SYNTHYSIS OF RAYON FROM DATE PALM FRONDS

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ABSTRACT

The artificial silk (Rayon) was produced from the fronds of date palms which was taken from date palm trees (type Al-Zahdi) from the Iraqi gardens. Two main parts of the frond, namely leaves and stalks were used in this study to produce rayon. The palm fronds were converted into a powder of 90-180 micrometers. Major steps were used to produce rayon; delignification, bleaching and finally dissolution. Modified organosolv method which uses organic solvent method was applied to remove high lignin content. Three variables were studied in the delignification process: temperature, the ratio of ethanol to water and digestion time. The results showed that the best percent of lignin removal was (97%) which occured at; digestion time (80 minutes), temperature (185^{o}C) and the ratio of ethanol: water of 50: 50 wt/wt. Statistical experimental design type Central Composite Design (CCD) has been used to find a mathematical relationship between the variables and the remaining lignin percent as a dependent variable. The effect of using different catalysts in delignification process have been studied and found that the best catalyst is sodium hydroxide at the concentration (0.025) mole/L which gave the same percent removal of lignin (97%) but with low digestion time about 30 min. In the next step, the cellulose was dissolved using. NaOH with different concentrations (4%-12%) and the results showed that the optimum concentration of sodium hydroxide was 8% at temperature - 20^{o}C. In order to improve cellulose dissolution, urea was added with proportion (6% NaOH + 4% urea). Finally, the cellulose was spinning with 10% H_2SO_4 to prepare rayon.

Keywords: Delignification, Rayon, Dissolution of cellulose, cellulose fibers, Fenton's reaction.

أنتاج الحرير الصناعي من سعف النخيل

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المستخلص

تم انتاج الحرير الصناعي من سعف نخيل التمر المأخوذ من أشجار نخيل التمر من البساتين العراقية (نوع الزهدي) ، وقد أستخدم جزئان أساسيان من السعف وهما الخوص والجريد (العضد)، حيث تم اخذ كميات من سعف النخيل وتقطيعه الى قطع صغيرة وتحويلها الى مسحوق بحدود 90 – 180 مايكرومتر.أهم الخطوات التي أستخدمت لتحضيرالحريرمن سعف النخيل هي أزالة اللكنين، القصر(التبيض) وأخيرا الأذابة. تم في هذه الدراسة تطبيق طريقة المذيب العضوي المعدلة (Modified organosolv) لازالة كمية اللكنين العالية. تم دراسة ثلاثة متغيرات في هذه العملية وهي : درجة الحرارة ، نسبة الأيثانول الى الماء و الوقت. من خلال النتائج التي تم الحصول عليها وجد أن افضل نسبة أزالة للكنين هي (97%) عند زمن هضم (80 دقيقة) و درجة حرارة 185 درجة مئوية ونسبة أيثانول : الماء تساوي 50: 50 نسبة وزنية. تم أستعمال طريقة (CCD) لايجاد علاقة رياضية تربط هذه المتغيرات مع نسبة اللكنين المتبقية بالنموذج. لقد تم دراسة تأثير استخدام عوامل مساعدة مختلفة وقد وجد أن افضل عامل مساعد هو هيدروكسيد الصوديوم بتركيز(0.025) مول لكل لتر حيث أعطى نفس نسبة اللكنين المزاله (97%) ولكن بزمن أقل حوالي 30 دقيقة. في الخطوة التالية، تم أذابة ألياف السيليلوز بأستخدام طريقة هيدروكسيد الصوديوم، بتراكيز مختلفة من هيدروكسيد الصوديوم (4٪ –12٪) وأظهرت النتائج أن التركيز الأمثل لهيدروكسيد الصوديوم كان 8٪ عند درجة الحرارة – 20درجة مئوية. تمت إضافة اليوريا بنسبة (6٪ هيدروكسيد الصوديوم + 4٪ اليوريا) وأخيرا تم حقن السليلوز المذاب بمحلول حامضي 10٪ من حامض الكبريتيك لتحضير نسيج الحرير.

الكلمات المفتاحية: أزالة اللكنين، الحرير الصناعي، اذابة الياف السليلوز، الياف السليلوز، كاشف فنتون.

