3	10.5	12.3	14.7	17.5	18.3	18.8	19

Bleaching

When sodium chlorite activated with TEA salt (TEA-HCl) is used for bleaching alkali-treated olive tree branches, several reactions are expected to occur. Among these reactions are (a) the gradual liberation of free acid from the TEA salt under the bleaching condition (95 °C) (reaction 1) and (b) the decomposition of sodium chlorite in the presence of the liberated free acid according to the following scheme (reactions 2 through 4):

$$\mathrm{TEA.HCl} \longleftrightarrow \mathrm{TEA} + \mathrm{HCl} \qquad [1]$$

$$4\mathrm{ClO_2}^- + 2\mathrm{H}^+ \longrightarrow 3\mathrm{ClO_2} + \mathrm{Cl}^- + 2\mathrm{OH}^- \qquad [2]$$

$$3\mathrm{ClO_2}^- \longrightarrow 2\mathrm{ClO_3}^- + \mathrm{Cl}^- \qquad [3]$$

$$\mathrm{ClO_2}^- \longrightarrow \mathrm{Cl}^- + 2\mathrm{O} \qquad [4]$$

In these bleaching trials, sodium chlorite activated with different triethanolamine salts was used to extract cellulose of olive tree branches. TEA-HCl was used as a model for the TEA salt in the bleaching process and the optimum conditions obtained from this systematic study were adopted for the other TEA salts (Abdel-Halim 2013). As shown by the above scheme (reactions 2 through 4), the decomposition of sodium chlorite in an acidic medium leads to the liberation of chlorine dioxide.

The rate of chlorine dioxide liberation had a remarkable effect on the extent of the bleaching process and its efficiency, in addition to the physiochemical properties of the bleached fibers. The bleaching process was achieved in two successive steps: first, the decomposition of the TEA salt, which is known to be a weak salt to its components TEA and acid, and second, the decomposition of sodium chlorite in an acid medium to its bleaching species, as illustrated in reactions 1 through 4.

Relation between TEA-HCl concentration and sodium chlorite decomposition

Several trials were carried out in bleaching the olive tree branches. Sodium chlorite concentration, pH, material-to-liquor ratio, and bleaching temperature were kept constant for all trails while and only varying the concentration of the activator TEA-HCl, used for sodium chlorite decomposition. This series of experiments was carried out to examine the role of sodium chlorite activator concentration on the percent decomposition throughout the reaction course, which in turn affects the efficiency of the overall bleaching process. The fixed reaction factors were to utilize the aqueous sodium chlorite solution (3 g/L), material-to-liquor ratio (1:20), bleaching bath temperature (95 °C), pH (7), and bleaching duration (240 min). Together with these fixed reaction conditions, the concentration of TEA-HCl was varied from 0 mmol/L to 10 mmol/L.

The data in Fig. 1 present a correlation between the bleaching reaction duration and the percent decomposition of sodium chlorite, when the bleaching is carried out at 95 °C and when different amounts of TEA-HCl are incorporated in the bleaching medium as an activator for sodium chlorite decomposition. The data recorded for sodium chlorite decomposition revealed a proportional relationship between the amount of activator TEA-HCl incorporated to the bleaching bath and the percent decomposition of sodium chlorite at a given duration; moreover, the data in Fig. 1 indicated that at a given TEA hydrochloride concentration, there was also a proportional relationship between the bleaching duration and the percent decomposition of sodium chlorite. In conclusion, the complete decomposition of sodium chlorite was achieved in one of two ways: first, a low concentration of TEA-HCl can be used to prolong the duration of the bleaching process and second, using a high concentration of TEA-HCl can shorten the duration of the bleaching process.

