



Utilization of The Combined Effect of Ultrasound Waves and Sodium Metperiodate in Preparation of Oxidized Galactomannan Fenugreek Gum for Medical and Other Purposes



A. Hebeish¹, A.A. Abd El-Rahman², S. H. Nassar², H. El-Sayad², N.S. Elshemy^{2*}

¹National Research Centre (NRC, Scopus affiliation ID 60014618), Textile Research Industrial Division (TRID), Pre-treatment and Finishing of Cellulose based Fibers Department (PFCFD), El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, Egypt

²National Research Centre (NRC, Scopus affiliation ID 60014618), Textile Research Industrial Division (TRID), Dyeing, Printing and Textile Intermediate Department (DPTID), El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, Egypt

A new oxidation system was developed for synthesis of oxidized galactomannan fenugreek gum (GMFG). The system is based on subjecting the (GMFG) to the combined effects of sonication and sodium metaperiodate (SMPI) oxidation under a variety of conditions. Variables studied include SMPI concentration and duration as well as pH and temperature of the treatment (synthesis) conditions. The as synthesized GMFG, that is, the oxidized GMFG samples were submitted to analysis whereby the carboxyl and carbonyl groups in addition to apparent viscosity and rheological properties were monitored. Results obtained signify that SMPI concentration, pH, temperature and duration of synthesis act in favor of carboxyl content, the latter increases by increasing the magnitude of the said variables. The reverse is the case with the carbonyl content and residual SMPI, i.e., the carbonyl and residual SMPI decreases by increasing the parameters controlling the synthesis conditions. Accordingly, the most appropriate conditions for synthesis of the oxidized GMFG under investigation refers to SMPI concentration of 0.5 gm/5 gm GMFG for a duration of 30 min while keeping the pH at 3 and the temperature at 50°C. It was also observed that the oxidized GMFG is quite stable for storing time up to two weeks; opposite to the non-oxidized GMFG which becomes mostly after only one day. It was further realized that sizing of cotton fabric with oxidized GMFG displays antibacterial activity against G⁺ bacteria and G⁻ bacteria but with the certainty that bacterial of G⁺ bacteria is greater than that of G⁻ bacteria. Furthermore, GMFG exhibits higher solubility and lower apparent viscosity than does its non-oxidized mate, indicating easier handling and removal of the oxidized GMFG. Indeed, the new methodology, outlined herein for the synthesis and micro chemical characterization of oxidized GMFG sound simpler and easier to perform than other oxidation methodologies. This together with energy and time-saving would advocate current research outputs as environment-friendly methodology for production of GMFG for use in medical and other purposes.

Key words: Sodium metaperiodate, Sizing, Ultrasonic wave, Galactomannan Fenugreek gum

*Corresponding author e-mail: nanaelshemy@hotmail.com

Received 29/9/2019; Accepted 7/10/2019

DOI: 10.21608/ejchem.2019.17500.2075

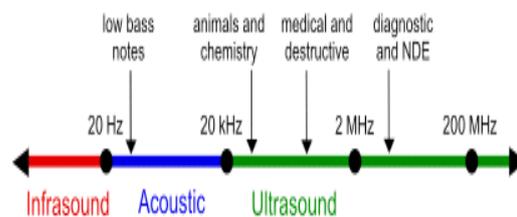
©2019 National Information and Documentation Center (NIDOC)

Introduction

Textile chemical processing consumes a lot of water, chemicals, and energy sources. From this point, many researchers worldwide are interested in the development and enforcement of new technology to impart different properties of textile fabrics while avoiding exclusive consumption of these sources. The application of ultrasonic waves in textile processing is adopted as an alternative heating source to the traditional heating methods to accelerate mass transfer in textile processes and reducing time, energy as well as water consumption [1–3]. Recently, the great efforts of these researchers have been devoted on the application of ultrasonic waves in different textile processing, such as sizing and de-sizing, bleaching and scouring [4–9], textiles dyeing [10–15] as well as dye effluent decolonization [16, 17].

Plentiful prospective advantages are gained through the use of ultrasound in different textile processing. By way of examples, mention is made of saving energy, reduced processing times, environmental improvements by reduced consumption of auxiliary chemicals, lower overall processing costs, and maintains or improves product quality. Nevertheless, there is an essential need to understand the relative operative processes, in order to make use of meaningful application of ultrasonic in textile processing.

Ultrasonic is defined as the oscillating sound waves with the frequency above the limits of human audibility, it is ranging between 20 kHz and 500 kHz, and it is oscillating with the frequencies above 20000/sec. When liquid is exposed to the ultrasonic waves, many microscopic bubbles are formed, via a phenomenon known as acoustic cavitation. As ultrasonic waves propagate, particles in the elastic medium oscillate, so the energy convey through the medium in the direction of propagation. In fact the diffuse effects of ultrasound arise from the way in which the sound is propagated through the medium. The waves can be propagated in two ways, 1) Longitudinal waves (in which the particles oscillate in a direction parallel to the wave propagation direction), 2) transverse waves (in which the particles oscillate in a direction perpendicular to that of wave propagation direction) [18]. In a solid state, both waves can be transmitted while in gas and liquids only longitudinal waves can be transmitted.



When ultrasonic waves are absorbed in the liquid system, the aforementioned bubbles repeat their expansion and contraction according to the pressure oscillation of an ultrasonic wave. And some bubbles or cavities collapse densely at the contraction phase of an ultrasonic wave. When the bubbles collapse, they produce tiny but powerful shock waves. It is also reported that the ultrasound acquires a pronounced effect on the rate of dyeing for several dye classes for various types of fibres [19-23].

The current work is targeted towards development of Novel textile auxiliaries for application in medical domains through oxidation of glactomannan fenugreek gum (GMFG) under the combined effects of ultrasonic and sodium metaperiodate (SMPI) oxidation. Quantitative analysis of microstructural features of the oxidized GMFG so obtained is performed in order to shed insights on the oxidized polysaccharide structure of GMFG vis-à-vis the non-oxidized gum. Same comparison will be undertaken with respect to stability and antibacterial activity of GMFG before and after oxidation.

Experimental and Methods

Materials

Fenugreek seeds

Clean, dry fenugreek seeds cultivated in Egypt were purchased from local market

Fabrics

Mill scoured, bleached and mercerized plain weave cotton fabric (135 g/m²) was kindly supplied by Misr Co. for Spinning and Weaving, El Mahalla EIKOBRA, Egypt.

Chemicals

Sodium metaperiodate, sodium thiosulphate, and sodium disulphate, were supplied by Sisco Research Laboratory PVT. Co. Hydroxyl amine hydrochloride was purchased from Oxford Lab Chem, India, Cas No: 5470-11-1. Phenolphthalein and methyl red were supplied by Fisher Scientific, Egypt. Sodium hydroxide, sulphuric acid,

hydrochloric acid, and absolute ethanol were all of laboratory grade chemicals.

Ultrasonic stirring systems

Ultrasonic Homogenizing involves a mechanical process to reduce particles in a liquid so that they become uniformly small and evenly distributed.

The optimum conditions for miniaturization obtained from Homogenizer were applied using the Ultrasonic stirrer (SONICS&MATERIALS, INC), Modle: VCX750, volts: 230 VAC 50/60 HZNOM, U.S.A.)

Methods

Separation of gum from seeds

Separation of the glactomannan fenugreek gum (GMFG) from fenugreek seeds was carried out according to the following three steps. In the 1st step the seeds were grinded and sifted to remove nucleus. In the 2nd step, the crunches were immersed in tap water and placed in a blender, soaked for approximately 24 h, then filtering it by using nylon net. In the final step, the resultant was precipitated by ethyl alcohol and dried at ambient temperature.

Oxidation of glactomannan fenugreek gum (GMFG) by Sodium Metaperiodate NaIO₄ (SMPI)

GMFG was prepared by adding 3 g of gum to 80 mL of tap water under mechanical stirring, and then adding different amounts of SMPI (0.25, 0.5, and 0.75) dissolved in 20 ml tap water. The mixture was kept at room temperature for 15 min with moderate stirring. The mixture was exposed to ultrasound wave at different temperature (30, 50, 60°C) for different time (320, 30, 50, 60 min). To this end, the reaction was stopped by adding 0.1 gm of sodium disulphate. The rheological properties of the oxidized gum were determined before precipitation. Then the oxidized gum was precipitated by drop wise addition of commercial ethanol under constant moderate mechanical stirring. The obtained gum was filtered and subjected to frequent washing with ethanol to remove the unreacted SMPI and finely dried in an oven for 2 h at 50°C. The dried gum was then milled into powder and the resultant oxidized gum was submitted to microquantitative analysis and rheological properties.

