Extraction of palm tree cellulose and its functionalization via graft copolymerization

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ABSTRACT

The work in this paper was planned with the aim of extracting the cellulosic component of palm tree waste and functionalizing this cellulose through graft copolymerization with acrylic acid. The cellulose extraction included hot alkali treatment with aqueous sodium hydroxide to remove the non-cellulosic binding materials. The alkali treatment was followed by an oxidative bleaching using peracid/hydrogen peroxide mixture with the aim of removing the rest of non-cellulosic materials to improve the fiber hydrophilicity and accessibility towards further grafting reaction. Optimum conditions for cellulose extraction are boiling in 5% (W/V) NaOH in a material to liquor ratio of 1:20 for 1 h then bleaching with 60 ml/l bleaching mixture at initial pH value of 6.5 for 30 min. The pH of the bleaching medium is turned to the alkaline range 11 and bleaching continues for extra 30 min. Graft copolymerization reaction was initiated by potassium bromate/thiourea dioxide redox system. Optimum conditions for grafting are 30 mmol of potassium bromate, 30 mmol of thiourea dioxide and 150 g of acrylic acid (each per 100 g of cellulose). The polymerization reaction was carried out for 120 min at 50 °C using a material to liquor ratio of 1:20.

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1. Introduction

Although bleaching of palm tree cellulose is to great extent the same as that of textiles based on cotton fiber, one has to consider two main factors in extraction and bleaching of palm tree cellulose. First, empty fruit bunch possesses ca. 17.2% lignin, 70% holocellulose, 42% alpha cellulose, 17.2% NaOH-soluble materials, 2.8 hot water-soluble materials and 0.7% ash content [1]. This is different from cotton, which acquires only 5% impurities, and the rest is α-cellulose. Second, empty fruit bunch is to some extent more sensitive to alkaline and oxidative treatments when compared to cotton fiber. In general, lignocellulosic fibers like flax, jute, bagasse, woody fibers contain various non-cellulosic materials like waxes, lignin, fats, pectins and naturally occurring colorants; etc. Removing of these impurities, efficiently through the successive preparatory steps scouring and bleaching treatments is a must to guarantee successful further processing [2–9]. Recently, there is much emphasis on the concept of energy conservation and accordingly, researchers made many different approaches to reduce the energy consumption during the successive processes involved in cellulose fibers pretreatments [10–12]. One important approach is activation of bleaching agents with different chemicals to increase

its efficiency and oxidation potential [13–22]. In recent years, much research has been devoted for production of the industrial raw materials from the agricultural and industrial processing wastes in order to secure cheaper costs [23–33]. The agricultural residues such as rice straw, sugar cane bagasse, cotton stalks, corn stalks, jute waste fibers, palm tree wastes and flax shaves are available as a vast reservoir of potentially available raw material. These residues can be subjected to pulping by the alkali boiling and the obtained cellulosic pulps are further functionalized and utilized as useful industrial products.

One of the most famous approaches to synthesize new materials is the graft copolymerization technique, where synthetic polymers have definite desired performance properties are grafted onto natural polymers, which may have lack in these properties, but have another desired properties. This graft copolymerization gather the desired properties of both polymers resulting in formation of new material with improved functional properties [34]. The most common way to prepare these graft copolymers is the redox initiation method [35–45], grafting assisted with microwave irradiation [46,47], γ-ray irradiation-initiated grafting [48–50], electron beam-initiated grafting [51–54] and many other different grafting techniques [55,56].

During this work extensive experimental work was planned to find the most suitable conditions to scour and bleach empty fruit bunch as part of palm tree wastes, taking into account the quality of bleached empty fruit bunch from the molecular weight point

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of view, the cost and the environmental impact of the bleaching process. The first part of the experimental activities in this work include the utilization of peracetic acid as bleaching system to clean up empty fruit bunch and make it accessible for further chemical modification. This part of the work involves firstly studying the factors affecting the bleaching process e.g. cooxidant concentration, duration, pH and bleaching medium temperature. Second monitoring the decomposition rate of the oxidant (peracetic acid and hydrogen peroxide), and this is achieved by estimating the decomposed percent of the oxidant throughout the reaction period. Third evaluation of the treated samples via determining the whiteness index, percent weight loss, carboxyl content and carbonyl content. The second part of the experimental activities includes functionalization of the bleached empty fruit bunch cellulose via graft copolymerization with acrylic acid to increase its carboxyl content. This requires studying the factors affecting the graft copolymerization reaction, like effect of initiator components concentrations potassium bromate and thiourea dioxide, acrylic acid concentration, material to liquor ratio and polymerization temperature. Finally the so prepared poly(acrylic acid)/cellulose graft copolymer is evaluated via following up the percent total conversion and calculating the graft yield.

2. Experimental

2.1. Materials and chemicals

Empty fruit bunch was collected from palm tree farm. Hydrogen peroxide, sodium hydroxide, glacial acetic acid, sodium carbonate, sulfuric acid, potassium permanganate, potassium bromide, potassium iodide, potassium bromate, thiourea dioxie, acrylic acid and sodium thiosulfate were all laboratory grade chemicals. The non-ionic wetting agent Texazym T was kindly supplied by Inotex Company.

2.2. Methods

2.2.1. Alkaline treatment of empty fruit bunch wastes

Sodium hydroxide solution was used to extract noncellulosic binding materials from empty fruit bunch composition. For this purpose, empty fruit bunch wastes were well air dried in sunny area. Then the empty fruit bunch wastes are finely grinded in an ordinary mill (Fig. 1).

After grinding, the empty fruit bunch wastes were treated, separately with sodium hydroxide solutions having concentrations ranging from 0.5% to 10% (W/V) and 2 g/l non-ionic wetting agent. The system was boiled under reflux for 60 min using the material to liquor ratio 1:20. At this end, the treated samples were removed from the alkaline solution by filtration, washed several times with hot distilled water, rinsed several times in cold distilled water until the rinsing water becomes neutral and finally dried in open air.

2.2.2. Preparation of the bleaching agent

Peracetic acid was prepared according to a reported method [57], that glacial acetic acid (0.5 mol) was mixed with concentrated sulfuric acid (0.375 mol) and the resulting mixture was allowed to cool to reach 0 °C. This cold acids mixture was then added, dropwise to hydrogen peroxide solution, so that the final reaction volume does not exceed 100 ml and at the end of addition, the system temperature was raised to 25 °C and maintained at this temperature for 90 min. The progress in the reaction of peracid formation was monitored by withdrawing samples from the reaction medium at different time intervals and estimating the amounts of consumed hydrogen peroxide and formed peracid throughout the reaction duration.

2.2.3. Bleaching

Alkali treated empty fruit bunch was treated with a bleaching liquor containing varying concentrations from the freshly prepared peracid mixture (20–120 ml/l) together with 2 g/l nonionic wetting agent. The bleaching reaction was allowed to proceed for different durations (15–240 min) and the bleaching runs were carried out at different pH values, which were initially adjusted by addition of sodium carbonate. Other bleaching trials were carried out at different reaction temperatures ranging from 30 °C to 70 °C, by use of material to liquor ratio 1:30.

