Dure Najaf Iqbal, Arif Nazir*, Munawar Iqbal and Muhammad Yameen

Green synthesis and characterization of carboxymethyl guar gum: Application in textile printing technology

https://doi.org/10.1515/gps-2020-0022
Received July 13, 2019; accepted December 09, 2019.

Abstract: This study focusses on the synthesis of carboxymethyl guar gum (CMG) via monochloroacetic acid under alkaline conditions. The reaction conditions were also optimized during the course of experiment. Guar derivative with variable degree of substitution (DS) were prepared and were confirmed by Fourier transform infrared (FTIR) spectroscopy. The DS was determined quantitatively by titration method for each derivative. The synthesized guar gum derivatives, being the natural thickners, have been used in textile printing technology. Substituted guar gum has been proved environmental friendly thickener as compared to synthetic thickeners. Penetration properties, fixation ability, colour fastness, levelness and fabric handling was compared with alginate thickener (commercially available). Guar gum thickeners showed enhanced properties versus alginate thickener and can be used as an alternative to synthetic thickeners in view of its green, non-hazardous and economical derivatives. Guar gum is the outstanding natural thickener, stabilizer, gelling agent and could possibly be used in various industrial units including food, cosmetic, textile, oil fracturing and mining.

Keywords: synthesis; reactive thickener agent; guar gum; alginate; printing; color properties

1 Introduction

The art of decorating fabric was initiated from the earliest periods using stamping process. It is known that ancients of Far East have practiced hand printing with wood blocks as early as 500 B.C. People of Moen Jo Daro (Sindh) and Egypt produced linen cloths of good construction and were also familiar with some form of textile printing [1-5]. Textile printing is the most versatile and vital methodolgy for introducing colour and design to textile fabrics. In printing, colour in induced on fabric using various technologies [6-8]. Screen printing is one of the oldest and versatile printing procedure involving a mesh for the formation of a desired design on fabrics [9-11]. Using screen printing methodology [12], greater amount of printing material can be applied to the substrate thus enhancing the thickness of print. This cannot be achieved via other methodologies for the formation of versatile effects. In textile printing with reactive dyes mostly sodium alginates or mixtures with carboxymethylated polysaccharides are usually used as thickening agent. It is due to their economical, green, washable, biodegradable nature and they cause no fabric stiffeness [3,13-15]. Grafting of partially carboxymethylated guar gum and N-vinyl formamide was synthesized for textile applications via free radical polymerization using 2,2-Azobis [2-(2-imadazolin-2-yl) propane]dihy-drochloride as an initiator [16-18]. Gong et al. [17] carried out carboxymethylation of guar gum with a multi-step process. The rotational viscometer was used to determine the rheological properties of printing pastes. The viscosity increased in the beginning and then decreased with storage time. Carboxymethylation of the gum produced from the seed of *Cassia occidentalis*, found very important industrial applications to replace the conventional gum. Copolymer of 4-vinyl pyridine and carboxymethylated guar gum was fabricated by using a bromate/thiourea redox pair as reaction promotes under inert atmosphere at 40°C. The graft copolymer is characterized by FTIR and thermal analysis. Solvent free synthesis of carboxymethyl galactomannans and other biopolymers were established via monochloroacetic acid in the presence of $NaHCO_3$.

Carboxymethylated derivative of guar gum have the potential to provide an efficient substitute methodology for the delivery of hydrophilic macromolecules orally [19]. Some ecofriendly bioactive products such as fibres, polysaccharides, dyes and pigments were reviewed for the expansion of bioactive textiles [20].

*** Corresponding authors: Arif Nazir,** Department of Chemistry, The University of Lahore, Lahore, Pakistan, e-mail: anmalik77@gmail.com
Dure Najaf Iqbal, Munawar Iqbal, Department of Chemistry, The University of Lahore, Lahore, Pakistan
Muhammad Yameen, Department of Biochemistry, Government College University Faisalabad, Pakistan

To prevent unacceptable fabric handling while printing with reactive dyes, sodium alginates or synthetic thickeners are typically used as thickening agents. Environment friendly reactive dying method has been established by Schneider et al. [7,21] using guar gum as a thickener. The use of very highly substituted guar gum as an alternative to alginates can be used in the printing of cotton with reactive dyes. The rheological, technological and colorimetric parameters of the mixed printing pastes were determined and used for comparison with the printing pastes of alginates [18,22-25].