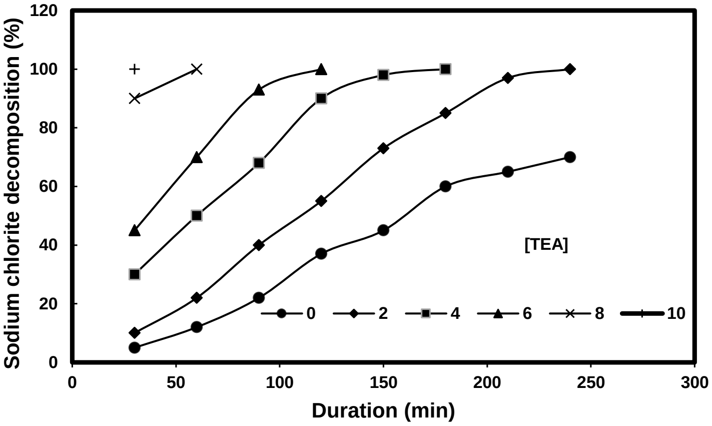

Fig. 1. Speed of sodium chlorite decomposition at varying TEA-HCl concentrations

Physiochemical properties of olive tree branch cellulose bleached using different concentrations from TEA-HCl

Table 2 presents the change in the physiochemical properties, whiteness index, loss in weight, and carboxyl content of the olive tree branch cellulose bleached by the use of different concentrations of TEA-HCl to activate the decomposition of the sodium chlorite. The results in Table 2 show that the TEA-HCl concentration of 6 mmol/L represents the optimum value to activate the decomposition of sodium chlorite, and this result is based on the highest recorded value for the whiteness index.

As shown in Fig. 1, one can notice that the utilization of 6 mmol TEA-HCl to activate the decomposition of the sodium chlorite resulted in decomposition of sodium chlorite in a gradual manner within 120 min. The gradual rate of sodium chlorite decomposition increased the benefit of olive tree branch cellulose from the oxidative species of the bleaching system, which led to gathering the highest value of whiteness index with a reasonable loss in weight. When using TEA-HCl concentrations lower than 6 mmol to activate the sodium chlorite decomposition, it is be mandatory to lengthen the bleaching duration in order to get full decomposition of the sodium chlorite. Even if the time was prolonged to attain full sodium chlorite decomposition at a low TEA-HCl concentration, there was no high enhancement noticed, neither in the weight loss nor in the whiteness index. Again, back to Fig. 1 and the physiochemical properties in Table 2, it is clear that incorporating a high concentration of TEA-HCl to activate the decomposition of sodium chlorite allowed the decomposition of sodium chlorite to take place in a shorter time, compared with the lower TEA-HCl concentrations; 100% sodium chlorite decomposition could even be attained in a period of 60 min upon using 8 mmol/L TEA-HCl and even up to 100% within 30 min upon using 10 mmol/L TEA-HCl. It was found that this fast decomposition of sodium chlorite, however, was useless for the olive tree branch cellulose, as no improvement was found in the whiteness index of the treated olive tree branch cellulose. Regarding the loss in olive tree branch weight upon utilization of a high concentration of TEA-HCl, it was found that there was incremental weight loss. The increase in weight loss upon increasing the TEA-HCl concentration did not happen in a continuous manner, and at a TEA-HCl concentration above 6 mmol/L the reverse was true. Moreover, the decrease in carboxyl content upon using TEA-HCl concentrations higher than 6 mmol/L could be better be understood in terms of the fast sodium chlorite decomposition in a manner that did not impart any bleaching effect on the treated olive tree branch.

Table 2. Physiochemical Properties of Olive Tree Branch Cellulose Bleached using Different Concentrations of TEA-HCl

TEA-HCl Concentration	Whiteness Index	Loss in Weight (%)	Carboxyl Content (m.equ./100g)
0	15.33	0.9	7.5
2	20.21	1.2	11.8
4	33.00	1.9	14.6
6	40	5.2	18.9
8	32	1.29	10.3
10	25	1	8.2
Raw OTBC	14.2	--------	6.7