The percent decomposed peracetic acid and hydrogen peroxide was followed up by estimating the residual peracid and hydrogen peroxide concentration throughout the reaction duration [58]. At the end of the bleaching reaction, the bleached samples were removed from the bleaching liquor by filteration and washed several times with hot water then rinsed thoroughly with cold water and finally dried in open air.
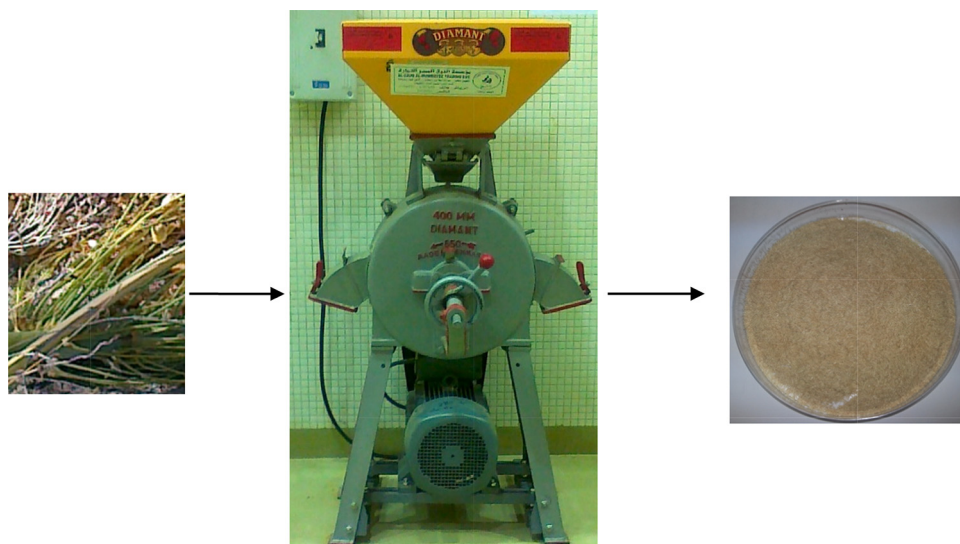

Fig. 1. Grinding of empty fruit bunch.

2.2.4. Graft copolymerization

Unless otherwise reported, poly(acrylic acid)/cellulose graft copolymer was prepared by the free radical polymerization, that empty fruit bunch was dispersed in water in a material to liquor ratio of 1:20. The system was stirred and at the same time, the temperature of the system was raised to the predetermined polymerization temperature. After attaining the desired reaction temperature, certain concentration of acrylic acid and the initiation components in aqueous solution were added consequently to the slurry. The polymerization reaction was left running for a duration of 120 min keeping continuous stirring. The residual double bonds were determined throughout the reaction period, from which the extent of polymerization was calculated as percentage total conversion [59].

2.3. Testing and analysis

2.3.1. Percent loss in weight

The loss in weight of empty fruit bunch as a result of scouring and/or bleaching was calculated according to the following general equation:

$$\%\,\text{weight loss} = (W1 - W2) \times \frac{100}{W1}$$

where $W1$ is the dry weight of empty fruit bunch sample before a given treatment and $W2$ is the dry weight of the empty fruit bunch sample after finishing the treatment.

2.3.2. Determination of percent decomposed hydrogen peroxide and peracid

The decomposition of peracid and/or hydrogen peroxide in percent was calculated by quantitative estimation of their concentrations according to a reported method [58].

2.3.3. Determination of degree of whiteness

The whiteness of the bleached empty fruit bunch samples in terms of whiteness index (WI) was measured by use of a Hunterlab Reflectometer (Model D25 M/L-2). The value of WI was calculated mathematically in terms of CIE Y (blue) and (green) reflectance components by applying the equation (ASTM Method E31373).

$$\text{W.I.} = \frac{4Z}{1.18} - 3Y$$

where Z and Y are the device readings.

2.3.3.1. Determination of carboxyl content and carbonyl content.
Reported methods were used to determine the carboxyl content [60] and the carbonyl content [61].

2.3.4. Determination of graft yield

The graft yield (G.Y) was calculated in percent by applying the following equation

$$\%\,\text{G.Y.} = \frac{W2 - W1}{WI} \times 100$$

where $W1$ and $W2$ are the dry weights of empty fruit bunch sample before and after grafting.

3. Results and discussion

3.1. Extraction of cellulose

As already indicated, the major emphasis of the research objective in this paper is concerned with the extraction of cellulose from the empty fruit bunch wastes and then to functionalize this cellulose through grafting with acrylic acid to prepare poly(acrylic acid)/cellulose graft copolymer. To achieve this goal, empty fruit bunch was subjected to alkaline treatment with sodium hydroxide, followed by bleaching with peracetic acid/hydrogen peroxide mixture to extract the cellulosic component. The extracted cellulose was then graft copolymerized with acrylic acid in order to prepare poly(acrylic acid)/cellulose graft copolymer. The reaction in each case was performed under different conditions to find the most optimum conditions for bleaching and grafting. The obtained results together with their detailed discussions are given below.

3.1.1. Alkali treatment of empty fruit bunch wastes

Table 1 shows the effect of NaOH concentration on the extent of impurities removal expressed as percent loss in weight. The alkali treatment was carried out using NaOH solution (0.5–10%) for 1 h. It is observed (Table 1) that, the loss in weight increases sharply with increasing NaOH concentration up to 5%. Increasing NaOH concentration above this limit is accompanied by further increment in the percent loss in weight but to a slower extent. The improvement in the impurities removal by increasing NaOH concentration up to 5% could be interpreted in terms of the increased swellability and in turn, the increased penetration of NaOH from the alkaline solution phase to the bulk of the fiber which leads to dissolution of the impurities. The slower extent of impurities removal at NaOH concentration above 5% reflects the lack of impurities at this limit and that the alkali starts to dissolve low molecular weight cellulosic fragments.

3.1.2. Preparation of peracetic acid

The term peracetic acid is known to be a solution consisting of acetic acid and hydrogen peroxide, in equilibrium state. Peracetic acid is prepared simply by the reaction of glacial acetic acid with concentrated hydrogen peroxide solution in presence of a strong mineral acid (sulphuric acid) as catalyst for removing water. Previous studies [62] which describe peracetic acid preparation by mixing concentrated hydrogen peroxide together with glacial acetic acid, in the presence of sulfuric acid catalyst suggest that the acetic acid is converted partially to peracetic acid according to Eq. (1) and suggest also that the role of sulfuric acid is to aid as an acid catalyst needed for removing water for the reaction to proceed in the direction of peracid formation.

$$H_2O_2 + CH_3COOH \xrightarrow{H_2SO_4} CH_3CO^\bullet O^\bullet OH + H_2O \tag{1}$$

Practically, it is possible to measure and assign exactly the concentrations of peracids in the whole mixture, but yet still the actual distribution of these peracids in the mixture unknown.

3.1.3. Oxidative bleaching treatment

According to the equation of peracid preparation, the peracid is an equilibrium mixture containing peracetic acid, water and hydrogen peroxide. The mechanism of peracetic acid decomposition is

Table 1
Effect of alkali concentration on the percent weight loss of empty fruit bunch.