Alginate thickeners are mostly used in reactive dying due to their inertness. Alternatives to these are polysaccharides which have sensitive –OH groups, which must be substituted before their use as thickeners in reactive printing. In present investigation, guar gum (Figure 1) was modified, characterized and employed as a thickner. Finally, properties were compared with commercial alginate thickner used in textile printing.

2 Materials and methods

Native guar gum was purchased from National gum industries, Karachi having molecular weight of 1.043×10^6 g/mol. All the chemicals and reagents used in this study were of analytical grade and were purchased from Merck, Germany. All solutions were prepared in distilled water. Nitrogen filled balloon was introduced through standard syringe techniques for moisture or air sensitive reactions. Glass apparatus was fully dried on flame used to avoid moisture.

Carboxymethylation was done from guar gum and monochloroacetic acid under heterogenous reaction conditions by the following method of Dodi et al. [19] with minor alteration. Guar gum (2 g) was dissolved in 100 mL distilled water for 30 min with continuous stirring under nitrogen gas. When fully swollen, NaOH (10% solution) was added over a period of 10 min with feeding rate of 1 mL/min. Reaction mixture was agitated for another 1 h at 50°C. Further a required volume of monochloroacetic acid was injected to the system with the same feeding rate. Temperature was raised to 60°C for 4 h. Reaction mixture was allowed to cool at room temperature before filtration. Final product was twice extracted with ethanol and filtered. The precipitates were washed with acetone and dried in oven for 24 h at 60°C.

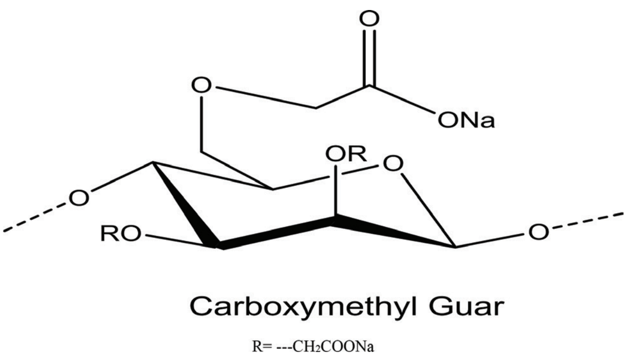


Figure 1: Structure of carboxymethyl guar gum.

1 g of CMG was added to 200 mL Erlenmeyer flask having 10 mL of distilled water to get a homogenous solution. Then NaOH (10 mL, 0.5 N) was added with continuous stirring and heated near boiling for 15 min. Then it was titrated with 0.5 N HCl using phenolphthalein as indicator. The amount of acid used was noted. D.S was figured out with the equation as follows:

$$\text{D.S.} = \frac{0.162\,\text{X}}{1-0.058\,\text{X}} \tag{1}$$

$$\text{X} = \frac{\text{AB}-\text{CD}}{\text{E}} \tag{2}$$

where: X – acid utilized per gram of sample, A – NaOH (mL) added, B – NaOH normality, C – HCl for titration of the excess NaOH, D – HCl normality, E – CMG (g) used.

Different organic solvents were used in order to test the solubility of CMG. 1% w/v solutions was prepared with constant stirring at room temperature [26,27]. The water holding ability/swelling ratio of guar gum derivatives was determined by following the method described in Abd El-Rahim et al. [28]. The solutions of CMG and native gum were prepared carefully in distilled water to study their swelling equilibriums. For this an accurate weight 1g of each compound were well dissolved in distilled water (50 mL) than kept for 24 h at STP to establish the swelling equilibrium. Next day, samples were filtered by a commercial sieve (681 µm, 30 mesh) to remove the excess water.

The equilibrium degree of swelling was measured by following equation:

$$\text{SR} = \text{W}_\text{f}\text{-W}_\text{i}/\text{W}_\text{i} \tag{3}$$

where: SR – Swelling ratio, W_f – Sample weight after swelling, W_i – Before swelling sample weight, DS was calculated by expression:

$$\text{DS} = \text{SR} \times 100 \tag{4}$$

Native guar gum as well as CMG samples were analyzed by FTIR spectrophotometer (Shimadzu IR-Prestige 21, Japan). For the FTIR, a blend of sample and KBr was prepared in a ratio of 1:99 it was squeezed under high pressure to form a pellet and dried in oven. Further it was observed in spectrophotometer at a resolution of 4 cm^{-1} having 50 numbers of scans and wave number of 4000-600 cm^{-1}.