The pH value of the bleaching liquor at different TEA-HCl concentrations

To show the effect of the initial concentration of TEA-HCl on the pH of the bleaching bath, the pH was monitored by analyzing samples withdrawn from the bleaching liquor at different time intervals. Both the pH and sodium chlorite decomposition were recorded. Figure 2 shows the relation between the pH of the bleaching bath and the bleaching duration for the different initial concentrations of TEA-HCl in the bleaching medium. The data presented in Fig. 2 show that for a given initial TEA-HCl concentration, as the bleaching duration was prolonged, the pH value decreased in a continuous manner; however, for a given fixed bleaching duration, increasing the initial TEA-HCl concentration was accompanied by a decrease in the bleaching bath pH value. It is clear from Fig. 2 that the utilization of initial concentration of TEA-HCl (6 mmol/L) led to a regular decrease in the bleaching bath pH until a pH value of 4 at a duration of 120 min, and at this point, the recorded percent decomposition of sodium chlorite was 100%. This observation leads to the conclusion that a TEA-HCl concentration of 6 mmol/L was optimum to activate the decomposition of sodium chlorite; this amount of TEA-HCl led to liberation of a reasonable amount of HCl to cause mild change in the bleaching medium, giving rise to a reasonable rate of sodium chlorite decomposition to its bleaching species. On the other hand, upon incorporating a higher initial TEA-HCl concentration to the bleaching medium, there was a sudden increase in the bleaching bath acidity, which in turn led to very fast and uncontrollable sodium chlorite decomposition in the very early stage of the bleaching duration without a real bleaching effect on the olive tree branch cellulose. The alkalinity of triethanolamine liberated as a result of TEA salt decomposition acted in fact as a buffering agent to prevent any sudden decrease in the pH of the bleaching bath. This buffering effect of triethanolamine led to decomposition of sodium chlorite in a uniform manner, resulting in the required bleaching effect. The absence of a buffering agent, like triethanolamine, would, of course, result in a sudden drop in bleaching bath pH, leading to uncontrollable decomposition of sodium chlorite without providing the required bleaching effect on the olive tree branch cellulose.

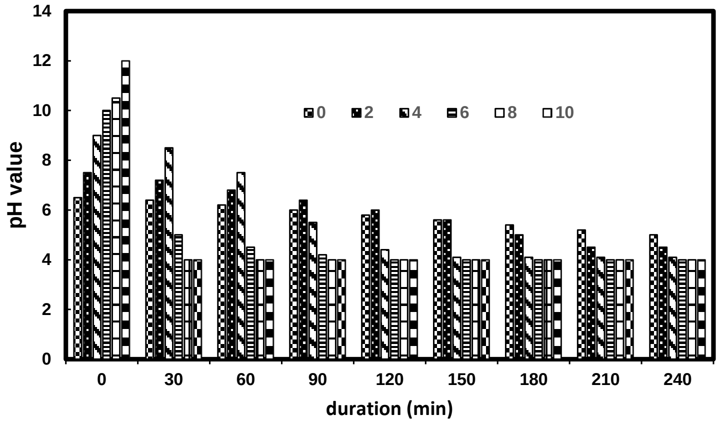

Fig. 2. pH value of the bleaching liquor at different TEA-HCl concentrations

Relation between bleaching bath temperature and decomposition of sodium chlorite

To show the relation between the bleaching bath temperature and sodium chlorite decomposition, several bleaching trials were carried out by using a fixed sodium chlorite concentration and TEA-HCl concentration and varying the bleaching bath temperature in the range of 50 °C to 95 °C. As shown in Fig. 3, generally, at any given reaction time the percent decomposed sodium chlorite was increased by raising the reaction temperature. On the other hand, the increase in sodium chlorite decomposition when changing the temperature of the bleaching from 50 °C to 70 °C at a time of 60 min was still small when compared to the corresponding increase upon changing the temperature of the bleaching bath from 70 °C to 95 °C. This difference in the percent decomposition of sodium chlorite at different bleaching temperatures shows the high energy of activation necessary to decompose sodium chlorite to its oxidizing components and reflects the favorable action of bleaching bath temperature on raising the kinetic energy of the molecules involved in the reaction. Moreover, upon carrying out the bleaching reaction at a temperature of 95 °C, complete sodium chlorite decomposition was reached within a duration of 120 min, but upon carrying out the bleaching reaction at lower temperatures, 100% sodium chlorite decomposition was not attained within the studied range of duration.