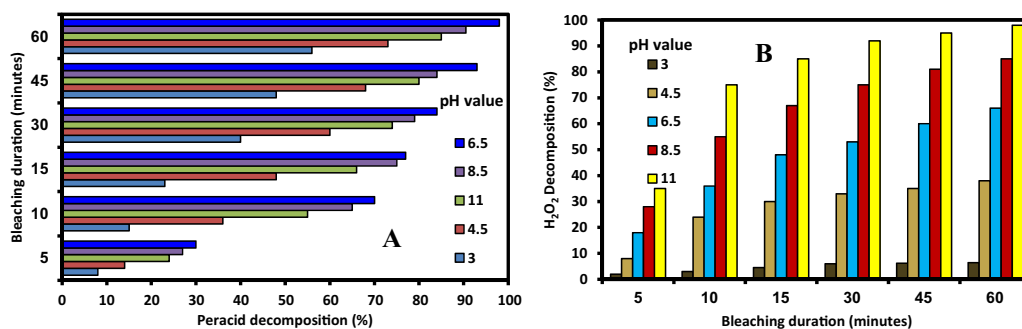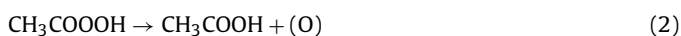| [NaOH], (W/V)	0.5	1	2	3	4	5	6	7	8	9	10
Loss in empty fruit bunch weight (%)	3	3.8	5.4	7.5	9	10	10.3	10.5	10.7	10.9	11.1

Fig. 2. Effect of bleaching medium pH on (A) peracid decomposition, (B) H₂O₂ decomposition.

somewhat the same as that of hydrogen peroxide decomposition as illustrated in Eq. (2).

$$CH_3COOOH \rightarrow CH_3COOH + (O) \qquad (2)$$

All factors which may affect the bleaching of empty fruit bunch cellulose were systematically studied in details. This includes changing the pH of the bleaching medium, changing the oxidant mixture concentration, changing the bleaching temperature and duration.

3.1.3.1. pH of the reaction medium. Fig. 2A and B shows, respectively, the percent decomposed peracid and hydrogen peroxide during the bleaching reaction course, when carrying out the bleaching reactions at different initial pH values. In all these bleaching trials, the same amount of the freshly prepared bleaching solution (60 ml/l) was used and the bleaching was carried out at fixed temperature of 70 °C, by use of material to liquor ratio 1:30 for a duration of 60 min [57].

On the other hand, Fig. 3A and B, respectively, present the total loss in the weight of empty fruit bunch cellulose (both loss due to scouring and that due to bleaching) and the whiteness index, when empty fruit bunch cellulose samples were bleached at different pH values.

Fig. 3C presents the chemical properties of empty fruit bunch cellulose samples subjected to bleaching reaction at different pH values.

It is clear from the data given in the aforementioned figures that the decomposition of both the peracid and hydrogen peroxide is enhanced significantly until a reaction duration up to 20 min, but on the other hand, increasing the reaction duration above this limit is characterized by a slower rate of decomposition for both peracid and hydrogen peroxide. It is also noticed that the decomposition of peracid as well as hydrogen peroxide is pH dependent and that the rate of decomposition for the peracid decrease in the order pH 6.5 > pH 8.5 > pH 11 > pH 4.5 > pH 2.5, while the rate of decomposition for hydrogen peroxide decrease in the order pH 11 > pH 8.5 > pH 6.5 > pH 4.5 > pH 2.5. The data indicate also that maximum percent loss in weight of empty fruit bunch cellulose and maximum improvement in its whiteness index is attained at pH 6.5.

Regarding the chemical properties, carboxyl content and carbonyl content, the data showed remarkable increase in their magnitudes by raising the bleaching medium pH up to pH 6.5, while further increase in the bleaching medium pH beyond this limit was found to have negative effect on both said chemical properties.

Generally and based on the above data, one can conclude that maximum benefit from the bleaching mixture in removing the non-cellulosic impurities and enhancing the fiber chemical properties is obtained by starting the bleaching reaction at initial pH value of 6.5, such that it continues at this pH value up to 30 min. During this 30 min, the peracid works very efficiently at this pH value and

attain percent decomposition of more than 80%, beside about 50% hydrogen peroxide composition. After 30 min, the pH of the bleaching medium is better to be turned to the alkaline range 11, where at this alkaline conditions hydrogen peroxide is known to function
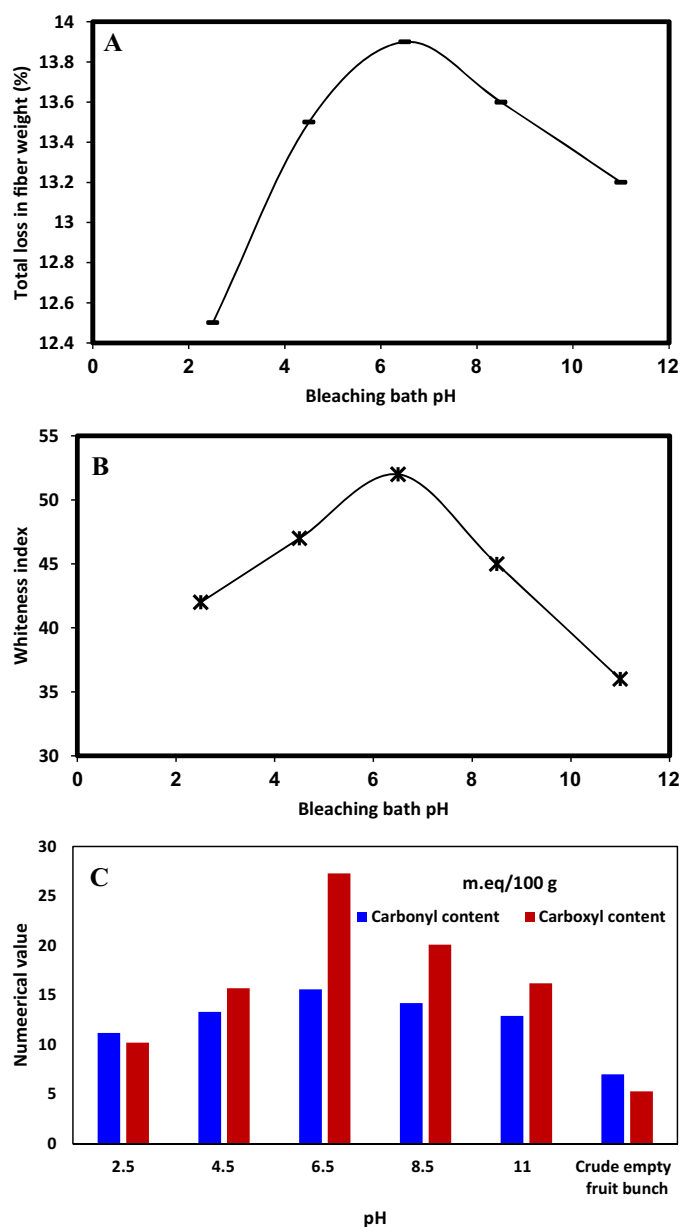