Quantitative chemical analysis and rheological properties of the oxidized glactomannan fenugreek gum

Determination of carboxyl and carbonyl groups content

The acidic (carboxyl) [24] and reducing (carbonyl) groups of GMFG before and after oxidation with SMPI were determined according to a method of Wing and Willett [24-26].

Rheological measurement

The rheological properties and apparent viscosity were carried out using Brookfield model DV-111, Programmable Rheometer, U.S.A. at different rates of shear range (between, 3.4 - 68s⁻¹), at 25°C according to a procedure reported elsewhere [26] by dissolving the purified samples in tap water at a concentration of 3%. The apparent viscosity was calculated using the following formula:

$$\eta = \tau / D$$

Where η = apparent viscosity in poise. τ = shearing stress (dyne / cm²), D = rate of shear (s⁻¹)

Sizing of Cotton fabrics

Light cotton fabric samples were treated with aqueous solution of GMFG before and after oxidation via impregnation coupled with squeezing to a wet pick up of 80% then dried at ambient temperature overnight. The sized cotton samples were monitored for increase in weight due to the treatment and antibacterial activity as well.

Antimicrobial test

Against E. coli as an example of gram negative bacteria (G⁻) and S. aureus as an example of gram positive bacteria (G⁺).

Antibacterial activity was tested by the filter paper disc diffusion method [27]. SMA and Mueller Hinton agar (Difco) containing 100 ppm of 2, 3, 5-triphenyltetrazolium chloride were used for antibacterial assay. 2, 3, 5-triphenyltetrazolium chloride was added to culture media to differentiate bacterial colonies and to clarify the inhibition zone [27]. Each plate was inoculated with bacterial, Escherichia coli as an example of gram negative bacteria (G⁻), Staphylococcus aureus as an example of gram positive bacteria (G⁺.1 ml) directly from the broth. All plates were incubated at 32°C for 4 days, after which the inhibition zones were measured and recorded in millimetres (mm). The scale of measurement was the following (disc diameter included): ≥ 28 mm inhibition zone is strongly inhibitory ≤ 16 to 10 mm inhibition zone is moderately inhibitory; and

≤ 12 mm is no inhibitory [26-28]. Control plates were prepared by placing antibiotic to evaluate culture for antibiotic resistance patterns that might affect sensitivity of assay. The antibiotic used was penicillin 10 IU [28].

Scanning Electron microscope (SEM)

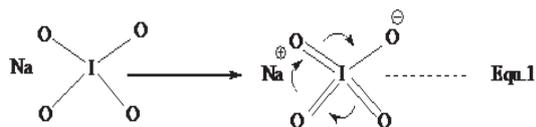
ZEISS LEO 1530 Gemini Optics Lens scanning electron microscopy (SEM) with 30 kV scanning voltages was employed to observe the morphologies of sizing cotton fibres with non-oxidizing and/or oxidizing GMFG.

Result and Discussion

As already stated current research initiatives are directed towards establishment of a new innovative method for oxidation of GMFG using sonication-SMPI combined system for synthesis of oxidized GMFG. To the author's knowledge, no work, has been published so far on harnessing the combined effect of sonication together with SMPI for modification via oxidation of GMFG despite the use of SMPI alone in oxidation of such gums. At any event, however, the oxidized GMFG fabricated as per the new method were analyzed for carboxyl and carbonyls contents as well as for rheological properties and apparent viscosity. Results obtained along with those brought about by alteration of the magnitude of the parameters controlling the conditions of synthesis of the oxidized GMFG are given under.

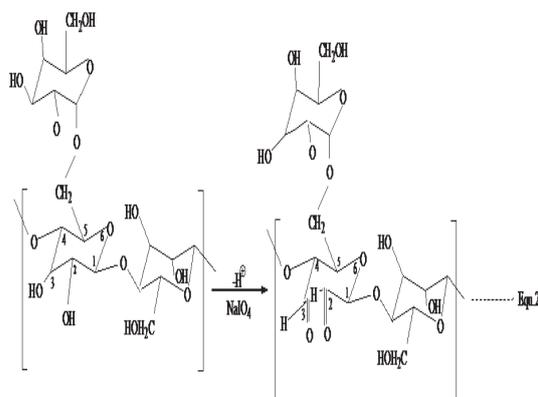
Provisional Mechanism of the Synthesis of Oxidized GMFG

Sodium metaperiodate (NaIO_4) is an inorganic salt, consisting of distorted IO_4^- ions with/ and Na^+ ions are surrounded by 4 oxygen atoms, when dissolve in water forms tetragonal crystals composed of a sodium cation and the periodate anion. It may also be regarded as the sodium salt of periodic acid. The solution of Sodium per iodate can be used to open saccharide rings between vicinal diols leaving two aldehyde groups (Eq.1).

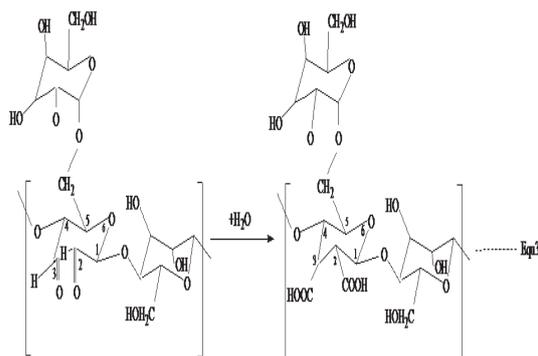


The oxidation effect is attributed to the presence

of periodate anion which can be used in solution to open saccharide rings between vicinal diol forming two aldehyde groups, Eq.2.



Similarly, glactomannan molecule is oxidized during treatment with SMPI by active oxidizing species brought about by decomposition of SMPI. As a result, formation of aldehyde groups occurs at C2, and C3, and this step is probably rate limited. Once the aldehyde groups are formed, they are rapidly oxidized to form carboxylic group (Eq.3).



Optimum conditions for the synthesis of oxidized GMFG

The effects of oxidizing parameters, such as oxidizing agent (SMPI) concentration, oxidizing bath pH, oxidizing temperature, as well as oxidizing time were investigated to obtain the optimum conditions for synthesis of oxidized GMFG extracted from fenugreek seeds by using SMPI coupled with ultrasound waves.

Effect of different parameter on:

Carboxyl and carbonyl groups content: GMFG before and after oxidation with the sonication-SMPI method -which was developed herein- were analysed for carboxyl and carbonyl groups. The magnitude of carboxyl and carbonyl groups is expressed as meq/5 g GMFG. Results in Fig.1 (a, b) shows the carbonyl, and carboxyl contents

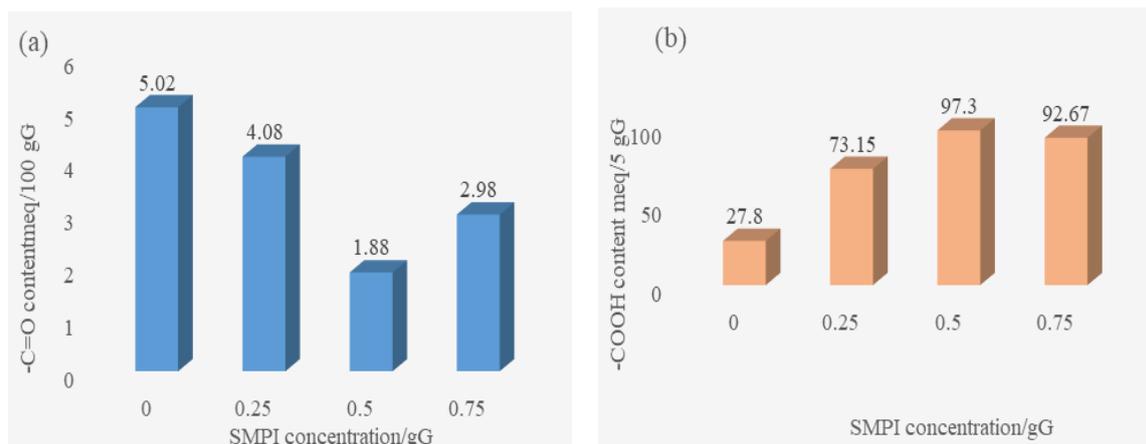


Fig.1 Effect of SMPI concentration on the (a) carbonyl content; (b) carboxyl content

of oxidized GMFG at three SMPI concentrations (0.25, 0.5, and 0.75 g/5g gum) oxidation was carried out at 60°C for 30 min, and pH3. Obviously, the increase in the concentration of SMPI (from 0.25–0.75 g/5 g gum) produces oxidized gum which is characterized by a marked increase in the carboxyl content. This is rather reasonable and could be attributed to abundance of active oxidizing species at higher concentrations of SMPI. The active species attack the-OH molecules at C₂ and C₃ and converting them to aldehyde groups (Equ.2) which are then rapidly oxidized to carboxylic groups (Equ.3). On the opposite side, carbonyl group decreased as SMPI increases. This is logical because the carbonyl groups undergo conversion through further oxidation to carboxyl groups as postulated above in the oxidation mechanism (equ.1-equ.3).