Two different reactive dyes named Reacxtive orange M2RJ and reactive yellow M3R of Dyestar company were used. Other reagents and cotton fabric were provided by Combined Fabrics Limited. CMG (thickener) was prepared in laboratory. Thickener and distilled water was well agitated to attain maximum swelling for 2 h. Printing blendes were prepared by mixing sodium chloride (1 g), citric acid (10 mL) and 4% PH buffer ACR for another 30 min. After attaining the required viscosity, dye was added to the solution. The solution was stirred well to get a homogenous paste. The screen was centered on white fabric to print. The fixation of the dyes was highly depends on the curing and bed of the sample.

M&R gas screen printing conveyor dryer curing machine (United Kingdom) was used to cure the printing sample. Sample was passed twice through machine having a curing temperature 170°C and cure time of 1.5 min. Printed piece was bed in heat transfer bed machine (Allied engineering works Faisalabad) operating at 150°C having a vertical static pressure of 5 psi and operating time of 15 s [29,30].

In this process, for color fastness to laundering test method of American Association of Textile Chemists and Colorists (AATCC 61) [31] was followed. The resistance to frequent wash was estimated to test the color fastness in laundries of textiles. Three home laundries were used for this purpose to test the color fastness of sample. The washing of printed fabric was carried under the following process. The sample was washed with cold water. Then it was soaped with detergent ICE 1 g/L at 50°C for 40 min duration. This laundry process was done in a Whirlpool Gold laundry machine (USA). Further sample was washed with cold water and dried. This soaping process was performed thrice.

The overall fastness properties were calculated through standard procedures [32]. The color fastness of print was tested under standard AATCC 8 [29]. This test was conducted on Crock meter James H. Heal & Co. Ltd. It was a manual crock meter which crocked the fabric at 45° angled. In this process a white cloth specimen of 5/13 cm was mounted on weave which rubs the sample in parallel direction. A 10 pass run test was performed. Color fastness to dry and wet crocking was tested. In dry crocking, dry white test piece was used where as in wet crocking; white test piece was damped with water.

Staining test was done under AATCC 2A [32] standard method. In this process, a multi-fiber was attached with sample in closed cup. 50 small steel balls and water was added to the cup and was covered with its lid. This cup was tightened in the machine having a hot water at 49°C having run time of 40 min. This test was done in Atlas Launder ometer (USA).

3 Results and discussion

Guar gum is one of the important naturally occurring non-ionic high molecular weight polysaccharide consists of galactomannan which has vast applications in various fields. CMG was synthesized via monochloroacetic acid under alkaline conditions and reaction conditions were optimized. Technological behaviour of CMG was studied in printing cotton fabric with reactive dyes. Major concern to textile printing is waste water pollution due to unfixed dyes and thickeners lost [33-38]. The properties of the derivatives were found comparable to native guar gum. Some ecofriendly bioactive products such as fibres, polysaccharides, dyes and pigments, polyphenols, oils and other biologically active compounds in textile industry were reviewed in recent studies. Printing was done from the resulting printing pastes. Printing paste viscosity was decreased by the increase in nitrogen content. The applied amount, penetration and fixation were assessed as the printing parameters. Most of the properties of the mixtures showed dye-dependent behavior. To prevent unacceptable fabric handle while printing with reactive dyes, sodium alginates or synthetic thickeners are typically used as thickening agents. Environment friendly reactive dying method has been established by Schneider et al. [7,21] using guar gum as a thickener.

Printing trials showed that its guar gum use can prevent fabric stiffness. The additives used have no significant effect on rheology and color strength but contributed to soft fabric handle even when guar gums were used as thickening agent. Many methods including rheological measurements and the technological behaviour of different guar thickeners were studied during the printing process and compared with the behaviour of other available printing thickeners. It was recognized from the analysis of waste waters that the guar thickeners are less damaging towards the environment, yielding comparable quality. The use of very highly substituted guar gum as an alternative to alginates can be used in the printing of cotton with reactive dyes . The rheological, technological and colorimetric parameters of the mixed printing pastes were determined and used for comparison with the printing pastes of alginates [18,22-25].