Fig. 3. Effect of bleaching medium (A) weight loss, (B) whiteness index, (C) chemical properties.
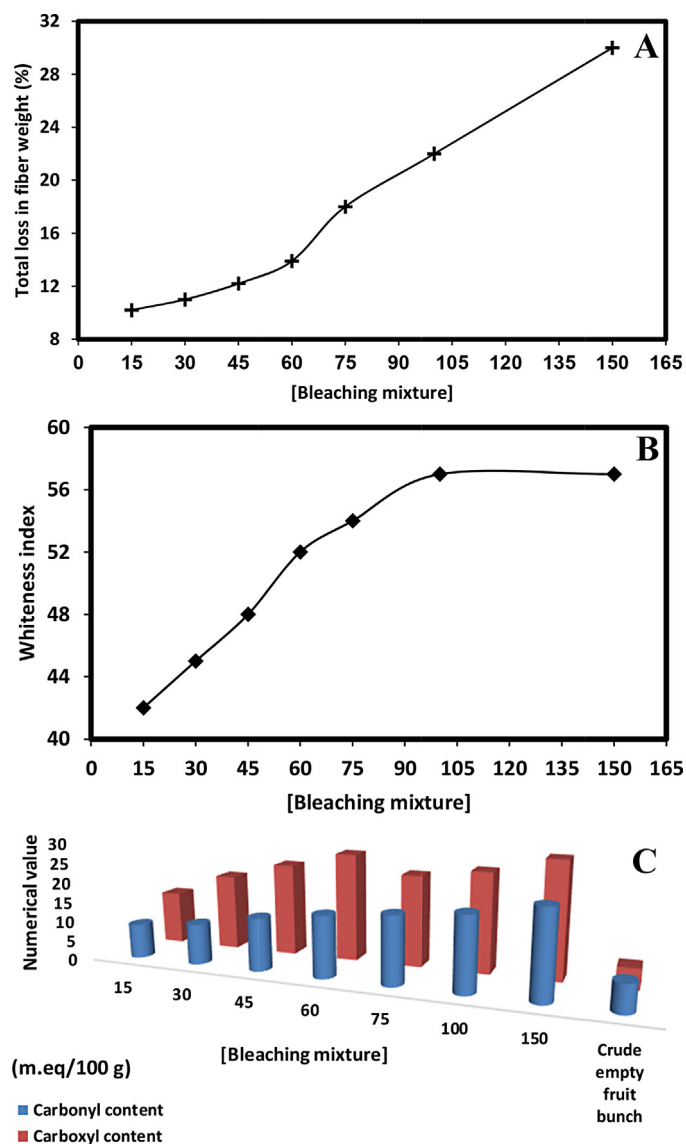
Fig. 4. Effect of bleaching mixture concentration on (A) weight loss, (B) whiteness index, (C) chemical properties.

very effectively and attain a decomposition rate of 100% and also complete the peracid decomposition to 100% [63].

3.1.3.2. Bleaching mixture concentration. Fig. 4A and B shows, respectively, the effect of peracid mixture concentration added to the reaction medium on the loss in weight of empty fruit

bunch cellulose and its whiteness index, while Fig. 4C presents the chemical properties of the bleached empty fruit bunch samples at different bleaching mixture concentrations. The bleaching treatment was carried out for a total duration of 60 min at 70 °C. The pH of the bleaching medium was adjusted initially at pH 6.5 and kept at this value for 30 min then the medium was turned alkaline by raising the pH to 11 and the treatment was prolonged for extra 30 min.

The obtained data for the physiochemical properties reveal that when the concentration of peracid mixture incorporated to the reaction medium increases up to 60 ml/l, this implies to increment in the percent loss of empty fruit bunch weight (Fig. 4A) and whiteness index (Fig. 4B). This is of course in addition to increase in the carboxyl content and the carbonyl content, when compared to the untreated empty fruit bunch samples (Fig. 4C). It is also noted from the recorded data that increasing the peracid mixture concentration above 60 ml/l leads to further increment in the above mentioned properties but this may be on the count of the fiber quality. Based on the above remarks, one can conclude that the optimum peracid mixture concentration to be used in the bleaching reaction to give satisfactory whiteness index together with reasonable loss in empty fruit bunch weight is 60 ml/l.

3.1.3.3. Bleaching temperature. The bleaching treatment was run using 60 ml/l of the peracid mixture at varying temperatures, namely, 30 °C, 50 °C and 70 °C. The bleaching treatment was run for 120 min using a material to liquor ratio of 1:30. The pH of the bleaching medium was adjusted initially at pH 6.5 and the bleaching continues for 30 min, then the medium is turned alkaline at pH 11 and the bleaching continues for extra 30 min. Fig. 5A and B shows, respectively, the rate of peracid decomposition and the rate of hydrogen peroxide decomposition. Fig. 6A, B and C shows the loss in weight of empty fruit bunch cellulose, the whiteness index of the bleached samples and the chemical properties of the bleached empty fruit bunch samples.

The data given in these figures indicate that the increase in the reaction temperature leads to enhancement in the rate of peracid and hydrogen peroxide decomposition, which is reflected on gradual increase in the loss in the weight of empty fruit bunch cellulose, improvement in the whiteness of empty fruit bunch bleached samples and increase in the chemical properties, carbonyl content and carboxyl content.

Based on previous discussion, it is concluded that the optimum conditions for bleaching empty fruit bunch with peracid is to utilize bleaching mixture concentration of 60 ml/l, by use of material to liquor ratio 1:30 at 70 °C. pH of the bleaching bath is better to be adjusted at pH 6.5 and bleaching continues for 30 min at this pH value, where peracid functions very well in this pH range. The bleaching medium is turned alkaline at pH 11 and the bleaching reaction is allowed to proceed for extra 30 min, where
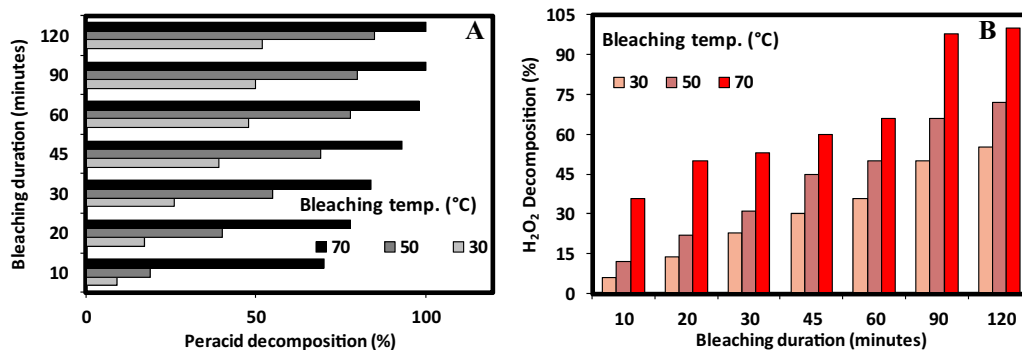