The results in Fig. 2 (a &b) show the carbonyl, and carboxyl contents of oxidized GMFG at different pH's (3, 7, and 9) using 0.5 g SMPI/5g GMFG at 60°C for 30 min. It is seen that increasing the pH of the oxidization medium from (3 to 9)

produces oxidizing gum which is accompanied by a marked decrease in the -COOH content; meanwhile there is an increase in -C=O group.

When the pH is less than 4, the carboxylic content increases by increasing pH of oxidation medium. However, once the pH value is more than 3, the carboxylic content of GMFG decreases by increasing the pH. This could be explained as follows: during the oxidation reaction, sodium periodate is first obliged to be transformed into the periodic acid under the acidic condition, and then the oxidization of GMFG is able to be liable for execution. Therefore, when the pH value is more than 3, it doesn't act in favour of the transformation of sodium periodate into the periodic acid. This lowers the efficiency of the oxidation. But the degree of the acetal or hemiacetal crosslinking formation increases because the aldehyde groups which are formed as the first step in the oxidation process reacted with the hydroxyl group between GMFG molecules or within GMFG molecules when the pH of the oxidization is more than 3. So, the suitable pH is considered to be 3 in this reaction.

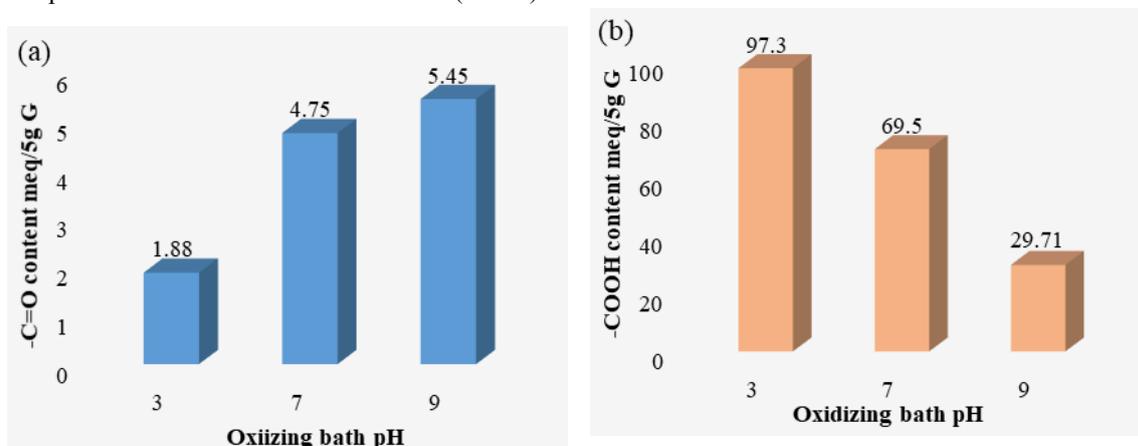


Fig. 2. Effect of pH of oxidation medium on (a) carbonyl content, (b) carboxyl content of GMFG

Factors like temperature significantly affect the reaction. With this in mind the reaction temperature was varied from 30 to 60°C in order to realize the temperature effect on oxidation process (0.5g/5g gum, pH 3, for 30 min). Figure 3, shows that when the reaction temperature is less than 50°C, the carboxylic content of GMFG increases by increasing the reaction temperature. On the contrary, when the reaction temperature is more than 50°C, the carboxylic content of GMFG decreases by increasing the reaction temperature up to 50°C. This may be explained as follows: raising the reaction temperature, coupled with the effect of ultrasound waves which causes the cavitation phenomena, the thermal motion of SMPI molecules is accelerated, thereby favouring the diffusion of SMPI into the particles. As a consequence, more hydroxyl groups on GMFG particles are oxidized. On the other hand, the elevated temperature would lead to the more side reaction of SMPI and the large expansion of the GMFG grains, which reduces the number of the holes on the GMFG grains. As a consequence, the effect of temperature on the oxidation reaction is realized. Hence, 50°C is regarded as the appropriate temperature for conducting the oxidation reaction using ultrasound waves-SMPI system.

Figure 4 (a &b) shows that, the carboxylic content of the oxidized GMFG increases by increasing duration of the reaction up to 30 min. Thereafter the carboxylic content of GMFG decreases basically with the increase of the reaction time. On the other hand, the carbonyl group content decreases significantly by prolongation of duration of oxidation to 30 min then it increases. The following may form a possible explanation for these findings, (i) as the reaction time increases the effective contact between the GMFG molecules and molecules of SMPI increases thereby working in conformation of the oxidization reaction, but the SMPI is depleted as the oxidization reaction proceeds. (ii) The particles of SMPI can penetrate more easily into the GMFG centre when ultrasonic waves are in use (cavitation or bubble formation phenomena), resulting in a more inner oxidation. (iii) The oxidization reaction processes would not continue to process after certain oxidation time because the concentration of SMPI is reduced to a certain value. Hence the suitable oxidation reaction time speaks of 30 min.

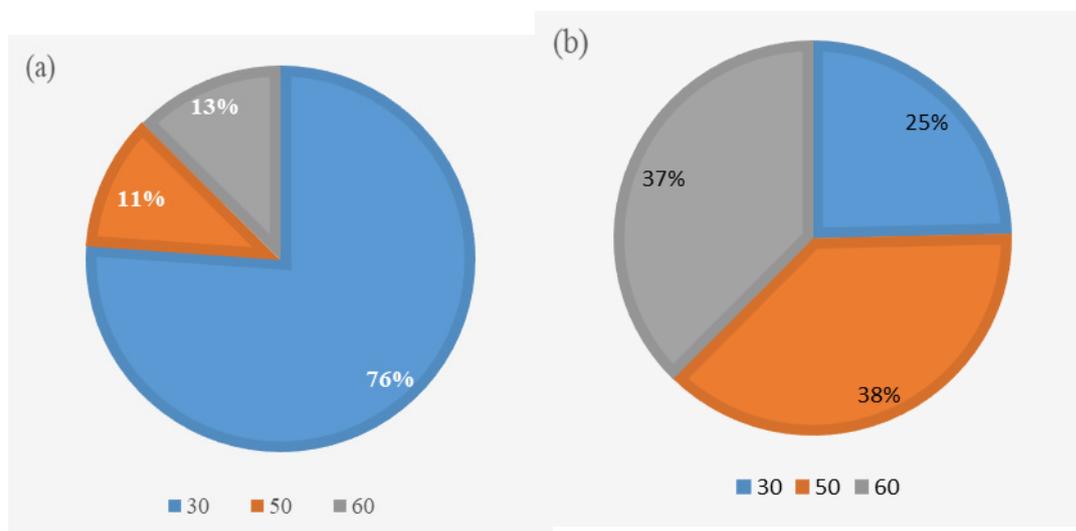


Fig. 3. Effect of oxidation temperature on (a) carbonyl content, (b) carboxyl content of GMFG

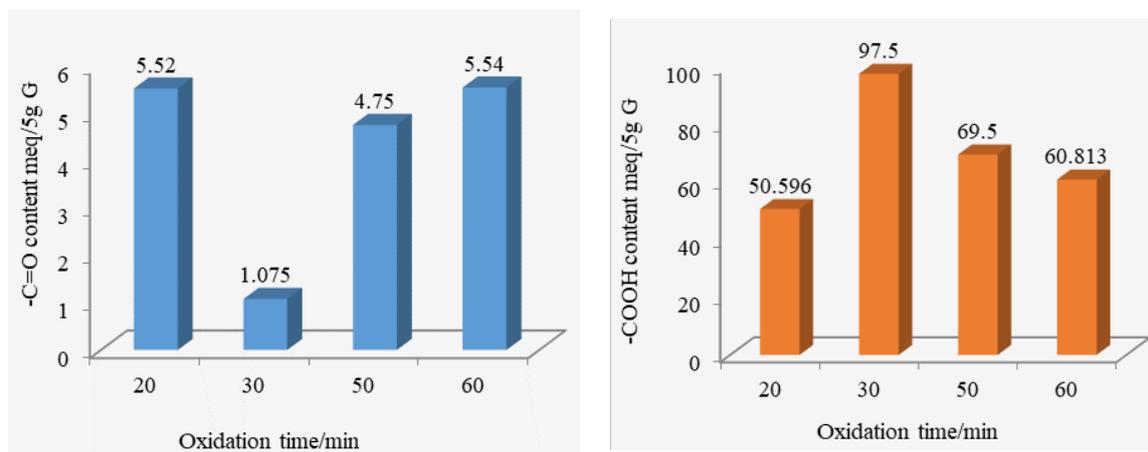


Fig. 4. Effect of oxidation time on (a) carbonyl content, (b) carboxyl content of GMFG.