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INTRODUCTION

Rayon is the oldest commercial manmade fiber. It was created from cellulose, the stringy material in plants that gives them their structure and quality. Cellulose which separated from wood is a noteworthy huge segment of rayon. Therefore, day after day the importance of lignocellulosic material was increased as an important source of sustainable energy and platform of chemicals. Furthermore, this source has significant importance in the pulping and textile industries (4). Several plants were used as sources for the synthesis of rayon, such as linter of cotton, bamboo and wood (8). Raw materials used in clothes industries are classified into plant materials, animal materials and industrial materials. The most common of these materials are cotton, linen, silk, wool, nylon and polyester (12). Due to the increasing demand for raw materials for the textile industry, many attempts were made to find alternatives that are characterized by abundance and high quality, therefore rayon was produced as an alternative to silk, which is cheaper and more available. In this study, the selection of date palm fronds was mainly due to two reasons. First, the local availability of a large number of date palm trees. Second, the palm fronds (stalks and leaves) contain a high percentage of cellulose materials reaching to about 52% which is important for the synthesis of rayon. Despite the availability of the large quantities of cellulosic fiber, the liberalization process fiber from lignocellulosic material and molding are still difficult. This is because of the influence of two other major wood fiber components; hemicellulose and lignin. To produce rayon, three main steps must be carried out; first is removing lignin and hemicellulose by delignification and bleaching process. The second step is dissolving cellulose fiber via appropriate dissolution process since the main component in biomass was cellulose which is only converted to rayon. The third step is spinning the dissolved cellulose in acid solution. Rayon historical development began with an "artificial silk" theory since natural silks were more expensive and incredibly tedious to produce. Many attempts, conducted to produce rayon, began from ***cotton linter*** because of a high content of cellulose. Cotton is composed of 87 -90% cellulose fibers which were polymer chains in both amorphous and crystalline forms. Although cotton linter contains a high percentage of cellulose; however, the yearly quantity of cotton linter produces an insufficient amount of rayon for consumer demand (6). Rayon also was produced from ***wood pulp*** by several chemical and manufacturing techniques. In 2002, rayon was manufactured from ***bamboo***, the plant which is widely available in China, and distributed to companies worldwide (16).

MATERIALS AND METHODS

In this section, the steps are divided into three sections. The first section is concerned with determination of the compositional analysis of date palm fronds (leaves and stalks). The second section deals with the delignification using modified organosolv pretreatment with and without catalyst while the last section discusses the dissolving of cellulose by sodium hydroxide (NaOH) method dissolution which leads to the production of rayon.

First: Composition analysis of date palm fronds

The composition of date palm fronds or other sources of lignocellulosic biomass are varying according to; the place where it will be growing, season and the part of the plant from which the samples are taken (1). The composition of biomass were measured such as the content of moisture, ash, lignin, extractive, protein and carbohydrate were determined according to National Renewable Energy Laboratory (NREL) LAPs for compositional analysis.

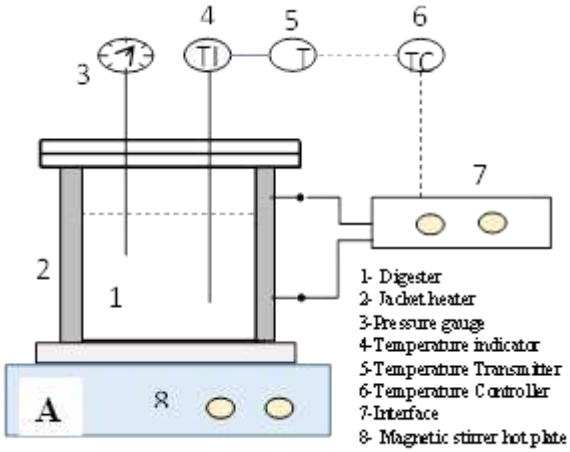
Second: Delignification of date palm fronds

The delignification process changes the biomass by hydrolysis of hemicellulose and cellulose. Potential targets include removal of lignin and disruption of the crystalline structure of cellulose. This process achieved with stainless steel reactor.

Description of the reactor

Two liters' stainless steel digester was used in this study with 11 cm in diameter and 21cm length. The reactor was heated from the side through a jacket-type heater, while heated from the bottom by magnetic stirrer hot plate as shown in (Fig. 1). The reactor was provided with a thermocouple equipped with a

temperature controller to control the temperature inside the reactor. The pressure of the digester was indicated using a pressure gauge.



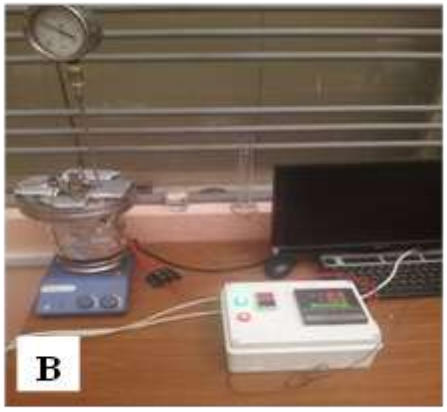


Fig. 1. A: Schematic diagram of the reactor. B: The reactor and its components used in experiments