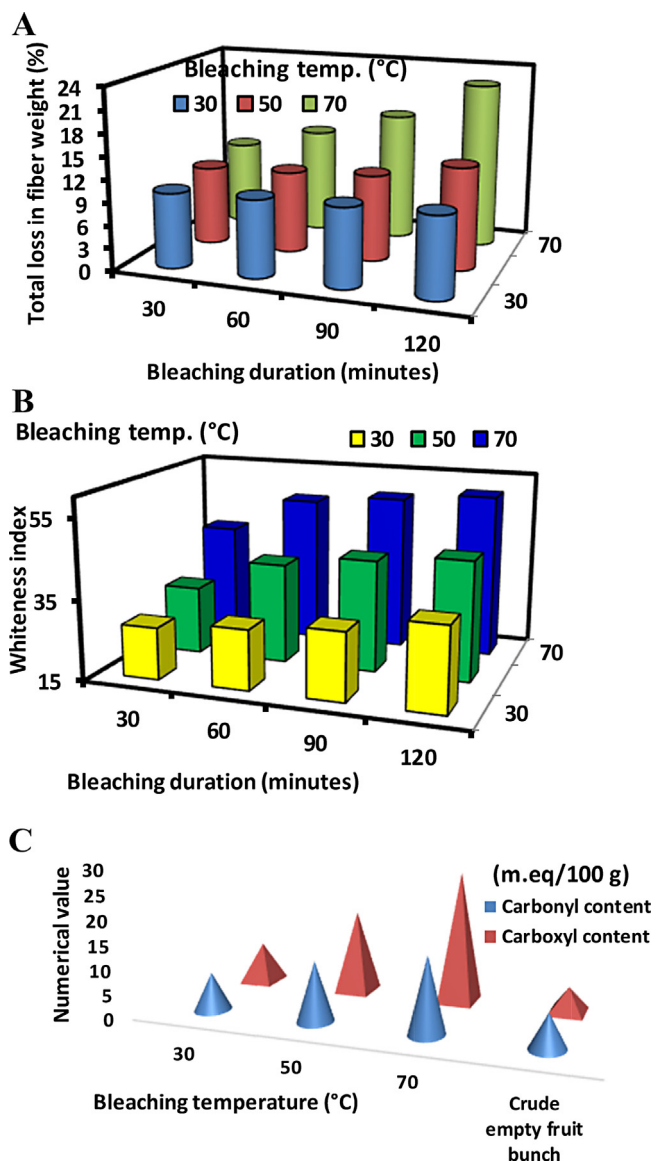**Fig. 5.** Effect of bleaching temperature on (A) peracid decomposition, (B) H_2O_2 decomposition.

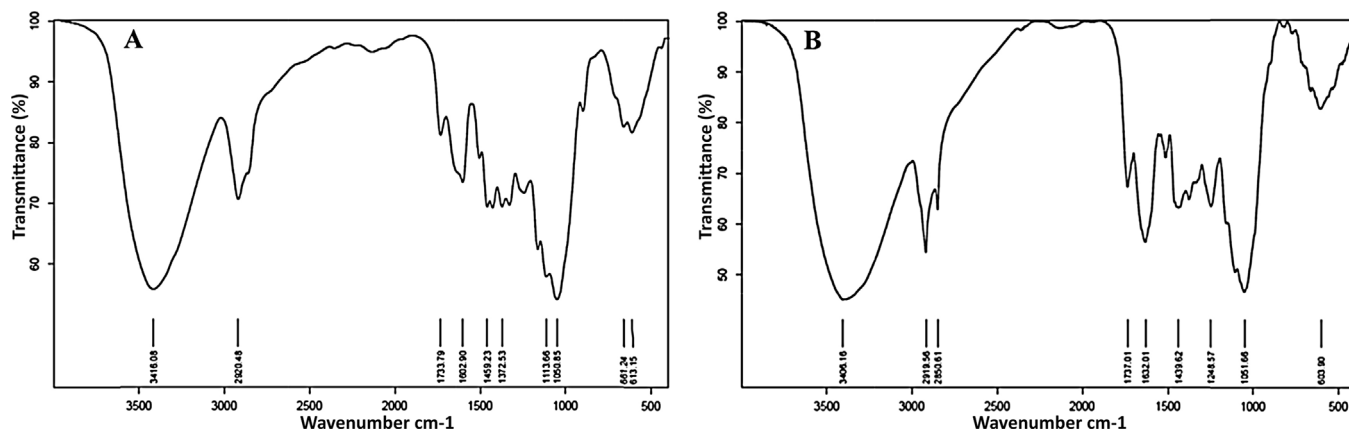**Fig. 6.** Effect of bleaching medium pH on (A) weight loss, (B) whiteness index, (C) chemical properties.

the residual hydrogen peroxide is full decomposed and gives maximum bleaching benefit in this alkaline range.

3.1.4. IR-Spectra of bleached empty fruit bunch cellulose

The infra-red spectra of raw empty fruit bunch cellulose is shown in Fig. 7A and that of bleached empty fruit bunch is shown in Fig. 7B. Having a look on both charts to compare the absorption bands characterizing the function groups, one can find easily the absorption band at 1730–1650 cm^{-1} characteristic for the C=O stretch of carboxyl group and also the absorption band at 1750–1625 cm^{-1} characteristic for the C=O stretch of ketone.

The areas of both beaks for bleached empty fruit bunch cellulose are higher than the corresponding areas for raw empty fruit bunch cellulose and this is logic as the oxidizing effect of hydrogen peroxide and peracid increases the carboxyl content by converting the primary hydroxyl groups to aldehydes then to carboxylic acids, and also increases the carbonyl content by oxidizing the secondary hydroxyl groups to ketones. This is in quite accordance with the noticed increase in the measured carboxyl and carbonyl content of bleached empty fruit bunch cellulose compared to the corresponding values measured for raw empty fruit bunch cellulose as illustrated in Figs. 3C, 4C and 5C.

3.2. Preparation and characterization of poly(acrylic acid)/cellulose graft copolymer

One of the routes for cellulose modification involves reaction with monomers, in particular vinyl monomers, through grafting process. Graft copolymerization of vinyl monomers onto cellulose can be initiated through generation of free radical along the stationary cellulose backbone. Among the various methods allowing the generation of free radicals, redox system initiated grafting has attracted the attention of many authors.

The main purpose of this section is to graft copolymerize acrylic acid onto the bleached empty fruit bunch cellulose using potassium bromate/thiourea dioxide redox system, with the aim of introducing more carboxyl groups to the cellulose backbone. The polymerization reaction was studied by varying the reaction conditions, like acrylic acid concentration, potassium bromate concentration and thiourea dioxide concentration, this is in addition to varying the initial polymerization temperature as well as the material to liquor ratio.

3.2.1. Effect of initiator components concentration
3.2.1.1. Potassium bromate concentration. The data presented in Fig. 8A demonstrates the great dependence of acrylic acid polymerization extent, expressed in terms of total conversion, on
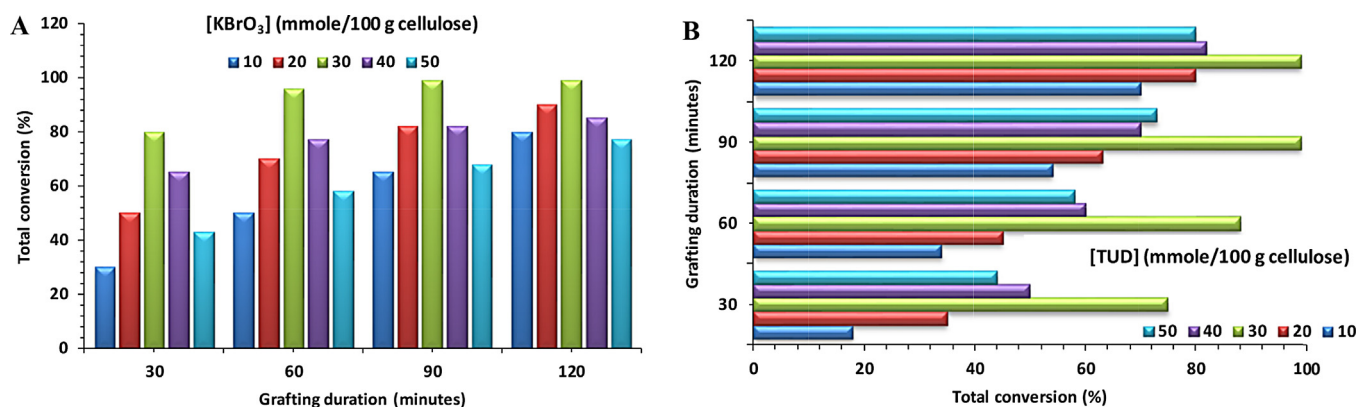

Fig. 7. IR-Spectra of (A) raw empty fruit bunch cellulose, (B) bleached empty fruit bunch cellulose.