Carboxymethylation of guar gum was accomplished by Willianson ether technique in which a two step reaction was performed. Starting from a strong base like NaOH that gives a free hydroxyl group to form an alkoxides which increased the nucleophilicity (Figure 2). The reaction between chloroaceticacid and alkoxides leads to the desired product. The side reactions in the process also give us the development of sodium glycoate by the reaction of sodium hydroxide and sodium chloroacetate. Different parameters were involved in the carboxymethlyation process [39]. The efficiency of the desired product was calculated by varying the reaction parameters i.e. solvent selection e.g water and DMF, concentrations and effect of volume of NaOH, monochloroacetic acid concentrations, temperature and time of reaction. Reaction conditions were optimized for each sample.The trials performed were summarized in the Table 1.

3.1 Degree of substitution

Each sugar unit of guar gum has 3 free hydroxyl groups available for substitution. More consistent, quick and inexpensive method for determination of carboxymethylation is titration method. It was done by back titration, which involved alkaline hydrolysis of substituted group (carboxymethyl group) and titration of excess alkali. By this method we quantitatively calculated number of hydroxyl groups substituted per sugar unit. Back titration was first time used in 1947 for carboxymethyl cellulose. Later on, it become greatly studied method for determination of DS of other polysaccharides.

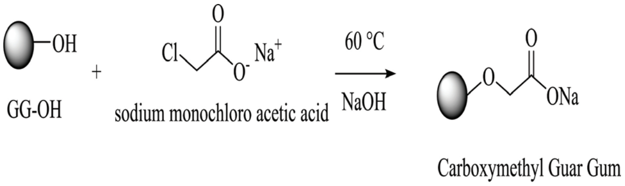


Figure 2: Synthesis of carboxymethyl guar (CMG).

Table 1: Carboxymethylation of guar gum following the method [19].

CMG product	V_{NaOH} (mL)	C_{NaOH} (%)	W_{CA} (g)	Time (h)	Temprature (°C)
1	15	5	2	3	50
2	15	10	4	3	50
3	10	15	6	4	50
4	10	30	10	4	60
5	10	10	2	4	60

Samples GG-1-GG5 were treated with acid (HCl) for acid hydrolysis of carboxymethyl groups, then converted into its sodium-salt by treating it with known amount of NaOH. Back titration of excess alkali was completed quantitatively determine the amount of liberated groups. Other methods used for DS of hydroxyl groups are IR, elemental analyses etc. The DS value was 0.35 with 66% yield and the main FTIR (KBr) Peaks are 3369 cm^{-1} (hydrogen bonded OH stretch) and 2927 cm^{-1} (aliphatic C–H stretch).

3.2 Determination of solubility

Cold water solubility even at very small amount makes guar gum different from other plant gums. Guar gum forms highly viscous gel like complex formation. Its water solubility depends upon mannose: galactose ratio. Large number of α-1-6-D–glucopyranosyl units enhance water solubility and vice versa. Guar is not organo-soluble which limits its applications [28,29]. The introduction of different functional groups on gum backbone might alter its solubility profile, but it depends upon substitution extent, nature of substituted group, temperature, type of solvent, molecular weight etc. Generally gum with DS more than 2 showed notable difference in solubility profile. Guar derivatives commercially available with DS lower than 1 is not soluble in typical solvents. Samples 1-5 showed good solubility in water. Sample 5 is soluble in DMF upon heating. All other samples are insoluble in all organic solvents.

3.3 Water holding ability of guar gum

Water-holding capacity (WHC) is an central aspect which determines commercial applications of gums. Swelling ratios or water holding capacity is ability of hydrogels to hold water after the equilibrium attained under certain conditions resulting in gel formation and loss of granular morphology (Table 2). Greater swelling capacity of guar

Table 2: Swelling index of modified guar gum samples.

Sample	Swelling index (%)
Guar gum	26.15 ± 2
1	25.17 ± 1
2	23.11 ± 2
3	22.23 ± 2
4	17.32 ± 2
5	14.54 ± 2

is associated with its hydrophilic nature when compared with other galactomannan. Its ability makes it ideal for improvement of texture of end products in diverse industrial formulations. It is requirement to verify swelling index of guar derivatives for its potential applications in cosmetics, food, pharmaceutical, and many other sectors [40,41]. Water holding capacity/swelling index of samples depends upon different factors. Relationship between swelling of guar gum and molecular structure is complex phenomenon. Different literature expressed similar effects depend upon experimental conditions. Carboxymethylation of gum induced hydrophobicity in gum backbone resultes decrease in swelling ability.