Organosolv method

Several types of delignification of lignocellulose were investigated such as microwave irradiation, steam pretreatment, liquid hot water, etc.(19). In this study, modified organic solvent (organosolv) method was applied to remove high lignin content in the date palm fronds. In this process, solvent (organic)-water is brought into contact with the lignocellulosic biomass at high temperature, using the stainless steel reactor (digester). Three variables were studied in this process: temperature, the ratio of ethanol to water and digestion time. Statistical experimental design type Central Composite Design (CCD) has been used to find a mathematical relationship between the variables and the remaining lignin percent as a dependent variable. The date palm fronds (biomass) were milled to about 0.18mm. A suspension of biomass-water-organic solvent (ethanol) was made (typically, 200 ml solvent per 20 g biomass). The effect of ethanol solvent is to hydrolyze lignin in the sample but has no effect on cellulose (15). In order to show the effect of catalyst, some experiments were conducted with adding catalyst and the other experiments without catalyst(control). This suspension was heated to a specific reaction temperature (in the range 150 -200^{o}C) while being stirred. This suspension was then kept at its set point during a certain reaction time (typically, 60 min) and subsequently cooled down. After filtration of the resulting slurry, the solid residue was washed with an identical organic solvent-water mixture and dried at 105^{o}C. From the filtrate solution, samples were taken for ultraviolet (UV) analysis.

Bleaching

Bleaching is a chemical process carried out on various types of wood pulp to remove the color of the pulp, so that it becomes white. The goal of bleaching chemical pulps is to remove essentially all of the residual lignin; hence the process is often referred to as delignification (10). Chlorine is the basis for the most common bleaching process**.** Three grams of dried sample was weighted and put into 500 ml flask, then 250ml of sodium chlorite solution (60 g/l sodium chlorite and 60 g/l sodium acetate) was added, the sample was soaked for four days (18). Then it was washed with distilled water for several times, followed by treating with 0.15 N NaOH twice and then washed with hypochlorite and distilled water thoroughly. Finally, the sample was freeze-dried. It was noted that the color was changed from dark brown to white as shown in (Fig. 2).

Fig. 2. A: The sample before bleaching .B: The sample after bleaching

Third: Dissolving of cellulose fiber and synthesis of rayon

Dissolving of cellulose fibers is a kinetic process where the forces that maintain the crystalline structure are overcome and lead to the disintegration of the structure of molecules (3). Forces include hydrogen bonds within the chain (intramolecular) and adjacent chains (intermolecular), as well as van der Waals forces and hydrophobic forces (17). Decomposition occurs when such a solvent is introduced into a polymer that is able to disturb the interplay between polymer molecules.

Dissolution using NaOH method

Fenton's reagent and preparation: Fenton's reagent is a solution used to oxidize contaminants or wastewaters which consist of ferrous iron (as a catalyst) with hydrogen peroxide. The traditional Fenton's reaction is the catalyzed decomposition of dilute hydrogen peroxide (H_2O_2) by iron (II) to form radicals of hydroxyl (11). In the 1890s, it was developed by Henry John Horstman Fenton as an analytical reagent.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \bullet OH + {}^{-}OH \quad \ldots\ldots\ldots (1)$$

$$H_2O_2 + Fe^{3+} \rightarrow HOO\bullet + H^{+} + Fe^{2+} \quad \ldots\ldots (2)$$

It can be prepared by: (80mM H_2O_2, 0.5mM $FeSO_4$, 10mM oxalic acid, 10mM sodium oxalate) by mixing between oxalic acid and sodium oxalate according to the following volume ratio: (1:13) to reach pH= 4.6-5 (22). Solutions of sodium hydroxide were prepared with different concentrations (4%, 6%, 8%, 10% and 12%) weight percent. For example, to prepare 4%, 4 g of NaOH is completed to 100 ml by adding 96g distilled water. The bleached sample was treated with Fenton's reagent by taking 0.2 g of the sample (mainly cellulose) with 10 ml reagent. Then placed in a plastic container (30 ml volume) and stirred for 24 hr using magnetic stirrer (21). After that, the sample was washed with deionized water and dried for 8 hours at 50 ^{o}C as shown in the (Fig. 3).

Fig. 3. The sample after treatment with Fenton's reagent

The treated sample was placed in a test tube and 10 ml of NaOH solution was added. The sample was left for 1 hr, then placed in a plastic container which contains ethyl glycol (38%) and put in the freezer for 24 hrs. The sample was removed from the freezer and left at least one hour at room temperature to melt it. Then the sample was centrifuged at 2500 rpm to separate the dissolved fibers from those undissolved. Undissolved fibers were washed with distilled water and weighted to calculate dissolution percent as Eq. (3).

$$\text{Cellulose dissolved}\% = \frac{C_b - C_a}{C_b} \times 100 \ldots (3)$$

C_b: Cellulose before dissolution.

C_a: Cellulose after dissolution

The dissolved fibers were injected in 10 % dilute sulphuric acid to form rayon, as shown in the (Fig. 4).