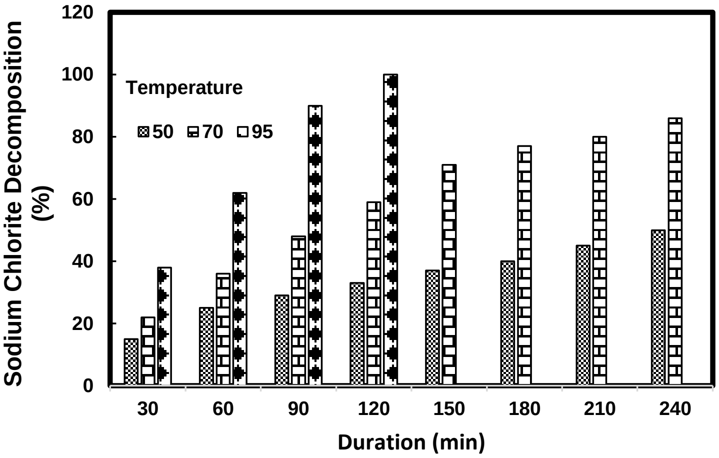

Fig. 3. Relation between bleaching bath temperature and sodium chlorite decomposition

Physicochemical properties of olive tree branch cellulose bleached at different temperatures

To show the relation between the bleaching bath temperature and the physicochemical properties of the bleached olive tree branches, several bleaching trials were carried out by using a fixed sodium chlorite concentration and TEA-HCl concentration and varying the bleaching bath temperature in the range of 50 °C to 95 °C. The concentration of sodium chlorite in these trials was fixed at 5 g/L, and the concentration of TEA-HCl was fixed at 6 mmol/L. The values of physiochemical properties presented in Table 3 for the bleached olive tree branch cellulose reveal the great dependence that the physiochemical properties of the bleached olive tree branch cellulose have on the temperature of the bleaching bath. It is clear from the data that the increase in the bleaching bath temperature was accompanied by incremental increase in the whiteness index of the bleached olive tree branch cellulose. The whiteness index increment upon raising the bleaching bath temperature can be better understood in terms of the activation effect that temperature has on sodium chlorite decomposition. Any increase in bleaching bath temperature will be accompanied by a corresponding increase in TEA-HCl decomposition to give its components HCl and TEA. In turn, HCl acts as an activator for sodium chlorite decomposition and give its bleaching species. The data recorded for the olive tree branch weight loss demonstrated a clear increase in the weight loss percent upon raising the bleaching bath temperature from 50 °C to 95 °C. There was also a proportional relationship between the increase in olive tree branch weight loss and the enhancement in whiteness index. These findings can be explained in terms of the increase in the efficiency of the bleaching reaction as a whole by increasing the bleaching temperature. The bleaching reaction was promoted, which resulted in higher removal of the non-cellulosic materials that are responsible for coloration of olive tree branches; accordingly, the whiteness index was increased.

The values recorded for the carboxyl content are also presented in Table 3 for different bleaching bath temperatures. The data show that in general there was a proportional relationship between the carboxyl content of the bleached olive tree branches and the temperature of the bleaching bath. This is due to the fact that when the bleaching bath temperature is raised from 50 °C to 95 °C, there will be an increase in the generation of active oxidizing species, which are responsible for the formation of more carboxyl groups.

Table 3. Physiochemical Properties of Bleached Olive Tree Branch Cellulose at Different Bleaching Temperatures

Bleaching Bath Temperature (°C)	WI	Loss in Weight (%)	Carboxyl Content (m.equ./100g)
50	22	3.1	11
70	29	3.9	14
95	40	5.2	18.9

Decomposition of sodium chlorite upon using different triethanolamine salts as activators

Based on the above discussion, it can be concluded that the optimum TEA salt concentration required to activate sodium chlorite decomposition was 6 mmol/L, as this concentration gave the exact amount of active species necessary for bleaching olive tree branches. For comparison, other TEA salts prepared from different organic acids and mineral acids were used to activate the decomposition of sodium chlorite. The salts were directly prepared through neutralization of TEA with HCl, H_2SO4, H_3PO_4, HCOOH, and CH_3COOH to yield the salts: triethanolamine hydrochloride, triethanolamine sulphate, triethanolamine phosphate, triethanolamine formate, and triethanolamine acetate, respectively. Five bleaching baths, each containing one of the different TEA salt activators, were prepared simultaneously by fixing the concentration of sodium chlorite at 5 g/L and incorporating, individually to the five bleaching baths, equal concentrations of the different five TEA salts. The bleaching bath pH was initially fixed at 7 before incorporating the TEA salt to the bleaching bath. The material-to-liquor ratio was fixed for all bleaching baths at 1:20, and the bleaching trials were conducted at 95 °C. Sodium chlorite decomposition was measured by withdrawing and analyzing a sample from the bleaching baths every 30 min.