Fig. 8. (A) Effect of thiourea dioxide concentration, (B) effect of potassium bromate concentration on acrylic acid total conversion.

the concentration of potassium bromate. It is also observed from Fig. 8A that regardless of the concentration of potassium bromate used in initiating the polymerization reaction, the change in total conversion is characterized by fast rate in the early stage of the polymerization reaction, followed by a slower rate. Obviously the total conversion should increases by increasing potassium bromate concentration and this is true up to a concentration of 30 mmol/100 g cellulose, then the total conversion decreases again by increasing potassium bromate concentration beyond this limit. The increase in conversion of acrylic acid to poly(acrylic acid) can be understood in terms of enhancement in the initiation redox process. The data presented in Fig. 8A show that maximum total conversion can be attained upon using the equimolar ratio from potassium bromate and thiourea dioxide 30:30 mmol/100 g cellulose. The decrease in the rate of polymerization reactions when using potassium bromate concentrations higher than 30 mmol/100 g cellulose can be accounted for by the inhibition effect of the liberated Br_2 gas (Eq. (3)), in addition to the action of the excessive bromate ion in the termination process.

$$BrO_3^- + 5Br + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (3)$$
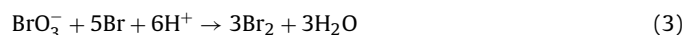
3.2.1.2. Thiourea dioxide concentration. Fig. 8B demonstrates the rate and extent of acrylic acid polymerization upon utilization

of varying concentrations from thiourea dioxide as an initiator. To study the effect of thiourea dioxide concentration on efficiency of polymerization, several trials were carried out at fixed temperature of 50 °C using fixed concentration from potassium bromate (30 mmol/100 g cellulose), fixed concentration from acrylic acid (100 g/100 g cellulose), and fixed material to liquor ratio of 1:10, for 2 h, while varying thiourea dioxide concentration (10–50 mmol/100 g cellulose. As is clear from Fig. 8B, the conversion of acrylic acid into poly(acrylic acid) is enhanced by increasing the concentration of thiourea dioxide up to 30 mmol/100 g cellulose. When thiourea dioxide concentration was increased above this limit, a significant decrease in the total conversion was noticed. This is in complete accordance with the fact mentioned previously that maximum total conversion is obtained upon using equimolar ratio from potassium bromate and thiourea dioxide (i.e. 30:30 m mole/100 g cellulose). The increase in total conversion upon increasing thiourea dioxide concentration up to 30 mmol/100 g
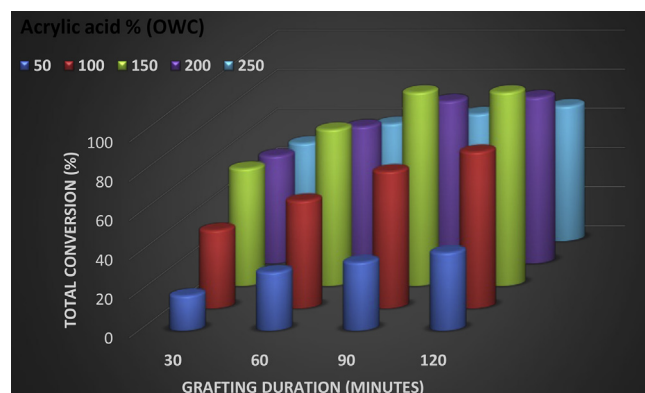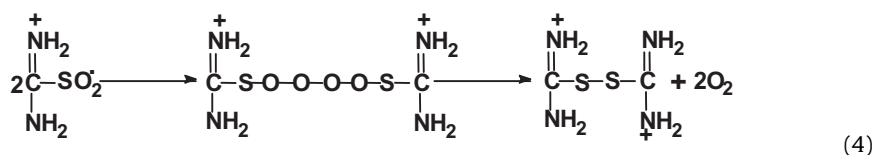

Fig. 9. Effect of acrylic acid concentration on total conversion.

cellulose is understood in terms of more active species formation, namely isothiourea dioxide free radicals. Moreover, at higher thiourea dioxide concentrations beyond 30:30 mmol/100 g cellulose, isothiourea dioxide free radicals tend to terminate each other resulting in the formation of inactive species as shown in the following equation:

(4)

3.2.2. Acrylic acid concentration

Fig. 9 shows the progress of total conversion with duration, when varying concentrations from acrylic acid (50–250%, based on weight of empty fruit bunch cellulose) are incorporated to the reaction medium. The data in Fig. 9 reveal that, the increase in the concentration of acrylic acid up to the limit of 150% (OWC) results in remarkable enhancement in the total conversion that it reaches 99% within a period of 90 min, when the used concentration is 150%. Using acrylic acid concentrations beyond 150%, namely 200% and 250% implies to unexpected decrease in the total conversion. The improvement in total conversion can be attributed to enhancement in the polymerization medium acidity. This leads to increase in the efficiency of potassium bromate as one of the initiation system components and enhances the stability of the formed isothiourea dioxide by the action of excessive protons available in the reaction medium (Eq. (5)). The negative total conversion trend upon using acrylic acid concentrations higher than 150% may be accounted for
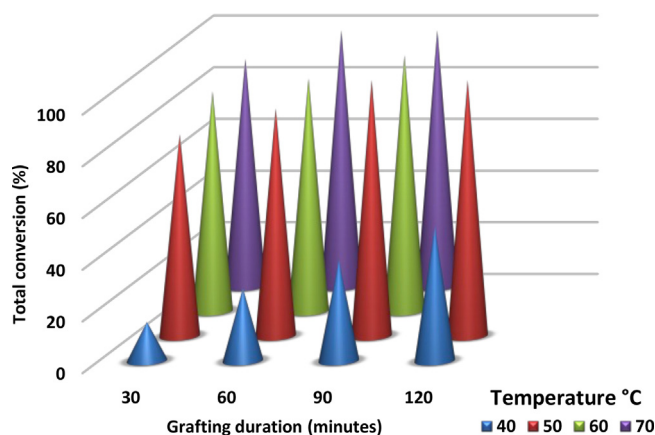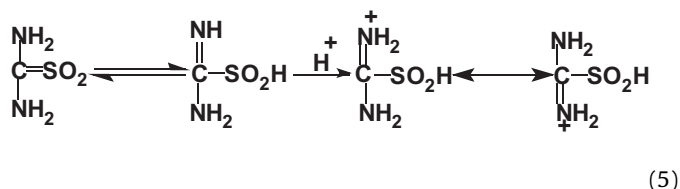
Fig. 10. Effect of polymerization temperature on total conversion.

Fig. 11. Effect of material to liquor ratio on total conversion.

by relative shortage in the amount of active species required to initiate this amount of monomer. Also, this highly acidic medium causes liberation of Br_2 gas which is known to cause oxidation rather than initiating the polymerization reaction.