Fig. 4. Rayon production using NaOH dissolution

RESULTS AND DISCUSSION

The results are divided into three sections. The first section is concerned with the results of the compositional analysis of date palm fronds (leaves and stalks). The second section deals with the results of delignification using modified organosolv pretreatment with and without catalyst while the last section discusses the results of dissolving cellulose by sodium hydroxide (NaOH) dissolution method which lead to the production of rayon

Compositional analysis of biomass

The compositions of date palm fronds (leaves and stalk) were determined according to National Renewable Energy Laboratory (NREL) (11). In the laboratories of biochemical engineering department / engineering college. (Table 1) shows the composition of fronds (leaves and stalks).

Table 1. The compositions of date palm fronds (leaves and stalk) based on dry weight

	Weight %, based on (dry basis)				
Sample	**Carbohydrate**	**lignin**	**Ash**	**Extractive**	**Protein**
Leaves	**51**	**27**	**8**	**10**	**4**
stalks	**59**	**23**	**7**	**8**	**3**

From (Table 1), it is noted that there is a relatively high percentage of carbohydrates in date palm fronds; this enhances the possibility of producing rayon from it.

Delignification (organosolv method)

Three parameters have been studied in the delignification process; (temperature, ethanol/water ratio and digestion time) with respective ranges (150-220) ^{o}C, (20-80) wt/wt and (20-80) min. The boundaries values of parameters were selected according to perceives work in the literature (20) Seventeen experiments were conducted in this study with the parameters values selected according to the statistical experimental design type central composite design (CCD). The experimental values were shown in (Table 2). The percent absolute error was calculated by Eq. (4).

$$|Error\ \%| = \frac{|\text{Experimental} - \text{Predicted}|}{\text{Experimental}} \text{x}100\%. \quad (4)$$

For example, for one run $|Error\ \%| = \frac{|3-3.31|}{3} \text{x}100\% = 10.3$

Table 2. Experimental parameters which studied in the delignification process.

Runs	Temperature ^{o}C	Ratio Ethanol :water wt/wt	Time min	Lignin % content		Percent absolute error
				experimental	predicted	
1	**185**	**50**	**80**	**3**	**3.31**	**10.3**
2	**150**	**50**	**50**	**9**	**9.6**	**6.67**
3	**205**	**67**	**67**	**5.5**	**5.17**	**6**
4	**164**	**67**	**32**	**12.5**	**11.92**	**4.64**
5	**185**	**50**	**50**	**6**	**6.17**	**2.83**
6	**185**	**80**	**50**	**8**	**8.81**	**10.1**
7	**220**	**50**	**50**	**5.5**	**5.8**	**5.45**
8	**185**	**20**	**50**	**10**	**10.09**	**0.9**
9	**164**	**32**	**32**	**11.5**	**11.15**	**3.04**
10	**164**	**67**	**67**	**6.8**	**6.27**	**7.79**
11	**185**	**50**	**20**	**8**	**8.59**	**7.38**
12	**164**	**32**	**67**	**6**	**5.85**	**2.5**
13	**185**	**50**	**50**	**6.2**	**6.17**	**0.48**
14	**205**	**32**	**32**	**8**	**7.86**	**1.75**
15	**205**	**32**	**67**	**7.5**	**7.41**	**1.2**
16	**185**	**50**	**50**	**6.3**	**6.17**	**2.06**
17	**205**	**67**	**32**	**6.5**	**5.97**	**8.15**

A second – order polynomial correlation was obtained as shown in Eq. (5). The coefficients of (Eq. 5) can be determined using computer software (Design Expert)

$$y = 6.17 - 1.10\ X_1 - 0.37\ X_2 - 1.53 X_3 - 0.66\ X_1 X_2 + 1.21\ X_1 X_3 - 0.088\ X_2 X_3 + 0.5\ X_1^2 + 1.09\ X_2^2 - 0.072\ X_3^2 \quad \ldots (5)$$

Where

B0, B1, B2…B9 are coefficients of Polynomial equation

X_1, X_2 and X_3 are the real variables (X_1: temperature, X_2: ethanol/water ratio, X_3: Time)

y is the remaining lignin percent

Correlation coefficient = 0.9681
Relative standard deviation = 3.6

Effect of temperature and ethanol/ water ratio on lignin content

According to the mathematical model of (Eq. 5) the effects of temperature and ethanol/water ratio were studied at a certain time. Figure (5) shows the contours of lignin percent content at different values of temperature and ethanol/water at constant time 20 min. Minimum value of lignin percent contained was 6.89% which was obtained at the lowest temperature of 191^{o}C and solvent ratio (ethanol: water equal to 50:50 wt/wt). Decreasing the temperature below 191^{o}C will led to increase the value of lignin% content in the sample. This is because decreasing the temperature will prevent full fractionation of lignocellulosic material and then the lignin percent will increase at temperature below 180^{o}C.