3.4 FTIR analysis

The FTIR results of native guar gum and CMG are showing in Figure 3. The native guar gum show that strong absorption band on 3391 cm^{-1} is due to hydrogen bonded OH bond (since the hydrogen boding decreases absorption frequency; Free OH appears at about 3600 cm^{-1}) where as the narrow peak on 2907 cm^{-1} is of aliphatic CH functional group. Absorption band appears on 1649 cm^{-1} indicated OH group which is due to presence of water molecule. The out of plane bending (twisting) of CH$_2$ group appear on 1457 cm^{-1} and bending at 1025 cm^{-1} indicates funcational group of CH$_2$–O–CH$_2$. The spectrum of CMG (Figure 3) indicates comparatively weaker (less intense) band at about 3418 cm^{-1} because of OH stretching indicated that substitution of few OH groups. Water band present on native guar gum is now missing in CMG product. The vibrations which are either symmetrical or asymmetrical at points 1429 cm^{-1} and 1615 cm^{-1} respectively revealed that substitution of carboxymethyl into guar gum at some points [42,43].

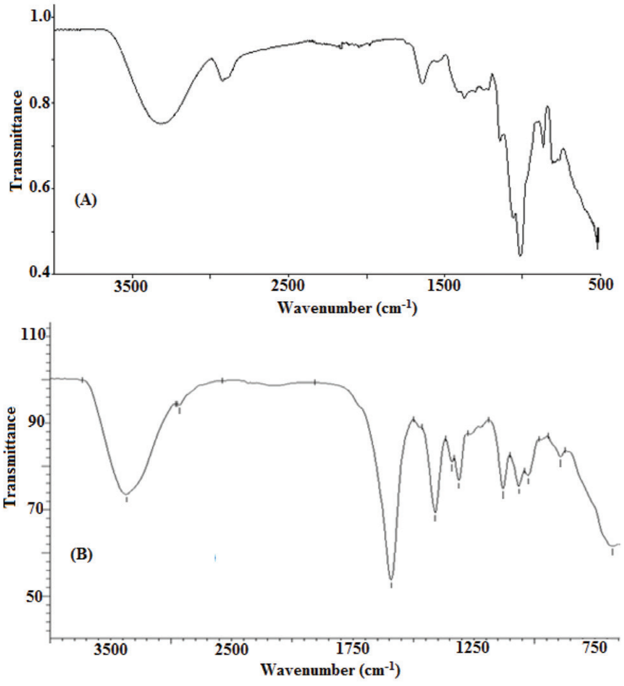
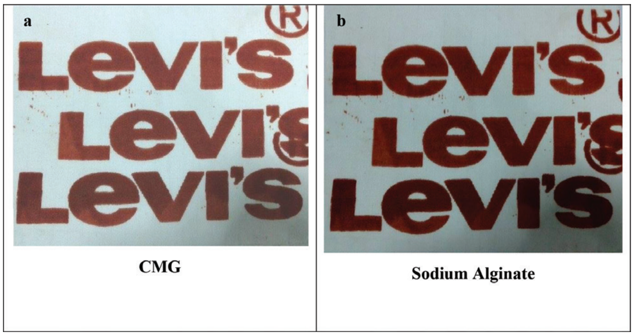


Figure 3: FTIR of (a) native guar gum and (b) carboxymethyl guar gum.



CMG

Sodium Alginate

Figure 4: Comparison of CMG thickener with sodium alginate.

Table 3: Parameters showing color fastness to crocking for different dyes.

Thickener	Reacxtive orange M2RJ	
	WET	DRY
CMG	3-4	3.5
Sodium alginate	3-4	4
	Reactive yellow M3R	
CMG	3-4	3.8
Sodium alginate	3-4	4

3.5 Color fastness

The printing trial of the thickener CMG and sodium alginate was carried out by two different dyes: reacxtive orange M2RJ and reactive yellow M3R (Figure 4). The printing was done instantaneously after paste prepration. After printing, the print was allowed to dry, fixation of dye was accomplished by curing and bedding in the machines. The printed samples were washed to check color fastness properties their results are summarized in Tables 3 and 4. The results showed that carboxymethyl guar gum easily replaced conventional thickeners without any compromise on printing results. It is less hazardous, economical, biodegradable and environmentally friendly thickener quite as good as sodium alginate. Its chemical structure caused no side reaction with dyes, esily washed out and causes no stiffeness to fabric. It has potential

Table 4: Color fastness to washing.