(5)

3.2.3. Polymerization temperature

Fig. 10 shows the total conversion of acrylic acid at different polymerization temperatures. By monitoring the progress in total conversion with time, at different temperatures, it could be concluded that the polymerization of acrylic acid is a temperature-dependent reaction, following the order 40 °C < 50 °C < 60 °C < 70 °C, that in case of using polymerization temperature of 40 °C, we got 52% TC in 120 min, while when the polymerization temperature is raised to 50 °C, we got 99% TC in 120 min. When we raise the polymerization temperature to 60 °C and 70 °C, we get the same
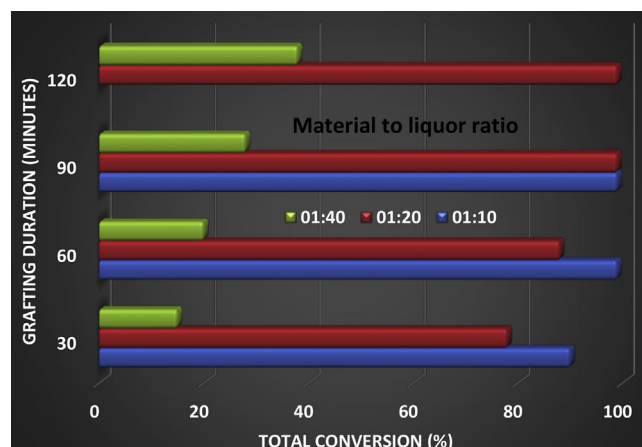
TC in shorter duration (90 min). This remark can be accounted for by the positive effect of temperature on enhancing the efficiency of the redox process. This is of course in addition to increasing kinetic energy of the reactant molecules or radicals. However, the temperature 50 °C was found to be the optimum polymerization temperature although it needs longer duration to attain 99% TC, because at the high temperatures 60 °C and 70 °C, homopolymerization takes place rather than graft copolymerization.

3.2.4. Material to liquor ratio

Fig. 11 shows the total conversion of acrylic acid to poly(acrylic acid) at different material to liquor ratios. It is clear from Fig. 11 that the total conversion depends to great extent on the ratio between empty fruit bunch cellulose and the total volume of the polymerization liquor. The enhancement in total conversion by reducing the material to liquor ratio was found to follow the order 1:40 < 1:20 < 1:10. This is absolutely logic because when the polymerization medium is diluted the reactants molecules become relatively far from each other and this results in reducing the number of molecular collisions, which give the chance for the reactant molecules to react with each other. However, 1:20 was found to be the optimum material to liquor ratio, based on the discussion stated above. Upon increasing the material to liquor ratio up to 1:40, the
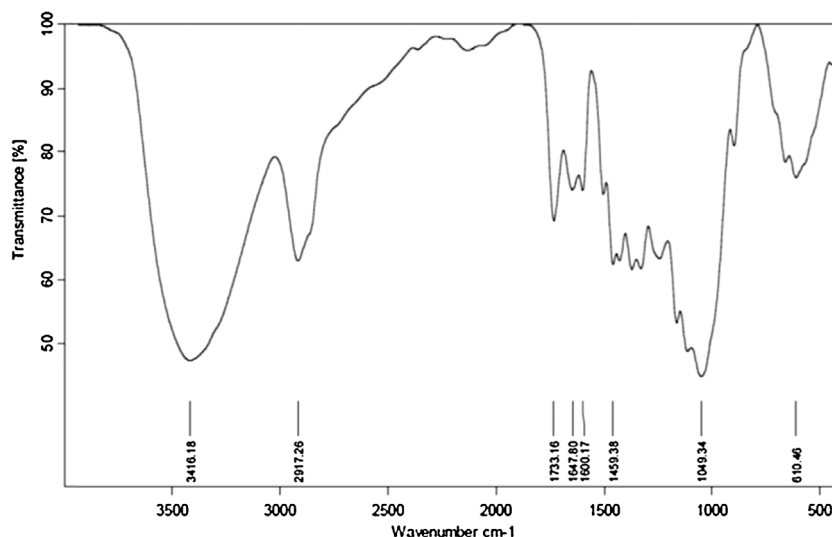

Fig. 12. IR-Spectra of poly(acrylic acid)/cellulose graft copolymer.

number of molecular collisions is reduced due to this high level of dilution and this will of course have a negative effect on the polymerization reaction as a whole, leading to low total conversion. On the other hand, at small liquor ratio 1:10, the reaction medium is very concentrated and the 99% total conversion is attained in shorter time but due to this high medium concentration, hompopolymerization will be favorable than graft copolymerization.

Based on the aforementioned discussion, it could be concluded that optimum conditions for graft copolymerizing acrylic acid onto empty fruit bunch cellulose are to use equimolar ratio of the initiator components KBrO$_3$:TUD, 30:30 mmol of each/100 g empty fruit bunch cellulose, together with 150% (OWC) acrylic acid, by use of material to liquor ratio 1:20 at polymerization temperature of 50 °C for a duration of 120 min. All grafted empty fruit bunch samples were characterized for their GY and the best value was found to be attained on using the above optimum conditions.

3.2.5. IR-Spectra of poly(acrylic acid)/cellulose graft copolymer

The infra-red spectra of bleached empty fruit bunch cellulose is shown in Fig. 7B and that of poly(acrylic acid)/cellulose graft copolymer is shown in Fig. 12. Having a look on both charts to compare the absorption bands characterizing the function groups, one can find easily the absorption band at 1730–1650 cm^{-1} characteristic for the C=O stretch of carboxyl group.

The area of this beak for poly(acrylic acid)/cellulose graft copolymer is higher than the corresponding area for bleached empty fruit bunch cellulose and this is logic as the graft copolymerization reaction introduces more poly(acrylic acid) chains to the backbone of empty fruit bunch cellulose and thus increases the carboxyl content.