Consumption of SMPI: Figures 5-8 show the residual amount of SMPI in the treating solution of sonication-SMPI oxidation of GMFG. Figure 5 shows that as the SMPI concentration increases (0.25 to 0.75 g/5gG) the residual SMPI decreases from 2.5 to 1.5. This may be attributed to the effect of the ultrasound waves. In liquid state, the sound is propagated as a longitudinal vibration which generates a series of compressions and rarefactions (i.e., areas of high and low pressure), low pressure in the rarefaction region can give rise to the formation of cavities and/or bubbles. These bubbles will be expanded and during the compression phase it collapses violently to generate the shock waves. The latter may lead to the response surface which was like the parabolic surface.

Figure 6 exhibits the effect of pH of oxidation medium on the residual amount of SMPI. It is seen that as the pH increases (3 to 9) the residual NaIO_4 decreases from 1.5 to 0.5. These results agree with

the above result; however, we can say the suitable pH is considered to be 3 for this reaction.

While Figure 7 depicts the effect of oxidation temperature ($^{\circ}\text{C}$) on the residual amount of SMPI. It is seen that as the oxidation temperature increases (20 to 60°C) the residual SMPI decreases. These results agree with the above results; however, it is possible that pH 3 is a suitable pH to essay out this reaction.

Finally, Figure 8 shows the effect of oxidation time in minute on the residual amount of SMPI. It is seen that as the oxidation time increases from 20 to 30 min the residual SMPI increases almost double. Further prolongation is accompanied by a decrease in residual SMPI. This is rather in full agreement with the above results, we can also consider an oxidation time of 30 min as the most appropriate time for oxidation of GMFG using the newly developed system, viz., sonication-SMPI system for oxidation of GMFG.

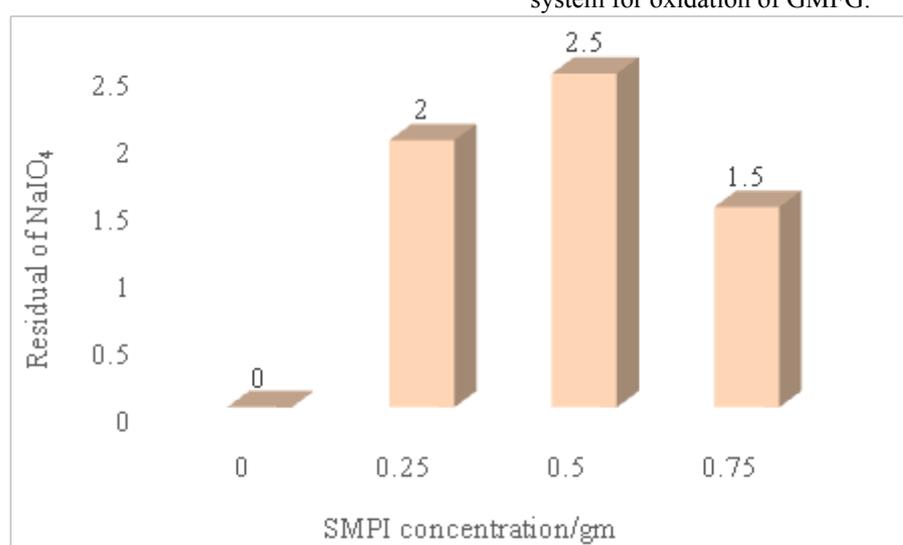


Fig. 5. Effect of SMPI concentration on the consumption of AMPI.

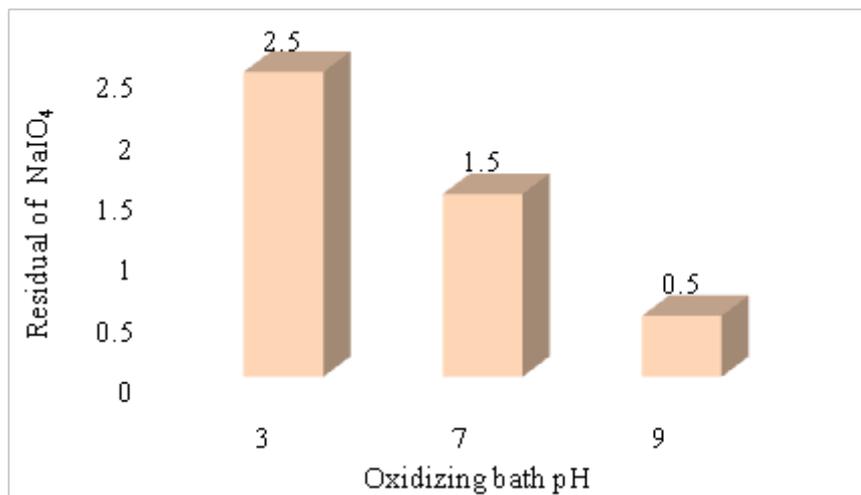


Fig. 6. Effect of pH of oxidation medium on the consumption of SMPI.

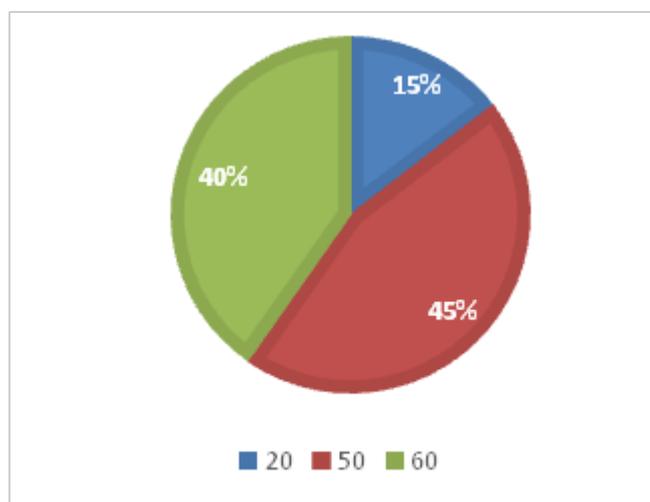


Fig.7. Effect of oxidation temperature on the consumption of SMPI.

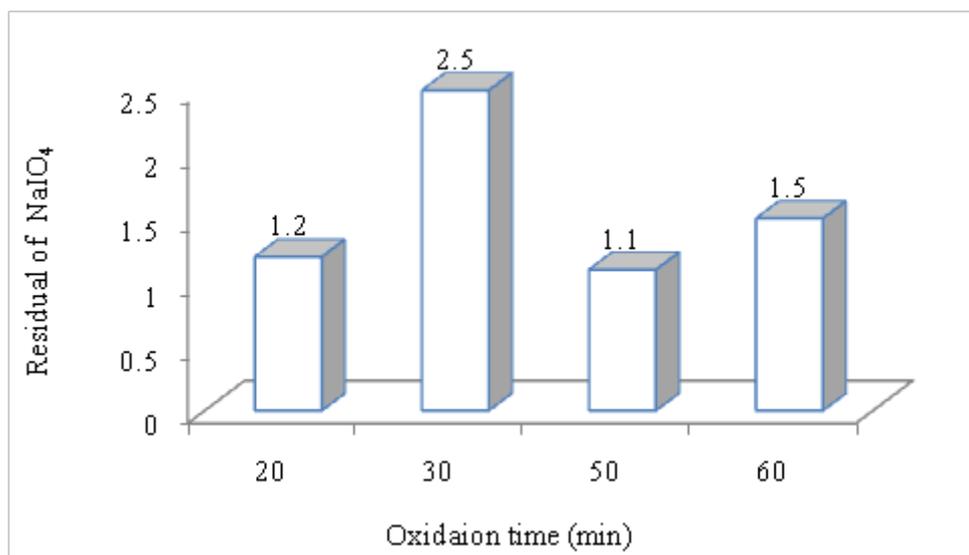


Fig. 8. Effect of time of oxidation on the consumption of SMPI.