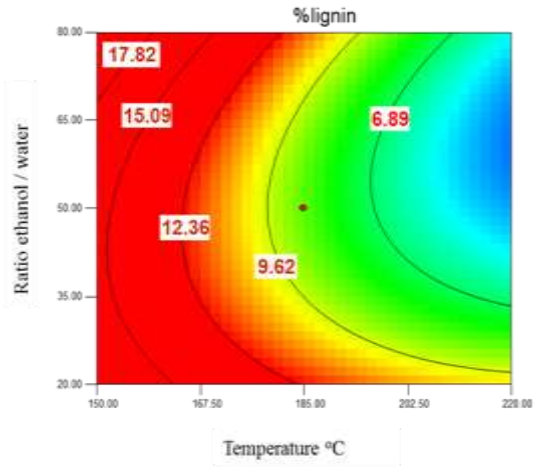


Fig. 5. Effect of temperature and ethanol/water ratio on lignin percent at constant time 20 min

Figure (6) shows the effect of temperature and ethanol/water ratio on the lignin percent content at constant time 50 min. The best lignin percent lie on contour 6.11% which was obtained at lowest temperature 185^{o}C and ethanol: water ratio at 50:50. On comparison with figure (5) at constant time 20 min, it can be concluded that increasing digestion time leads to decrease the temperature as well as improve the removal of lignin. Although increasing temperature will lead to decrease the lignin content, but it is not recommended to exceed the digestion temperature above 185^{o}C because many changes will happen to the cellulose structure and destroy it (25).

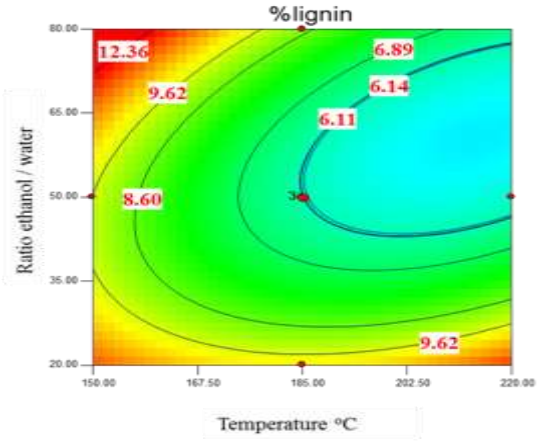


Fig. 6. Effect of temperature and ratio on lignin percent at constant time 50 min

Figure (7) shows that best lignin percent content (3.08%) was obtained using digestion time 80 min at temperature is 185^{o}C and solvent ratio of 50:50. So this is the optimum operating condition for lignin removal.

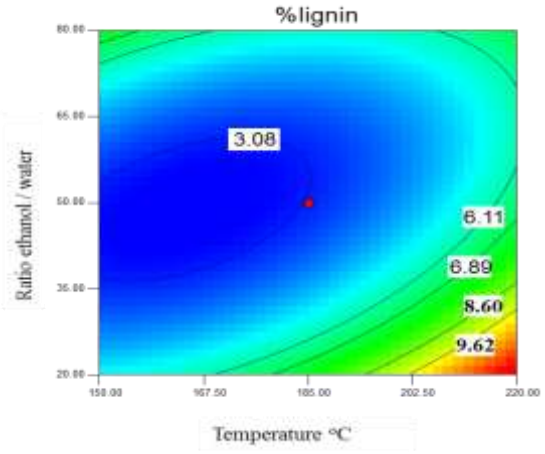


Fig. 7. Effect of temperature and ratio on lignin percent at constant time 80 min

Effect of using Catalyst

The time of digestion is very important parameter in a delignification process and time 80 min gave perfect lignin percent content, but this time is too long therefore; a possibility to improve the organosolv process might be the application of a catalyst. In the literature catalysts were used with concentration of 0.025M for each of H_2SO_4 and NaOH and 0.05M for Ca (OH) $_2$. The experiments were conducted at 180^{o}C and ratio of ethanol: water equal to 50:50. Figure (7) shows that the treated sample without catalysts gave 3% lignin content and 80 min digestion time, while all catalysts reduced the digestion time to 30 min, but lignin percent content was

minimum (3%) when using NaOH as shown in Figure (8).

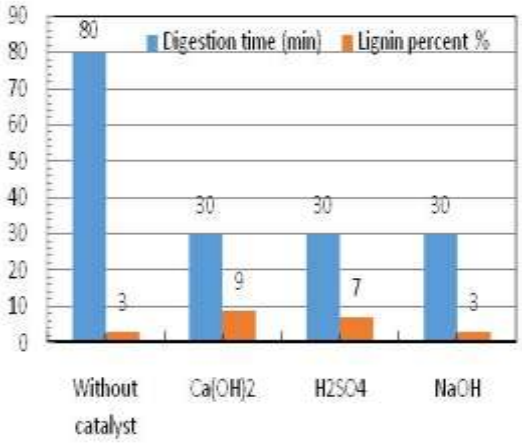


Fig. 8. Effect of different catalysts on lignin percentage content. Conditions are 185°C, and ratio ethanol: water = 50:50