Sample	Change in color of sample	Change in color of material	
		wool	cotton
CMG	3-4	5	4
Sodium alginate	3-4	5	4

to replace more favourite thickener sodium alginate in reactive printing. The results exhibited the possible application of guar gum as thickening agent in textile printing. Under the current scenario of environmental pollution, the technique is green, non-hazardous, economical and environmental friendly [44-50].

4 Conclusions

Guar gum derivative, carboxymethyl guar was synthesized via monochloroacetic acid under alkaline conditions and reaction conditions were optimized. The synthesized guar gum derivatives were employed as thickener in textile printing. Substituted guar gum has been proved environmental friendly thickener as compared to synthetic thickeners. Penetration properties, fixation ability and colour fastness were comparable with commercial alginate thickener. These premilinary results revealed that guar gum could possibly be used as thickener in textile printing, which is green, non-hazardous, economical and environmental friendly.

References

[1] López-Mata M.A., Gastelum-Cabrera M., Valbuena-Gregorio E., Zamudio-Flores P.B., Burruel-Ibarra S.E., Morales-Figueroa G.G., et al., Physicochemical properties of novel pectin/Aloe gel membranes. Iran. Polym. J., 2018, 27(8), 545-553.

[2] Zhao Q., Zhao L., Ma C., Synthesis and properties of fluorinated hydrophobic association polyacrylamide as thickener for hydraulic fracturing fluid. Iran. Polym. J., 2017, 26(8), 589-595.

[3] Weibel M.I., Mengatto L.N., Luna J.A., Rintoul I., Accurate prediction of shape and size of polyvinyl alcohol beads produced by extrusion dripping. Iran. Polym. J., 2018, 27(3), 161-170.

[4] Sabzevari A., Kabiri K., Siahkamari M., Induced superabsorbency in polyester fiber. Iran. Polym. J., 2016, 25(7), 635-646.

[5] Dawson T., Hawkyard C., A new millennium of textile printing. Rev. Prog. Color. Rel. Top., 2000, 30(1), 7-20.

[6] Šostar-Turk S., Schneider R., Printing properties of a high substituted guar gum and its mixture with alginate. Dyes Pigments, 2000, 47(3), 269-275.

[7] Schneider R., Šostar-Turk S., Good quality printing with reactive dyes using guar gum and biodegradable additives. Dyes Pigments, 2003, 57(1), 7-14.

[8] Sharma G., Sharma S., Kumar A., Al-Muhtaseb A.A.H., Naushad M., Ghfar A.A., et al., Guar gum and its composites as potential materials for diverse applications: A review. Carbohydr. Polym., 2018, 199, 534-545.

[9] Scarpello M.L., Kazani I., Hertleer C., Rogier H., Ginste D.V., Stability and efficiency of screen-printed wearable and washable antennas. IEEE Anten. Wire. Propagat. Lett., 2012, 11, 838-841.

[10] Sobhanimatin M.B., Pourmahdian S., Study on the inverse emulsion copolymerization of microgels based on acrylamide/2-acrylamido-2-methylpropane sulfonic acid. Iran. Polym. J., 2016, 25(5), 405-413.

[11] Luo Y., Luo G., Gelinsky M., Huang P., Ruan C., 3D bioprinting scaffold using alginate/polyvinyl alcohol bioinks. Mater. Lett., 2017, 189, 295-298.

[12] Fijan R., Basile M., Lapasin R., Šostar-Turk S., Rheological properties of printing pastes and their influence on quality-determining parameters in screen printing of cotton with reactive dyes using recycled polysaccharide thickeners. Carbohydr. Polym., 2009, 78(1), 25-35.

[13] Zhang X.-S., Xia Y.-Z., Shi M.-W., Yan X., The flame retardancy of alginate/flame retardant viscose fibers investigated by vertical burning test and cone calorimeter. Chin. Chem. Lett., 2018, 29(3), 489-492.