Comparison between major important properties of Glactomannan Fenugreek Gum (GMFG) before and after oxidation using Sonication- SMPI system: GMFG was subjected to oxidation according to the newly developed method which is based on the combined effect of sonication and SMPI system. Details of the oxidation conditions are described in the foregoing sections. Thus obtained oxidized GMFG samples are compared with the non-oxidized GMFG as shown in Fig. 1-4.

Obviously, the viscosity and carboxyl (-COOH) groups of the oxidized GMFG are much lower and the carbonyl (-C=O) groups are much higher than those of the non-oxidized GMFG. The use of the new method in oxidation of GMFG makes it more soluble and easier to remove during the desizing process. Also noticed is that the oxidized GMFG assumes high stability as it could stand storing for two weeks (Fig.9b) without significant changes; opposite to the non-oxidized GMFG which becomes musty after one day storing (fig.9 a). Regardless of SMPI concentration used, the oxidized GMFG displays much higher carboxyl (-COOH) and carbonyl (-C=O) contents than the non-oxidized GMFG. However, the SMPI concentration determines the magnitude of the carboxyl and carbonyl contents. This could be ascribed to the abundance of oxidizing species at

higher concentration of SMPI. The active species attack the hydroxyl (-OH) group on the repeating unit (molecule) of the polysaccharide at C₂ and C₃ and converting them to aldehyde groups (Eq.2).

Sizing of cotton fabric with GMFG before and after oxidation using sonication-SMPI system at different concentration of SMPI: GMFG before and after oxidation under the combined effect of sonication-SMPI system using different concentration of SMPI was used in sizing of cotton fabrics. Results of percent increase in fabric weight due to sizing using oxidized GMFG samples and non-oxidized samples are set out in Tables 1-4. As is evident the size add-on on fabric increases by increasing concentration of SMPI in the oxidation system. It is also clear that the oxidized GMFG samples and the non-oxidized GMFG sample afford good sizes for cotton fabrics. It is certain however, that the percent increases in size add-on obtained with the oxidized GMFG samples are much higher than that obtained with non-oxidized GMFG samples. The highest percent increase in fabric weight (size add-on) is obtained when the fabric was sized with oxidized GMFG prepared using sonication in presence of 0.5 g SMPI/5g GMFG. The latter seems to present the most appropriate concentration to be used in the sonication-SMPI oxidation system.

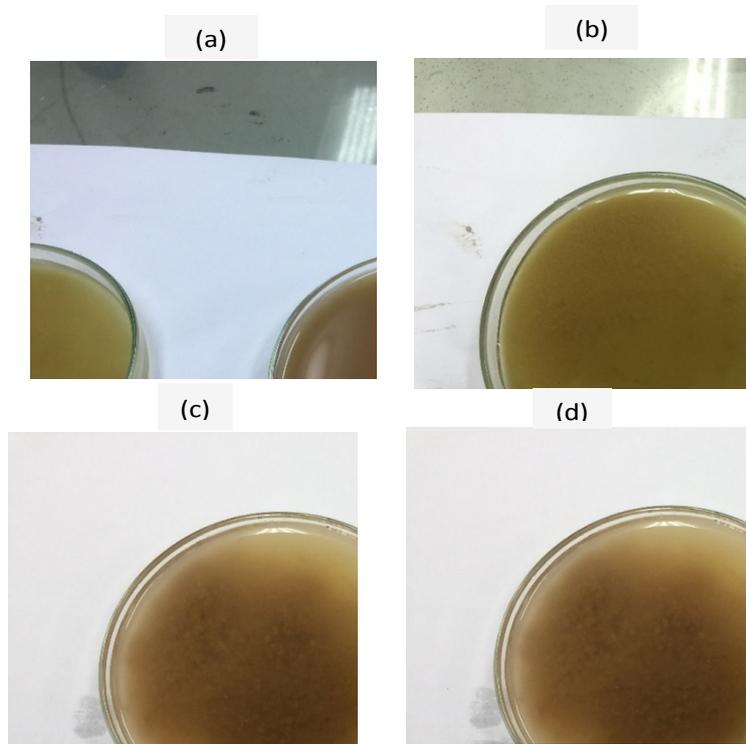


Fig. 9 a. Non-Oxidized GMFG: a) Fresh, b) after 1 day, (c) after 2 days and d) after 3 days

Table 1. sizing of cotton fabrics using oxidized GMFG samples and non-oxidized GMFG, the oxidized sample were synthesized using sonication-SMPI method (at different SMPI concentrations).

SMPI conc.	Weight of fabric		Increase in fabric weight %
	Before sizing	After sizing	
0	0.799	0.827	3.567
0.25	0.891	0.925	3.815
0.50	0.837	0.905	8.124
0.75	0.827	0.879	6.288

Table 2. Effect of oxidation of GMFG at different pH on the weight increase of cotton fabric after sizing

Oxidizing bath pH	Weight of fabric		Size add on %
	Before sizing	After sizing	
3	0.920	1.027	11.630
7	0.975	1.028	5.436
9	0.910	0.980	7.692

Table 3. Effect of oxidation of GMFG at different temperatures on the fabric weight after sizing with the prepared oxidized GMFG samples

Oxidizing bath temp./ °C	Weight of fabric		Size add on %
	Before sizing	After sizing	
30	0.70	0.75	7.14
50	0.70	0.77	10.000
60	0.70	0.74	5.7143

Table 4. Effect of sizing of cotton fabrics with GMFG oxidized for different duration of oxidation on the % increase in fabric weight

Duration of oxidation (min)	Weight of fabric		Increase in fabric wt. %
	Before sizing	After sizing	
20	0.947	0.971	2.534
30	0.700	0.770	10.000
50	0.900	0.931	3.444
60	0.934	0.964	3.212

A close examination of the results of Table 1-4 would reveal that cotton fabric sized with non-oxidized GMFG exhibits an increase in size add-on of 3.567%. This is against size add-on of 8.124% obtained with fabric sized with oxidized GMFG when oxidation was carried out using the sonication-SMPI (0.5 g/5 gm) system. Such a remarkable difference in the size add-on using non-oxidized reflects variations particularly in molecular size, particle size, solubility and uniformity.

Oxidation under the combined effect of sonication-SMPI is anticipated to decrease the molecular size and the particle size thereby leading to more uniformity and solubility in aqueous solution. Once this is the case, larger amount of the size solution of the oxidized GMFG is transferred to the fabric as compared with the size solution of non-oxidized GMFG

Antimicrobial activity: In the foregoing sections, we have shown that the non-oxidized GMFG is not stable and becomes musty within one-day time. On the contrary oxidized GMFG using the newly developed sonication-SMPI method enhance the stability and prolonged the stability up to two weeks' time without being musty.

Result given in Table 5 speak of: (i) antibacterial activity of cotton fabric treated with the prepared oxidized gum is greater than the untreated fabric, (ii) the antibacterial activity of sized cotton fabric against G^+ bacteria is greater than the activity against G^- , (iii) the antibacterial activity of un-treated cotton fabric against G^+ bacteria was less than the activity against G^- , (iv) the antibacterial activity increase as the concentration of SMPI increases until 0.5 g/5g gum then it decreases again in both (G^+ & G^-).

Results of Table 6 display that: (i) the antibacterial activity of sized cotton fabric against G^+ bacteria is greater than the activity against G^- , (ii) the antibacterial activity decreases as the pH of oxidation increase, and (iii) the sized fabric weight slightly decreases, as pH of oxidation increases (Table 6)

Here too, results of Table 8 highlight: (i) that the antibacterial activity of sized cotton fabric against G^+ bacteria is greater than the activity against G^- , (ii) that the antibacterial activity

increases as the oxidation temperature increases, and (iii), that there is only a slight increase in the weight of the sized samples are noticed (Table 6)

The Antibacterial activity of Oxidized GMFG was examined and results obtained are shown in Table 8. Evidently the antibacterial activity of the sized cotton fabric against G^+ bacteria is greater than the activity against G^- . It is also clear that the antibacterial activity increases as the temperature of oxidation increases. Meanwhile, there is a slightly increase in the weight% of the sized cotton samples (Table 8), results of table 8 exhibit an increase in fabric weight due to sizing.