Cellulose dissolution

Three parameters were studied in the dissolution process; sodium hydroxide concentration, path cooling temperature and Fenton's reaction time. The ranges of these parameters were (4 %-12%) weight percent, two temperatures (-15 and -20) °C and (1-48) hours respectively (26). Two types of samples were used; sample was treated with reagent and a sample without treatment. Experiments were repeated four times and average values of cellulose dissolution were taken

Effect of Fenton's reaction treatment

To study the effect of Fenton's reagent, use on cellulose dissolution, several values of Fenton's reaction time were studied within the range (1-24) hr. Fenton's reaction produces radicals which break the hydrogen bonds for cellulose and make it ready to dissolve in NaOH solution. From (Fig. 9) it was concluded that cellulose dissolution increased with increasing time until time 24 hr, beyond which the solubility of cellulose fibers begin to decrease. This is because the structure of cellulose fibers distorted and leads to decrease dissolution of cellulose fibers. The optimum value of cellulose dissolution was 30 wt % which occurred at reaction time 24hr. Budtova and Navard studied the dissolution of cellulose fibers for cotton and found that the perfect Fenton's reaction time was 18 hr to give maximum cellulose dissolution of 23% (5).

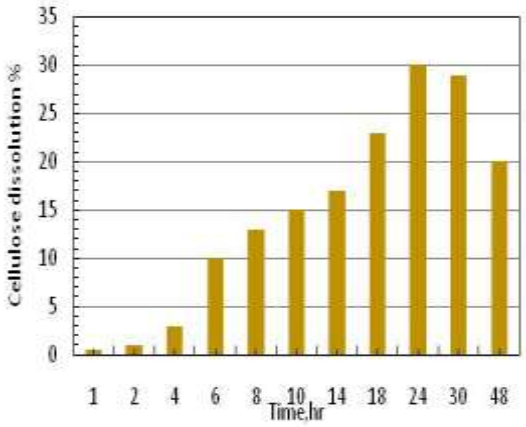


Fig. 9. Effect of Fenton's reagent duration on cellulose dissolution.

Effect of NaOH concentration

To study the effect of alkaline concentration for cellulose dissolving, four values of concentration were taken (4%, 6 %, 8 % and 12 wt %). Two sets of experiments were conducted. In the first set, the samples were treated with Fenton's reagent for 24 hr while in the second set the samples were untreated. (Fig. 10) shows that for both sets at (-15°C) , the best value of NaOH concentration was 8% which causes cellulose dissolution of 30 wt% for samples treated with Fenton's agent and 23% for samples untreated. Wang (25) studied cellulose dissolution for cotton linter (as a cellulose fibers source) using NaOH solution with different concentrations and different cooling bath temperatures and found that the best cellulose dissolution percent was 20 wt% when using 9 wt% NaOH concentration

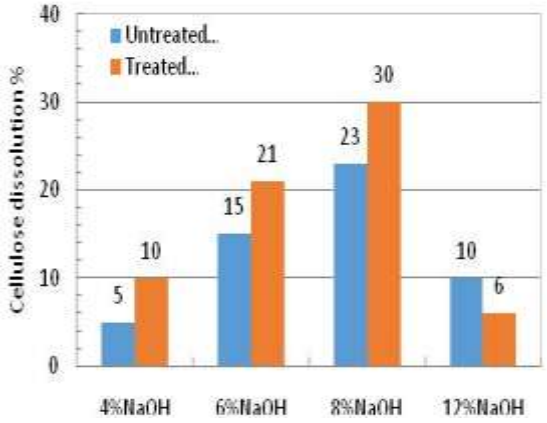


Fig. 10. Percentage of cellulose dissolution at different NaOH weight concentrations at temperature - 15 ±2°C

The same two sets of experiments were conducted at -20°C. Figure(11) shows that the best cellulose dissolution for the sample treated with Fenton's reagent was 42% which

occurred also at 8% NaOH concentration while for untreated sample the maximum cellulose fibers dissolution was 28% this implies that decreasing the temperature to -20°C will enhance the solubility of cellulose in NaOH solution.