[14] de Jesus J.Y., de Carvalho Dantas E.S., Serafini M.R., dos Passos Menezes P., Cardoso J.C., Albuquerque-Jr R.L.C., et al., Development and physicochemical properties of extract of Morinda citrifolia Linn/pectin-based membranes. J. Therm. Anal. Calorim., 2016, 123(3), 2003-2012.

[15] Tummalapalli M., Berthet M., Verrier B., Deopura B., Alam M., Gupta B., Composite wound dressings of pectin and gelatin with aloe vera and curcumin as bioactive agents. Int. J. Biol. Macromol., 2016, 82, 104-113.

[16] Mishra M.M., Mishra D.K., Mishra P., Behari K., Synthesis and characterization of a novel graft copolymer of partially carboxymethylated guar gum and N-vinylformamide. Carbohydr. Polym., 2015, 115, 776-784.

[17] Gong H., Liu M., Chen J., Han F., Gao C., Zhang B., Synthesis and characterization of carboxymethyl guar gum and rheological properties of its solutions. Carbohydr. Polym., 2012, 88(3), 1015-1022.

[18] Gong H., Liu M., Zhang B., Cui D., Gao C., Ni B., et al., Synthesis of oxidized guar gum by dry method and its application in reactive dye printing. Int. J. Biol. Macromol., 2011, 49(5), 1083-1091.

[19] Dodi G., Hritcu D., Popa M., Carboxymethylation of guar gum: Synthesis and characterization. Cell. Chem. Technol., 2011, 45(3), 171-176.

[20] Shahid M., Mohammad F., Perspectives for natural product based agents derived from industrial plants in textile applications - a review. J. Clean. Prod., 2013, 57, 2-18.

[21] Schneider R., A study of fabric stiffness with guar gum in reactive printing. Dyes Pigm., 1999, 41(3), 167-175.

[22] Šostar S., Schneider R., Guar gum as an environment-friendly alternative thickener in printing with reactive dyes. Dyes Pigments, 1998, 39(4), 211-221.

[23] Thombare N., Jha U., Mishra S., Siddiqui M.Z., Guar gum as a promising starting material for diverse applications: A review. Int. J. Biol. Macromol., 2016, 88, 361-372.

[24] Tripathy J., Mishra D.K., Srivastava A., Mishra M.M., Behari K., Synthesis of partially carboxymethylated guar gum-g-4-vinyl pyridine and study of its water swelling, metal ion sorption and flocculation behaviour. Carbohydr. Polym., 2008, 72(3), 462-472.

[25] Liyanage S., Abidi N., Auld D., Moussa H., Chemical and physical characterization of galactomannan extracted from guar cultivars (*Cyamopsis tetragonolobus* L.). Indus. Crop. Prod., 2015, 74, 388-396.

[26] Zhang L.M., Zhou J.F., Hui P.S., A comparative study on viscosity behavior of water-soluble chemically modified guar gum derivatives with different functional lateral groups. J. Sci. Food Agr., 2005, 85(15), 2638-2644.

[27] Karande V.S., Bharimalla A.K., Vigneshwaran N., Kadam P.G., Mhaske S.T., Cotton linter nano-fibers as the potential reinforcing agent for guar gum. Iran. Polym. J., 2014, 23(11), 869-879.

[28] Abdel-Halim E., Emam H., El-Rafie M., Utilization of hydroxypropyl cellulose and poly (acrylic acid)-hydroxypropyl cellulose composite as thickeners for textile printing. Carbohydr. Polym., 2008, 74(4), 938-941.

[29] Reife A., Dyes, environmental chemistry. Kirk-Othmer Encyclopedia of Chemical Technology, 1993.

[30] Kale R.D., Jadhav N.C., Pal S., Fabrication of green composites based on rice bran oil and anhydride cross-linkers. Iran. Polym. J., 2019, 28(6), 471-482.

[31] Deng B., Cai R., Yu Y., Jiang H., Wang C., Li J., et al., Laundering durability of superhydrophobic cotton fabric. Adv. Mater., 2010, 22(48), 5473-5477.

[32] Sarkar A.K., Seal C.M., Color strength and colorfastness of flax fabrics dyed with natural colorants. Cloth. Text. Res. J., 2003, 21(4), 162-166.