Apparent viscosity and Rheological properties of oxidized GMFG:

GMFG before and after oxidation with the sonication-SMPI method-which was developed herein- were analysed for apparent viscosity. The oxidation was carried out using different concentration of SMPI. Table 9 depicts the apparent viscosity as a function of SMPI concentration at shearing rates ranging from 0 to 93. As is evident, the apparent viscosity of the non-oxidized GMFG decreases as rate of share increases within the range studied different situation is encountered with the oxidized GMFG whereby the apparent viscosity depends on the concentration of SMPI in the oxidation system under investigation. For instance, increasing the concentration of SMPI from 0.25 to 0.5/5g GMFG enhances significantly the apparent viscosity. The opposite holds true upon raising the SMPI concentration to 0.758/5g GMFG. At this latter concentration there are very sharp drops in apparent viscosity irrespective of the rate of share; the apparent viscosity tends to level off at higher rates of share..

The viscosity of the oxidized GMFG significantly decreases by increasing the concentration of SMPI oxidizing agent. This could be associated with breaking down the glucoside linkages during the oxidation processes. Decrement in apparent viscosity may be associated with glucosidic bond during violent oxidation under the combined effect of ultrasound waves and SMPI which leads to decrement in the molecular weight of GMFG. SMPI oxidation of GMFG produces aldehyde groups at C_2 and C_3 , a situation which eases cleavage of the glucosidic linkages. Thus the magnitude of GMFG oxidation depends on the SMPI concentration and the weakened position of glucose unit opening and completes of the oxidation processes.

Table 5. Antibacterial activity of sized cotton fabrics using the oxidized GMFG as sizing agent

SMPI conc.	G ⁺	G ⁻
0	2.5	0.5
0.25	7.5	6.6
0.50	22.5	18.0
0.75	15.0	14.0

Table 6. Antibacterial activity of sized cotton fabrics using oxidized GMFG at different oxidizing pH

pH of oxidation medium	Type of bacteria	
	G ⁺	G ⁻
3	19.5	18
7	22.5	18.0
9	18.0	15.5

Table 7. Antibacterial activity of sized cotton fabrics using oxidized GMFG prepared at different oxidation temperatures

Oxidizing bath temp./ °C	Type of bacteria	
	G ⁺	G ⁻
30	14.5	13.0
50	19.5	16.0
60	22.5	18.0

Table 8. Antibacterial activity of cotton fabrics sized using GMFG oxidizing at different oxidation temperatures

Oxidizing bath temp./ °C	Type of bacteria	
	G ⁺	G ⁻
20	14.5	13.0
30	22.5	18.0
50	17.0	15.0
60	17.0	15.0

Table 9. Effect of SMPI concentration on apparent viscosity of oxidized GMFG

Conc. Of NaIO ₄ (g/5gGMFG)	0	0.25	0.5	0.75
	RS cm ⁻¹	Apparent Viscosity in centipoise		
9.30	105	10.0	-	-
18.60	97.5	40.0	163	15.0
27.90	95.0	46.0	200	20.0
37.20	96.0	56.3	219	25.0
46.50	94.0	58.0	225	25.5
55.80	93.3	63.5	242	27.5
65.10	90.0	64.5	250	28.6
74.40	88.1	68.4	251	28.8
83.70	87.0	68.8	253	28.9
93	85.0	78.5	269	28.9

60°C, pH 3, for 30 min at different concentration of SMPI

Table 10 shows the apparent viscosity of GMFG oxidized under different pH's using sonication-SMPI method. The apparent viscosity at shear rates from 0 to 93 cm⁻¹. It is observed that for a given rate of share, the apparent viscosity displays a value at pH 3 which is almost 3 fold higher than that of pH 7. The situation is more aggravated at pH 9 where the apparent viscosity at the highest rate of share 93 cm⁻¹ acquires a value of 3.50 centipoise. This is against apparent viscosity value of 90 centipoise at pH 7. At pH 3 periodic acid seems to be the oxidizing component in combination with sonication.

It is logical that the periodic acid at pH3 is the oxidizing agent in acombined effect with sonication. At pH 7 and pH 9 the main oxidant is SMPI with much less oxidizing power than periodic acid.

At any event, however, the significant decrements of the apparent viscosity of oxidized GMFG by increasing the pH of the oxidation medium may be attributed to breaking down the glucosidic linkages during the oxidation processes. Decreases in apparent viscosity should be due to a combination of breaking down the glucosidic bond during violent oxidation which gives rise to a decrease in the molecular weight of GMFG.

Table 11 illustrates the apparent viscosity of GMFG oxidized at different oxidation temperatures. The results indicate that when the oxidation temperature increases the apparent viscosity increases. Similarly the apparent viscosity increases by increasing the rate of shear.

Table 12 shows the apparent viscosity of oxidized GMFG obtained at different oxidation time. The results indicate that the apparent viscosity increases by increasing the duration of oxidation. Similar treated is observed by increasing the rate of shear.

Enhancement on apparent viscosity of the oxidized GMFG brought about by increasing the time of oxidation and rate of shear suggests that GMFG undergoes changes in molecular size, particle size and shape, as well as solubility among the different entities of GMFG under the effect of the side factors, i.e. the time and the rate of shear. As a consequence, the state of the oxidized GMFG in solution assumes formation of more uniform aggregates and clusters with

great tendency for intimate association thereby enhancing the viscosity of GMFG solution

Figure 10a exhibits the experimental rheograms for the oxidized GMFG which was extracted from fenugreek seeds. The figure makes it evident that the relation between the shearing stress and the rate of shear is not linear and the up and down flow curves are not coincident. It is understandable that the oxidized GMFG display a non-Newtonian pseudo plastic behaviour. This means, when the viscosity (resistance to flow) of oxidised GMFG is measured a large applied force (shearing stress) must be used which cause a high-velocity flow (shear rate), i.e., the apparent viscosity is less than that of the same paste determined using a smaller force and a slower rate of flow [29, 30]. It is worthy to remark that in pseudo plastic solution no time-dependent effects are detected [30].

Figure 10b shows the rheograms of GMFG oxidized with SMPI at different PH'S. It is clear that the relation between the shearing stress and the rate of shear is not linear and the up and down flow curves are not coincident for all the samples examined. All the samples are, therefore, characterized by non-Newtonian pseudo plastic behaviour. The figure 9b shows also that the rheogram location with respect to the rate of shear axis depends on the pH values of the oxidation medium, thereby elucidating difference in the apparent viscosity.

Fig. 10c shows the experimental rheograms for GMFG oxidized at different temperatures (50, 60, 75°C.). It is evident that, all samples are characterized by non-Newtonian pseudo plastic behaviour. It is also clear from the rheograms that as the oxidation temperature increases, the location of the rheograms is shifted towards the rate of shear axis illuminating a decrease in its viscosity. It is further observed that the location of rheogram with respect to the rate of shear axis depends on the temperature of oxidation medium, which elucidate difference in the apparent viscosity.

Fig. 10d revels the experimental rheograms for GMFG oxidized for different times (20, 30, 50, 60 min.). It is obvious that all the samples are characterized by non-Newtonian pseudo plastic behaviour since the relation between rate of shear and shearing stress is not linear and the up and down flow curves are not coincident. It is also clear that as the oxidation time increases, the location of the rheograms is shifted towards the rate of shear axis elucidating a decrease in the viscosity of the GMFG.