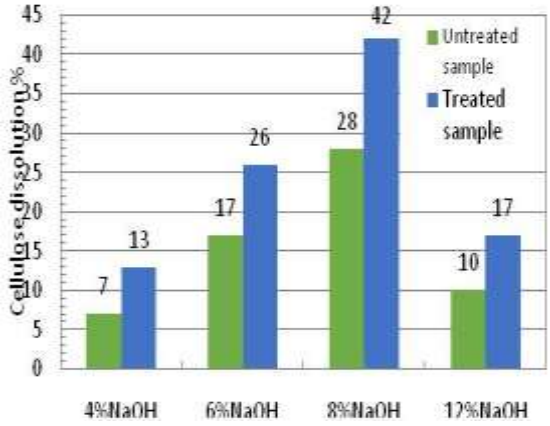


Fig. 11. Percentage of cellulose dissolution at different NaOH weight concentrations at temperature -20 ±2°C

From figures (10and 11), it was concluded that the best NaOH concentration for cellulose dissolution process was 8%. Furthermore, the samples treated with Fenton's reagent show better dissolution in NaOH solution the untreated ones. Figure 12 illustrates how the hydrodynamic of hydrate ions was affected by the concentration of ion solution. At low solution concentration, the ions are surrounded by a large amount of water molecules and thus pairs of separated ions are existing. At high solution concentration, the ions will be surrounded by fewer amounts of water molecules resulting in lower hydrodynamic diameter. The cellulose crystallite diameter is 10 nm and inter-sheet distance is of about10 Å (24). At low concentration of NaOH, the hydrodynamic diameter is too large to penetrate cellulose crystalline region, while at high NaOH concentration the hydration of NaOH will be insufficient to break hydrogen bonding which makes the cellulose to mercerize (not dissolved). Therefore; there is a certain concentration of NaOH solution which is appropriate to penetrate the cellulose and start to dissolution. This value of concentration is called turn point concentration (critical concentration) (2). In the current study, it was found that the turn point concentration was 8%. This finding is agreement with that found by Wang (25) who found that the turn point concentration of cellulose (cotton linter) was 9%.

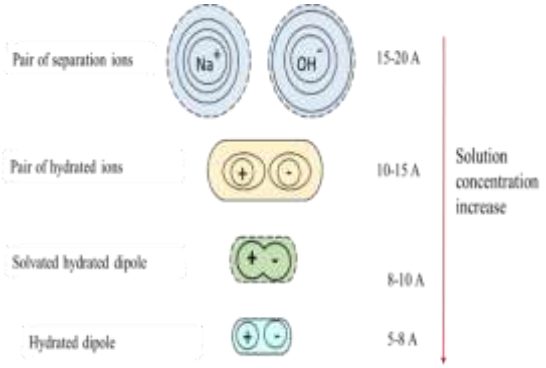


Fig. 12. Hydrodynamic diameter of hydrates with respect to NaOH solution concentration (23).

3.1.3 Effect of temperature

With a view to study the effect of temperature on solubility of cellulose fiber, two values of temperatures were used (-15 °C and -20 °C) depending on previous studies (7, 14). Figure (13) shows that at -20 °C, the best cellulose dissolution for sample treated with Fenton's reagent was 42% and for untreated sample the maximum cellulose fibers dissolution was 28%. While at temperature (-15°C), the cellulose dissolution percent was 30 % for treated sample and 23% for untreated sample. This implies that decreasing temperature to (-20 °C) will enhance the solubility of the cellulose in NaOH solution

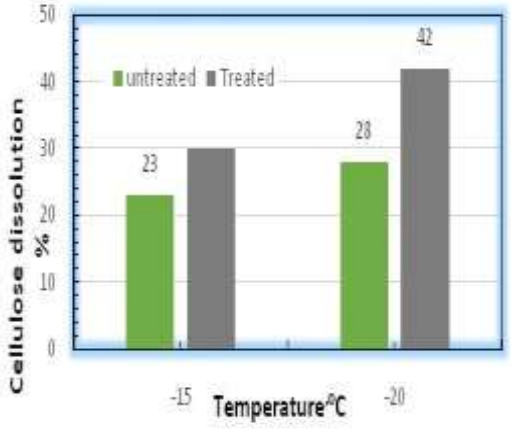


Fig. 13. Effect of temperature on cellulose dissolution at 8% alkaline solution

Effect of urea addition

The effect of adding urea in NaOH solution on cellulose fibers dissolution was studied, a solution of NaOH and urea with proportion (6%NaOH and 4% urea) was used to enhance cellulose fibers dissolution or stimulate crystalline polymerization (15).Figure (18) shows that at temperature -15°C the maximum

cellulose fibers dissolution was 62% for the samples treated with Fenton's reagent and 35% for untreated ones. Figure (15) shows the results of cellulose dissolution at temperature -20^{o}C. For the sample treated with Fenton's reagent the maximum cellulose fibers dissolution was 35% while for an untreated sample was 28%. These results for treated samples indicate that adding urea will increase the solubility from 30% to 62% at (-15^{o}C) while at (-20^{o}C) adding urea will decrease the cellulose fibers dissolution from 42% to 35%.