[33] Majolagbe A.O., Adeyi A.A., Osibanjo O., Adams A.O., Ojuri O.O., Pollution vulnerability and health risk assessment of groundwater around an engineering Landfill in Lagos, Nigeria. Chem. Int., 2017, 3(1), 58-68.

[34] Nouren S., Sarwar M., Muhi-ud-Din G., Yameen M., Bhatti H.N., Soomro G.A., et al., Sweet Lime-Mediated Decolorization of Textile Industry Effluents. Pol. J. Environ. Stud., 2019, 28(1), 283-289.

[35] Nisar N., Ali O., Islam A., Ahmad A., Yameen M., Ghaffar A., et al., A Novel Approach for Modification of Biosorbent by Silane Functionalization and its Industrial Application for Single and Multi-Component Solute System. Z. Phys. Chem., 2019, 233, 1603-1623.

[36] Khan N.U.H., Bhatti H.N., Iqbal M., Nazir A., Decolorization of Basic Turquise Blue X-GB and Basic Blue X-GRRL by the Fenton's Process and its Kinetics. Z. Phys. Chem., 2019, 233(3), 361-373.

[37] Kamran U., Bhatti H.N., Iqbal M., Nazir A., Green Synthesis of Metal Nanoparticles and their Applications in Different Fields: A Review. Z. Phys. Chem., 2019, 233, 1325-1349.

[38] Jabeen S., Ali S., Nadeem M., Arif K., Qureshi N., Shar G.A., et al., Statistical Modeling for the Extraction of Dye from Natural Source and Industrial Applications. Pol. J. Environ. Stud., 2019, 28(4), 2145-2150.

[39] Priyanka P., Dixit A., Mali H.S., High strength Kevlar fiber reinforced advanced textile composites. Iran. Polym. J., 2019, 28(7), 621-638.

[40] Elleuch M., Bedigian D., Roiseux O., Besbes S., Blecker C., Attia H., Dietary fibre and fibre-rich by-products of food processing: Characterisation, technological functionality and commercial applications: A review. Food Chem., 2011, 124(2), 411-421.

[41] Sánchez-Gálvez V., Gálvez F., Sancho R., Cendón D., A new analytical model to simulate high-speed impact onto composite materials targets. Int. J. Impact Eng., 2017, 108, 322-333.

[42] Chikwe T.N., Onojake M.C., Characterization of some crude oil samples from Niger delta area of Nigeria using infrared absorption spectrometric technique. Chem. Int., 2018, 4(3), 163-169.

[43] Aal R.M.A., Gitru M.A., Essam Z.M., Novel synthetized near infrared cyanine dyes as sensitizer for dye sensitized solar cells based on nano-TiO_2. Chem. Int., 2017, 3(4), 358-367.

[44] Awwad A.M., Salem N.M., Aqarbeh M.M., Abdulaziz F.M., Green synthesis, characterization of silver sulfide nanoparticles and antibacterial activity evaluation. Chem. Int., 2020, 6(1), 42-48.

[45] Iwuoha G.N., Akinseye A., Toxicological symptoms and leachates quality in Elelenwo, Rivers State, Nigeria. Chem. Int., 2019, 5(3), 198-205.

[46] Iqbal M., Abbas M., Nazir A., Qamar A.Z., Bioassays based on higher plants as excellent dosimeters for ecotoxicity monitoring: A review. Chem. Int., 2019, 5(1), 1-80.

[47] Hassen E.B., Asmare A.M., Predictive performance modeling of Habesha brewery wastewater treatment plant using artificial neural networks. Chem. Int., 2019, 5(1), 87-96.

[48] Igwe O., Nwamezie F., Green synthesis of iron nanoparticles using flower extract of Piliostigma thonningii and antibacterial activity evaluation. Chem. Int., 2018, 4, 60-66.

[49] Ibisi N.E., Asoluka C.A., Use of agro-waste (*Musa paradisiaca* peels) as a sustainable biosorbent for toxic metal ions removal from contaminated water. Chem. Int., 2018, 4(1), 52-59.

[50] Djehaf K., Bouyakoub A.Z., Ouhib R., Benmansour H., Bentouaf A., Mahdad A., et al., Textile wastewater in Tlemcen (Western Algeria): Impact, treatment by combined process. Chem. Int., 2017, 3(4), 414-419.