Table 10. Effect of pH of the oxidation media on apparent viscosity of oxidized GMFG

Oxidation pH medium RS cm ⁻¹	3	7	9
	Apparent Viscosity in centipoise		
9.30	-	5.0	-
18.60	163	50.0	-
27.90	200	65.0	-
37.20	219	75.0	-
46.50	225	82.0	1.25
55.80	242	83.7	1.75
65.10	250	85.0	2.0
74.40	251	85.1	2.22
83.70	253	86.1	2.75
93	269	90.0	3.50

60°C, for 30 min, 0.5g SMPI/5g GMFG at different pH

Table 11. Effect of temperature of oxidation medium on apparent viscosity of oxidized GMFG

Oxidizing bath temp ./°C RS cm ⁻¹	30	50	60
	Apparent Viscosity in centipoise		
9.30	20	-	-
18.60	115	125	163
27.90	125	142	200
37.20	138	169	219
46.50	132	170	225
55.80	133	183	242
65.10	135	186	250
74.40	139	191	251
83.70	139	194	253
93	139	195	269

At 60°C, pH 3, for 30 min, 0.5g SMPI/5g GFG

Table 12. Effect of oxidizing bath time on apparent viscosity of oxidized GMFG

Oxidizing bath time ./min RS cm ⁻¹	20	30	50	60
	Apparent Viscosity in centipoise			
9.30	150	-	125	-
18.60	158	163	138	-
27.90	175	200	183	33.3
37.20	188	219	185	50
46.50	200	225	189	60
55.80	204	242	193	66.7
65.10	206	250	194	71.4
74.40	207	251	195	80.6
83.70	208	253	196	81.3
93	209	269	197	82.5

At 60°C, pH 3, for different time, 0.5g SMPI/5g GFG

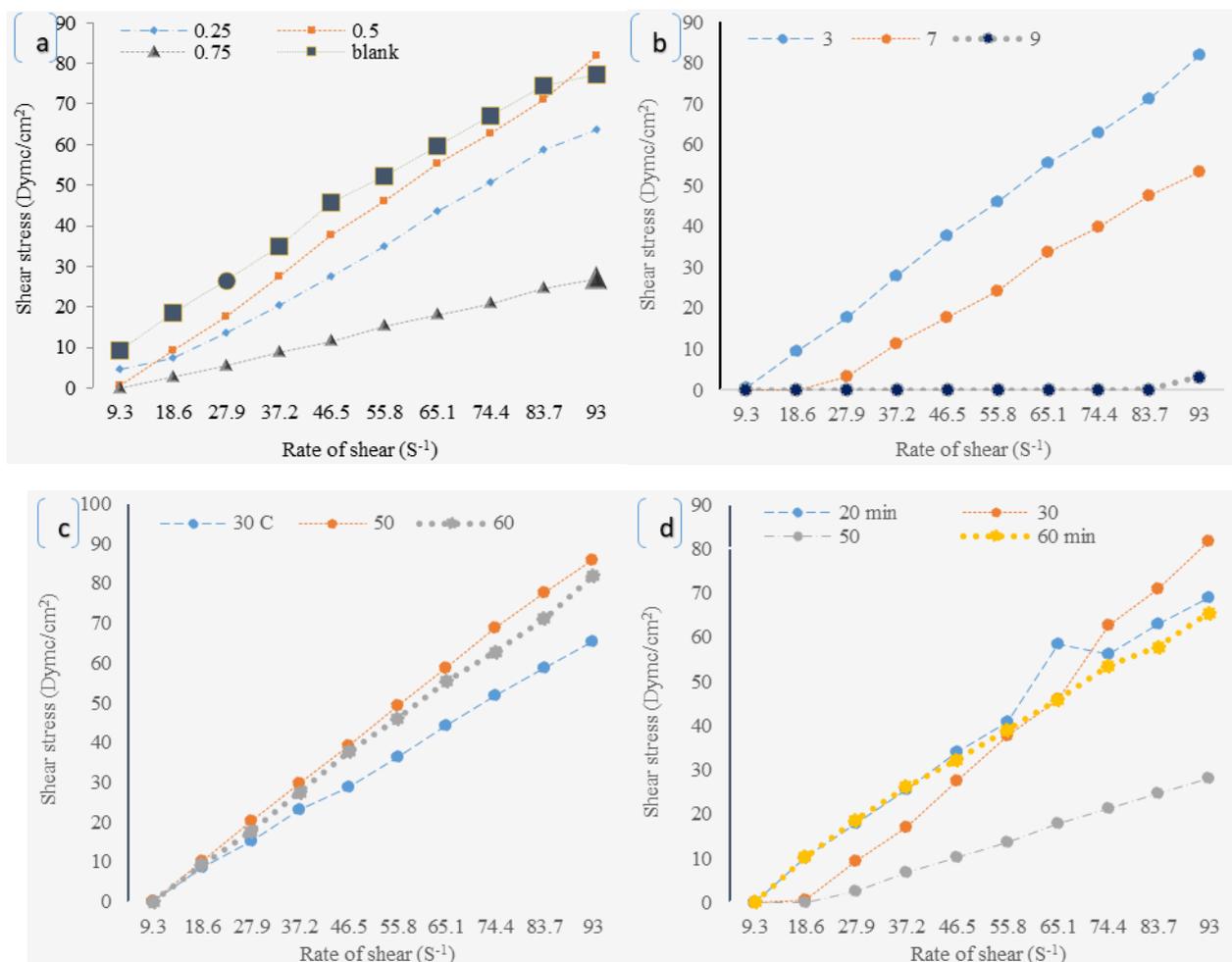


Fig 10. Effect of (a) SMPI concentration, (b) oxidizing medium PH, (c) oxidation temperature, (d) oxidation time on the rheological properties of oxidized GMFG

Scanning electron microscopy (SEM)

To get insight into the morphology of the oxidized GMFG under the combined effects of ultrasonic and SMPI oxidation, scanning electron microscopy (SEM) characterization was performed to detect the incorporation of SMPI on the fibre surfaces, Fig.11. The surface of the blank cotton fibre in absence of oxidized GMFG (Fig. 11a) shows the flocculation behavior while

in presence of non-oxidizing GMFG (Fig. 11b) shows aggregates fibre with small fibre diameter. The image of the pristine sizing cotton fibre with oxidizing GMFG combined with ultrasonic and SMPI system shows clear and smooth longitudinal fibril structure surface (Fig. 11c) which combined with increasing in fibre diameter which permit to more penetration of oxidized GMFG into the cotton molecules.

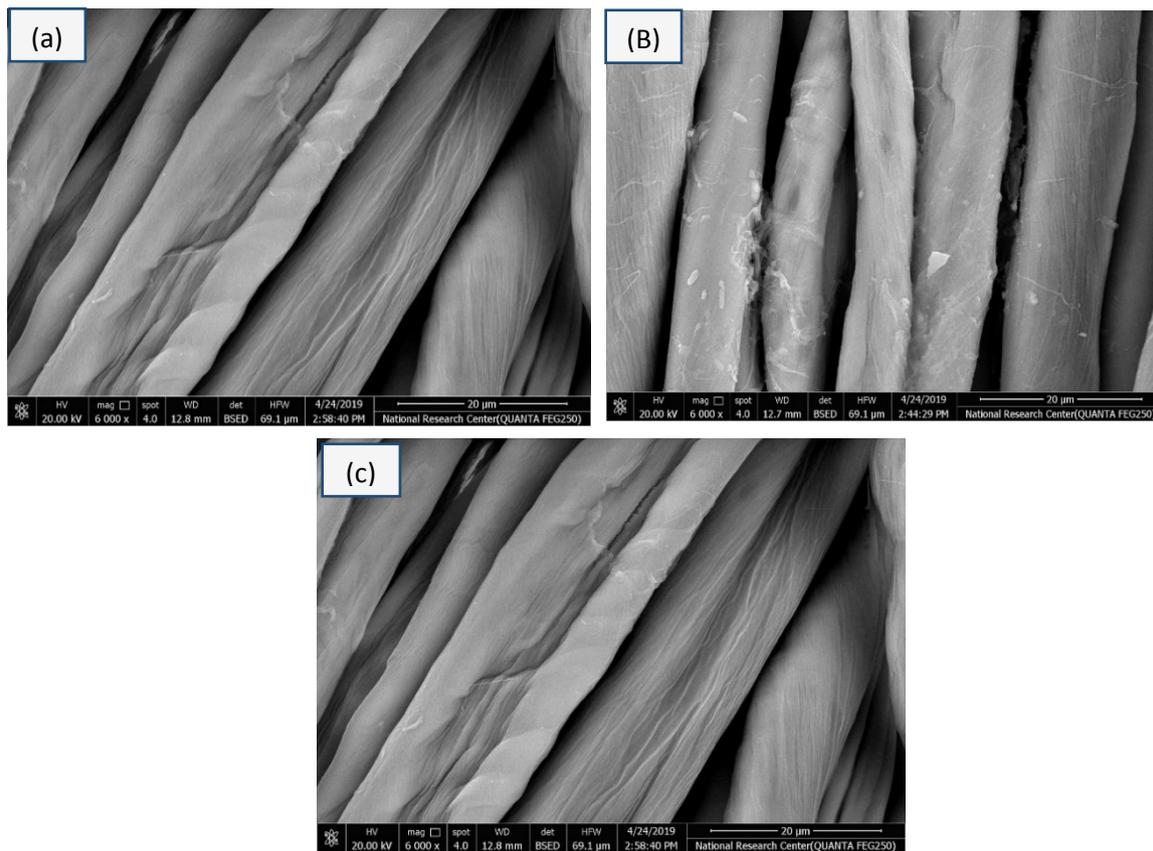


Fig.11. (a) Scanning electron microscope image for blank cotton fibre, (b) SEM for sizing cotton fibre with non-oxidizing GMFG, (c) SEM for sizing cotton fibre with oxidizing GMFG.