The data presented in Fig. 4 show the relation between the kind of triethanlamine salt used to activate decomposition of the sodium chlorite and the percent of sodium chlorite decomposition. The kind of TEA salt utilized to activate sodium chlorite decomposition strongly affected the sodium chlorite decomposition. For example, at a given bleaching time of 120 min, hydrochloric salt resulted in the greatest sodium chlorite decomposition followed by sulphate salt, phosphate salt, formate salt, and acetate salt. This order implies that generally the inorganic salts of triethanolamine were more capable of activating the decomposition of sodium chlorite than the organic salts of triethanolamine were; moreover, among the series of inorganic triethanolamine salts, the hydrochloride was found to be the most efficient salt, while the phosphate salt was the lowest. The efficiency of a given triethanolamine salt in activating the decomposition of sodium chlorite reflects to a great extent the power of the acid resulting from its decomposition and the ability of such an acid to increase the acidity of the bleaching bath, which in turn enhances the decomposition of sodium chlorite. Because of the weakness of the acids resulting from the decomposition of organic triethanolamine salts, these acids were not capable of increasing the bleaching medium acidity to the required limit; this is why the bleaching trials run by use of these salts to activate the decomposition of sodium chlorite did not show complete decomposition of the sodium chlorite before a bleaching duration of 3 h.

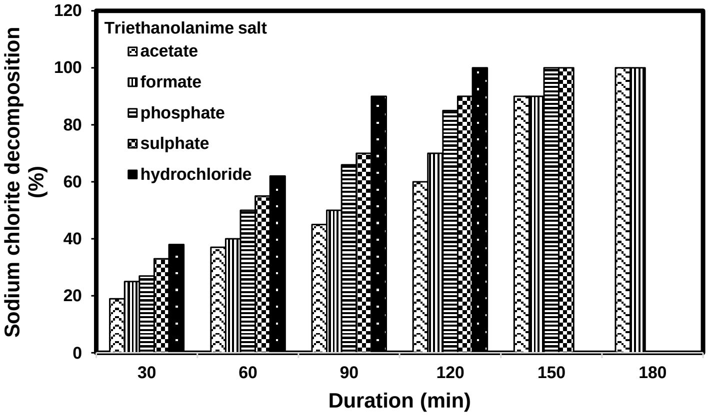

Fig. 4. Percent decomposition of sodium chlorite upon using different triethanolamine salts as activators

Physiochemical properties of olive tree branch cellulose bleached by the use of different triethanolamine salts

Table 4 shows the physiochemical properties of the olive tree branch samples resulting from bleaching with sodium chlorite decomposition activated by the use of different TEA salts.

Table 4. Physiochemical Properties of Olive Tree Branch Cellulose Bleached by the use of Different Triethanolamine Salts

TEA Salt	WI	Loss in Fabric Weight (%)	Carboxyl Content (m.equ./100g)
Acetate	30	2	10
Formate	33	2.10	11.25
Phosphate	37	4.2	14.93
Sulphate	37.5	5.2	16.12
Hydrochloride	40	5.2	18.9

As mentioned, the bleaching bath used to treat the olive tree branch cellulose contained basically sodium chlorite (5 g/L) and a TEA salt (6 mmol/L). The bleaching bath pH was initially adjusted to a value of 7, and the bleaching temperature was adjusted to 95 °C. A material-to-liquor ratio of 1:20 was used, and the treatment was left to run at these conditions for a duration of 180 min. The data presented in Table 4 illustrate that activation of sodium chlorite decomposition by the use of an inorganic TEA salt resulted in olive tree branch cellulose having improved physiochemical properties, when compared with olive tree branch cellulose bleached by the use of an organic TEA salt to activate sodium chlorite decomposition. This again emphasizes the effect of the strength of the acids resulting from inorganic triethanolamine salt decomposition in increasing the acidity of the bleaching medium to the extent required to initiate and complete the decomposition of sodium chlorite to its oxidizing species necessary for bleaching, thus leading to high improvement in both whiteness index and carboxyl content.