Acknowledgement

References

[1] K.C. Khoo, M.N.M. Yusoff, T.W. Lee, Research Pamphlet No. 107, 1991, pp. 1.
[2] E.S. Abdel-Halim, Carbohydr. Polym. 88 (2012) 1201.
[3] E.S. Abdel-Halim, S.S. Al-Deyab, Carbohydr. Polym. 86 (2011) 988.
[4] A. Farooq, S. Ali, N. Abbas, G.A. Fatima, M.A. Ashraf, J. Cleaner Prod. 42 (2013) 167.
[5] E.S. Abdel-Halim, W. Konczewicz, M. Zimniewska, Salem S. Al-Deyab, Mohamed H. El-Newehy, Carbohydr. Polym. 82 (2010) 195.
[6] M. Joshi, M. Nerurkar, P. Badhe, R. Adivarekar, J. Mol. Catal. B: Enzym. 98 (2013) 106.
[7] E.S. Abdel-Halim, H.M. Fahmy, Moustafa M.G. Fouda, Carbohydr. Polym. 74 (2008) 707.
[8] M. Montazer, S. Morshedi, Int. J. Biol. Macromol. 50 (2012) 1018.
[9] E.S. Abdel-Halim, M.H. El-Rafie, R. Kohler, Polym.–Plast. Technol. Eng. 47 (2008) 58.
[10] N.A. Ibrahim, N.M. Abdel Moneim, E.S. Abdel Halim, M.M. Hosni, J. Cleaner Prod. 16 (2008) 1321.
[11] S. Palamutcu, Energy 35 (2010) 2945.
[12] A. Hasanbeigi, L. Price, Renewable Sustainable Energy Rev. 16 (2012) 3648.
[13] E.S. Abdel-Halim, Carbohydr. Polym. 96 (2013) 64.
[14] X. Long, C. Xu, J. Du, S. Fu, Carbohydr. Polym. 95 (2013) 107.
[15] E.S. Abdel-Halim, S.S. Al-Deyab, Carbohydr. Polym. 92 (2013) 1844.
[16] C. Xu, X. Long, J. Du, S. Fu, Carbohydr. Polym. 92 (2013) 249.
[17] E.S. Abdel-Halim, Carbohydr. Polym. 90 (2012) 316.
[18] F. Si, K. Yan, X. Zhang, Carbohydr. Polym. 103 (2014) 581.
[19] A. Hou, X. Zhang, Y. Zhou, Carbohydr. Polym. 82 (2010) 618.
[20] E.S. Abdel-Halim, Carbohydr. Polym. 88 (2012) 1233.
[21] M. Bösing, B. Krebs, B. Nestler, M. Seebach, G. Reinhardt, M. Wohlers, U. Dingerdissen, Appl. Catal., A: Gen. 184 (1999) 273.
[22] T. Tzanov, S.A. Costa, G.M. Gübitz, A. Cavaco-Paulo, J. Biotechnol. 93 (2002) 87.
[23] A. Hebeish, M. Ramadan, E.S. Abdel-Halim, A. Abo-Okeil, Clean Technol. Environ. Policy 13 (2011) 713.
[24] F.A. Abdel-Mohdy, E.S. Abdel-Halim, Y.M. Abu-Ayana, S.M. El-Sawy, Carbohydr. Polym. 75 (2009) 44.
[25] A. Hashem, E.S. Abdel-Halim, Kh.F. El-Tahlawy, A.A. Hebeish, Adsorpt. Sci. Technol. 23 (2005) 367.
[26] E.S. Abdel-Halim, S.S. Al-Deyab, Carbohydr. Polym. 87 (2012) 1863.
[27] H.A. Hegazi, HBRC J. 9 (2013) 276.
[28] A.K. Anupam, P. Kumar, G.D. Ransinchung R.N., Procedia—Soc. Behav. Sci. 104 (2013) 264.
[29] B. Singha, S.K. Das, Colloids Surf., B: Biointerfaces 107 (2013) 97.
[30] E.S. Abdel-Halim, Arabian J. Chem. 7 (2014) 362.
[31] D. Sud, G. Mahajan, M.P. Kaur, Bioresour. Technol. 99 (2008) 6017.
[32] T.A.H. Nguyen, H.H. Ngo, W.S. Guo, J. Zhang, S. Liang, Q.Y. Yue, Q. Li, T.V. Nguyen, Bioresour. Technol. 148 (2013) 574.
[33] M. Bilal, J.A. Shah, T. Ashfaq, S.M.H. Gardazi, A.A. Tahir, A. Pervez, H. Haroon, Q. Mahmood, J. Hazard. Mater. 263 (2013) 322.
[34] E.B. Ly, J. Bras, P. Sadocco, M.N. Belgacem, A. Dufresne, W. Thielemans, Mater. Chem. Phys. 120 (2010) 438.
[35] J. Zhu, X. Dong, X. Wang, Y. Wang, Carbohydr. Polym. 80 (2010) 350.
[36] E.S. Abdel-Halim, Salem S. Al-Deyab, Int. J. Biol. Macromol. 68 (2014) 33.
[37] G. Kayık, N.Ş. Tüzün, J. Mol. Graphics Modell. 49 (2014) 55.
[38] E.S. Abdel-Halim, Carbohydr. Polym. 90 (2012) 930.
[39] X. Liu, Y. Xu, J. Yu, S. Li, J. Wang, C. Wang, F. Chu, Int. J. Biol. Macromol. 67 (2014) 483.
[40] E.S. Abdel-Halim, React. Funct. Polym. 73 (2013) 1531.
[41] E.S. Abdel-Halim, S.S. Al-Deyab, Carbohydr. Polym. 86 (2011) 1306.
[42] Y. Sheng, H. Huang, M. Yu, X. Zhang, L. Cheng, Z. Liu, W. Liu, Q. Huang, J. Yi, W. Yang, J. Ind. Eng. Chem. 20 (2014) 419.
[43] E.S. Abdel-Halim, H.E. Emam, M.H. El-Rafie, Carbohydr. Polym. 74 (2008) 783.
[44] O.S. Taskin, I. Erel-Goktepe, M.A.A. Khan, S. Pispas, Y. Yagci, J. Photochem. Photobiol., A: Chem. 285 (2014) 30.
[45] E.S. Abdel-Halim, H.E. Emam, M.H. El-Rafie, Carbohydr. Polym. 74 (2008) 938.
[46] B.S. Kaith, A.S. Singha, S. Kalia, Autex Res. J. 7 (2007) 119.
[47] A.Y.A. Alfaifi, M.H. El-Newehy, E.S. Abdel-Halim, S.S. Al-Deyab, Carbohydr. Polym. 106 (2014) 440.
[48] Z. Xu, Y. Yang, Y. Jiang, Y. Sun, S.Y. Pang, Molecules 13 (2008) 490.
[49] A. Hashem, E.S. Abdel-Halim, H.H. Sokker, Polym.–Plast. Technol. Eng. 46 (2007) 71.
[50] A. Hashem, H.H. Sokkar, E.S. Abdel-Halim, A. Gamal, Adsorpt. Sci. Technol. 23 (2005) 455.
[51] E.S. Abdel-Halim, F.A. Abdel-Mohdy, M.M.G. Fouda, S.M. El-Sawy, I.A. Hamdy, S.S. Al-Deyab, Carbohydr. Polym. 86 (2011) 1389.
[52] E.S. Abdel-Halim, M.M.G. Fouda, I.A. Hamdy, F.A. Abdel-Mohdy, S.M. El-Sawy, Carbohydr. Polym. 79 (2010) 47.
[53] J.F. Madrid, Y. Ueki, N. Seko, Radiat. Phys. Chem. 90 (2013) 104.
[54] M.M. Nasef, H. Saidi, K.Z.M. Dahlan, Nucl. Instrum. Methods Phys. Res. Sect. B: Beam Interact. Mater. At. 265 (2007) 168.
[55] E.S. Abdel-Halim, F.A. Abdel-Mohdy, S.S. Al-Deyab, M.H. El-Newehy, Carbohydr. Polym. 82 (2010) 202.
[56] E.S. Abdel-Halim, S.S. Al-Deyab, A.Y.A. Alfaifi, Carbohydr. Polym. 102 (2014) 550.
[57] M.H. El-Rafie, E.S. Abdel-Halim, H.E. Emam, Egypt. J. Text. Polym. Sci. Technol. 11 (2007) 197.
[58] A.I. Vogel, Quantitative Inorganic Analysis, third ed., Longman Group Limited, London, 1961.
[59] R.W. Wallace, D.G. Young, J. Polym. Sci., A: Polym. Chem. 4 (1966) 1179.
[60] M.F. Mattisson, K.A. Legendre, Anal. Chem. 24 (1952) 1942.
[61] K. Tihlérik, M. Pasteka, Starch 44 (1992) 385.
[62] R.B. Chavan, D.P. Chattopadhyay, J.K. Sharma, Colourage 47 (2000) 15.
[63] N. Zhang, X.F. Zhou, J. Mol. Catal. A: Chem. 365 (2012) 66.