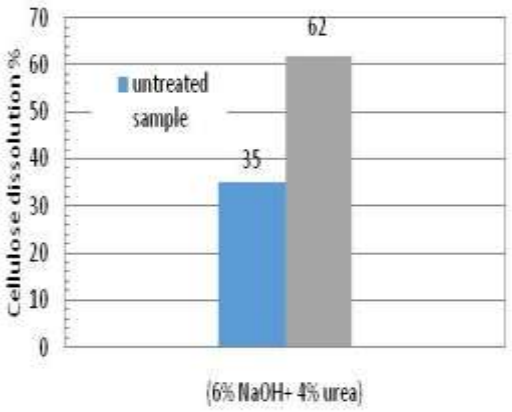


Fig. 14. Effect of urea addition on cellulose dissolution at temperature - 15 ±2^{o}C

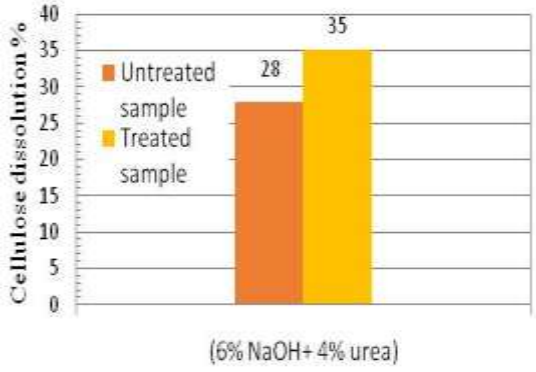


Fig. 15. Effect of urea addition on cellulose dissolution at temperature -20 ±2^{o}C

The cellulose fibers dissolution is a thermodynamic process and can be represented by Gibbs free energy equation:

$\Delta G = \Delta H - T.\Delta S$…… (6)

For cellulose dissolution process (breaking cellulose crystal) with NaOH solution without urea, values of entropy and enthalpy change are -2.23 kJ /mol K and -495.48 kJ /mol respectively. While for the treatment with NaOH and urea, values are -0.546 kJ /mol K and -61.83 kJ /mol respectively (14). At temperature 258 k (-15^{o}C), ΔG=80.55 kJ /mol for treatment without urea and ΔG=79.01 kJ /mol for treatment with urea. The decrystallization reaction is exothermic because of the negative value of enthalpy so lower temperature is favorable. Figure (16) shows the plot of Gibbs free energy verses temperature for dissolution of cellulose by NaOH solution with and without urea. The two straight lines intersect at temperature 258k (-15^{o}C). At temperature greater than 258K (-15^{o}C), the treatment with NaOH and urea solution has lower ΔG than that without urea which is better for decrystallization reaction. While at temperatures less than 258k (-15^{o}C) NaOH without urea has lower ΔG so it is better for decrystallization. In the current study the lowest temperature was 253K (-20^{o}C).

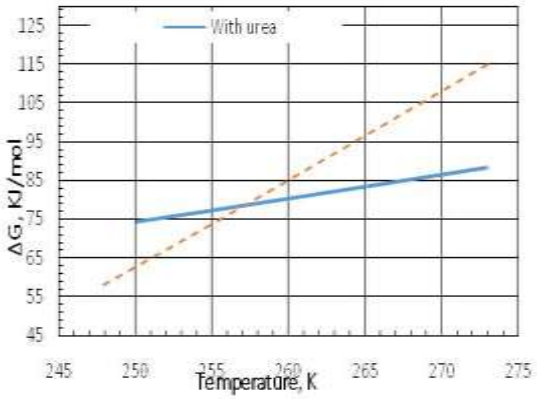


Fig. 16. Gibbs free energy for cellulose dissolution by NaOH with and without urea (25).

In this study; date palm fronds analysis, delignification, cellulose dissolution and rayon production were investigated. The most important conclusions are: There is a possibility to delignify the date palm fronds using modified organosolv method in which the lignin is destroyed by solvent and temperature. The more effective parameters in the delignification process were: temperature, ethanol /water ratio and digestion time. The optimum conditions for the delignification process were: temperature 185^{o}C, ethanol: water 50:50 and digestion time 80 min. Design of experiments (DOE) program using Central response technique has been used to find a mathematical relationship between these three variables and the independent variable, remaining lignin % in the sample. A second – order polynomial correlation was obtained as shown in Eq.(5):

$y = 6.17 - 1.10\ X_1 - 0.37\ X_2 - 1.53 X_3 - 0.66\ X_1 X_2 + 1.21\ X_1 X_3 - 0.088\ X_2 X_3$

$+0.51\ X_1^2+1.09\ X_2^2- 0.072\ X_3^2$ …(5)

In order to modify organosolv, sodium hydroxide (0.025M) was used as catalyst which reduces the digestion time from 80 min to 30 min. Sodium hydroxide dissolution is used to dissolve pure cellulose in a short time. The optimum NaOH concentration was found to be 8% and reaction temperature -20^{o}C. The cellulose dissolution is affected by different parameters; temperature, sodium hydroxide concentration, and the addition of urea. The addition of urea to sodium hydroxide (4 % urea and 6% NaOH) to reduce the reaction temperature from -20^{o}C to -15^{o}C.

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