FTIR spectroscopy

The FTIR spectra of the olive tree cellulose before and after extraction treatment are presented in Fig. 5. The main goal of subjecting the raw olive tree cellulose to the alkali treatment and bleaching is to remove the binding and cementing non-cellulosic materials including pectin, lignin, and hemicellulose to liberate and extract the pure cellulosic fibers. The extent of cellulose extraction or removal of the non-cellulosic materials can be evaluated by comparing the absorption bands characterizing pectin, for example, in the FTIR spectra of the raw lignocellulose material and the extracted cellulose.

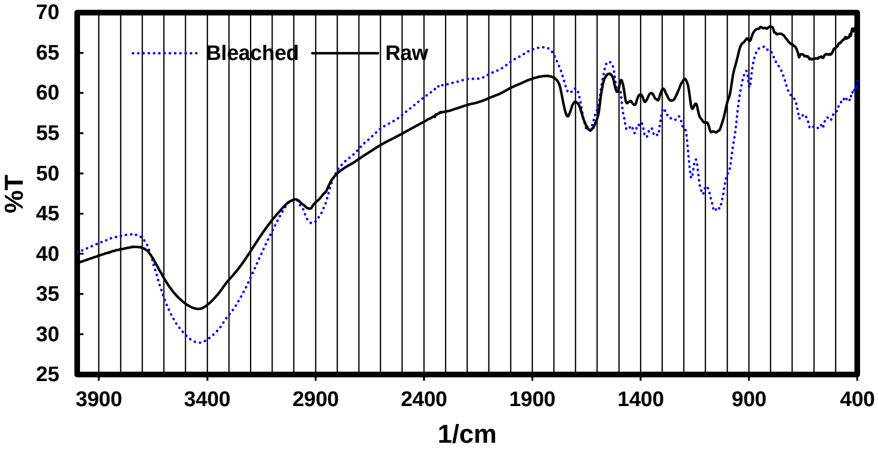

Fig. 5. FTIR spectra of the raw and bleached olive tree cellulose

The main difference between the raw and bleached cellulose was that the chemical treatments (scouring and bleaching) had removed part (not all) of the non-cellulosic materials present in the composite-like structure of the lignocellulosic materials, *i.e.* the olive tree branches. So the FTIR spectrum of raw and bleached olive are expected to be similar, except in the intensities of the peaks characteristic for the non-cellulosic materials, which had been partially removed due to these chemical treatments.

In the spectrum of raw olive cellulose there are two vibration bands near to 1740 cm^{-1}. These bands represent the carbonyl of an ester group $v(C=O)_{ester}$ and the carbonyl of a carboxyl group $v(C=O)_a$. As shown in the spectrum of the extracted olive cellulose, the intensities of these two bands decreased, compared to their values in the spectrum of raw olive cellulose. This is due to treatment of olive cellulose with sodium hydroxide, which is known to remove pectin from the composite structure of lignocellulosic materials. On the other hand, the pectate salt with its two characteristic carboxylate stretching bands, $v_s(COO^-)$ at 1410 cm^{-1} and $v_{as}(COO^-)$ at 1620 cm^{-1}, appeared at high intensities in the spectrum of the extracted olive cellulose, compared to their corresponding intensities in the spectrum of raw olive cellulose.

CONCLUSIONS

1. Olive tree branches were ground into fine powder and subjected to successive alkaline scouring and sodium chlorite bleaching to extract cellulose fibers from the composite structure of the lignocellulosic material. Sodium chlorite decomposition was activated by the use of different triethanolamine salts and it was found that the efficiency of salts derived from mineral acids were higher than those derived from organic acids.
2. Among the mineral acids from triethanolamine salts, triethanolamine hydrochloride was found to be the most efficient sodium chlorite activator.
3. FTIR spectra of raw and bleached olive cellulose confirmed the success of the extraction process, as the intensities of the bands characteristic to pectin in the spectrum of bleached fiber were lower than those of raw olive cellulose.

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