Conclusion

A new method was established for synthesis of oxidized galactomannan fenugreek gum (GMFG) extracted from fenugreek seeds under the combined effect of ultrasound waves and sodium metaperiodate (SMPI). The oxidation process was carried out under a variety of conditions encompassing the parameters SMPI concentration, oxidation pH medium and temperature and duration of oxidation. The resultant oxidized GMFG samples, along with the non-oxidized gum, were submitted to quantitative determination of micro structural analysis, namely, carboxyl and carbonyl group as well as apparent viscosity and rheological properties. Conclusion arrived at from these studies are given below:

- a. The aforementioned parameters affecting oxidation of GMFG using ultrasonic-SMPI system act in favour of GMFG oxidation. For instance, increasing the magnitude of these parameters is accompanied by a marked increase in both carbonyl content and residual of SMPI (NaIO_4).
- b. GMFG oxidized by using sonication-SMPI method is more stable than the non-oxidized gum during storing for a long time
- c. The obtained results show that the suitable concentration of SMPI is 0.5g/5g GMFG when SMPI is used as an oxidizing agent in combination with sonication to produce oxidized GMFG. Besides, the oxidation condition involves pH of 3 at 50°C for 30 min.
- d. The non-oxidizing GMFG is musty after one day while the oxidized is not musty before two weeks.
- e. The cotton fabric sized by using oxidized GMFG acquires antimicrobial activity which advocates it for medical textiles.
- f. Oxidized GMFG displays increased solubility and decreased apparent viscosity by increasing the extent of oxidation in comparison with the non-oxidized GMFG. This recommends utilization of currently developed sonication-SMPI system as green oxidizing agent for fabrication of water soluble and easily removable GMFG with wider domains for application.
- g. The image of the pristine sizing cotton fibre with oxidizing GMFG combined with ultrasonic and SMPI system shows clear and smooth longitudinal fibril structure surface which combined with increasing in fibre diameter which permit to more penetration of oxidized GMFG into the cotton molecules

References

1. Vouters M, Rumeau P, Tierce P, Costes S (2004) Ultrasounds: an industrial solution to optimise costs, environmental requests and quality for textile finishing. *Ultrason Sonochem* 11:33–38 3.
2. Ma J, Chen S, Liu C, Xu W, Wang S (2008) The influences of ultrasonic on embedding nanoparticles into porous fabric materials. *Appl Acoust* 9:763–769
3. Hurren C, Cooksona P, Wang X (2008) The effects of ultrasonic agitation in laundering on the properties of wool fabrics. *Ultrason Sonochem* 15:1069–1074
4. Khajavi R, Azari P (2007) Effects of ultrasound irradiation on wet wool chlorination treatment. *Pak J Biol Sci* 10:2732–2735
5. Guebitz GM, Caco-Paulo A (2008) Enzymes go big: surface hydrolysis and functionalisation of synthetic polymers. *Trend Biotechnol* 26:32–38
6. Araujo R, Casal M, Cavaco-Paulo A (2008) Application of enzymes for textile fibres processing. *Biocatal Biotransformation* 26:332–3492
7. Parvinzadeh M (2007) Effect of proteolytic enzyme on dyeing of wool with madder. *Enzyme Microb Technol* 40:1719–1722
8. Karabogã C, Koçulu AE, Duran K, Bahtiyari M_I (2007) Use of ultrasonic technology in enzymatic pretreatment processes of cotton fabrics. *Fibres Text East Eur* 15:97–100
9. Basto C, Tzanov T, Cavaco-Paulo A (2007) Combined ultrasound-laccase assisted bleaching of cotton. *Ultrason Sonochem* 14:350–354.

10. Lee KW, Chung YS, Kim JP (2003) Characteristics of ultrasonic dyeing on poly(ethylene terephthalate). *Text Res J.* 73:751–755
11. Kamel MM, El-Shishtawy RM, Youssef BM, Mashaly H (2007) Ultrasonic assisted dyeing. IV. Dyeing of cationised cotton with lac natural dye. *Dyes Pigm.* 73:279–284
12. Kamel MM, El-Shishtawy RM, Hanna HL, Ahmed NSE (2003) Ultrasonic-assisted dyeing: I. Nylon dyeability with reactive dyes. *Polym Int.* 52:373–380
13. Kamel MM, El-Shishtawy RM, Yussef BM, Mashaly H (2005) Ultrasonic assisted dyeing. III. Dyeing of wool with lac as a natural dye. *Dyes Pigm.* 65:103–110
14. Merdan N, Akalin M, Kocak D, Usta I (2004) Effects of ultrasonic energy on dyeing of polyamide (microfibre)/Lycra blends. *Ultrasonics*, 42:165–168.
15. Vajnhandl S, Le Marechal AJ (2005) Ultrasound in textile dyeing and the decolouration/mineralization of textile dyes. *Dyes Pigm.* 65:89–101
16. Singla R, Grieser F, Ashokkumar M (2009) Sonochemical degradation of martius yellow dye in aqueous solution. *Ultrason Sonochem.* 16:28–34
17. Vajnhandl S, Le Marechal AJ (2005) Ultrasound in textile dyeing and the decolouration/mineralization of textile dyes. *Dyes Pigment*, 65:89–101
18. Singla R, Grieser F, Ashokkumar M (2009) Sonochemical degradation of martius yellow dye in aqueous solution. *Ultrason Sonochem.* 16:28–34
19. Hassabo, A.G., Novel Synthesis of Nano-emulsion Butyl Methacrylate/Acrylic Acid via Micro-emulsion Polymerization and Ultrasonic Waves. *Journal of Textile and Apparel, Technology and Management*, 2016. 10(1).
20. Thakore, K. “Application of ultrasound to textile wet processing.” *American Dyestuff Reporter*, 79, no. 10 (1990): 3044-.
21. Vajnhandl, Simona, and Alenka Majcen Le Marechal. “Ultrasound in textile dyeing and the decolouration/mineralization of textile dyes.” *Dyes and Pigments*, 65, no. 2 (2005): 89-101.
22. McNeil, S. J., and R. A. McCall. “Ultrasound for wool dyeing and finishing.” *Ultrasonics Sonochemistry* 18, no. 1 (2011): 401406-.
23. Ning, Xun-an, Hong Chen, Jianrong Wu, Yujie Wang, Jingyong Liu, and Meiqing Lin. “Effects of ultrasound assisted Fenton treatment on textile dyeing sludge structure and dewaterability.” *Chemical Engineering Journal* 242 (2014): 102108-.
24. Moholkar, V. S., V. A. Nierstrasz, and M. M. C. G. Warmoeskerken. “Intensification of mass transfer in wet textile processes by power ultrasound.” *AUTEX Research Journal* 3, no. 3 (2003): 129138-.
25. Kuakpetoon, D.; Wang, Y.-J. *Carbohydr. Res.*, 341, 1896, (2006)
26. Dulong, V.; Mocanu, G.; Picton, L.; Le Cerf, D. *Carbohydr. Polym.*, 87, 1522, (2012).
27. Hebeish A., El-Rafie M. H., Rabie A. M., El-Sheikh M. A., Mehrez E. El-Naggar1, “Ultra-Microstructural Features of Perborate Oxidized Starch”, *J. APPL. POLYM. SCI.*, DOI: 10.1002/APP.40170, (2014)
28. Elgayyar, M., Draughon, F. A., Golden, D. A., & Mount, J. R., Antimicrobial activity of essential oils from plants against selected pathogenic and saprophytic microorganisms. *Journal of Food Protection*®, 64, 2001, 1019-1024.
29. Baliarsingh, S., Behera, P.C., Jena, J., Das, T. and Das, N.B., 2015. UV reflectance attributed direct correlation to colour strength and absorbance of natural dyed yarn with respect to mordant use and their potential antimicrobial efficacy. *Journal of Cleaner Production*, 102, pp.485-492.
30. Nagla El-Shemy, Karima Haggag, Elham El-Kharady, Hosam El-Sayed, “Synthesis and Applications of Nano Binder Based on Plant Oils”, *Journal of Natural Fibers*, Taylor & Francis, 1-16, (2016)
31. Tyrone, L. V. *Textile processing and properties, preparation, dyeing, finishing and performance.* Amsterdam – London – New York – Tokyo (1994)