Synthesis, characterization and evaluation of amphoteric galactomannan derivative for the mitigation of malachite green and congo red dye from aqueous solution

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Abstract Biopolymeric materials have been utilized for water treatment since ancient times. Consequently, novel sustainable, inexpensive and natural biobased alternatives have been explored persistently. Amphoteric derivatives of galactomannans are still unexplored and rarely used materials to treat industrial wastes. The present study was explored to synthesize and characterize the amphoteric derivative of galactomannan, obtained from Cassia tora seeds, by applying ‘Taguchi design’ (L’9), for its application in mitigation of cationic (Malachite green) and anionic (Congo red) dyes. The derivative was also studied for the conditioning of water using kaolin suspension. The results signify that the amphoteric derivative (anionic DS ~ 0.52 and cationic DS 0.197) is effective in maximum adsorption of Malachite green (73%) and Congo red (17%) dyes and as a flocculant at a minimum dose of 10 ppm. The amphoteric derivative was characterized by X-ray-diffraction, TG analysis and spectroscopic techniques.
Introduction

The developing concerns of water scarcity and environmental sustainability consciousness have renewed the global awareness towards the functional reuse, and treatment of extremely contaminated wastewater (Grant et al. 2012). Water pollution and its threat to the environment have significantly attracted worldwide attention (Xie et al. 2014). Water-soluble dyes comprising of cationic, anionic, and non-ionic groups are widely being used in diverse industrial segments causing water pollution due to their persistent growth and progress in numerous industries such as textiles, leather, paper production, pharmaceutical, and food industry, etc. (Cripps et al. 1990; Reed et al. 1998; Karadag et al. 2006; Gharbani et al. 2008; Gupta, 2009; Chen et al. 2009). It is estimated that approximately 0.7 million tons of dyes are synthesized every year worldwide and, over 10,000 different dyes and pigments are used industrially (Zhou et al. 2019). The presence of dyeing effluents produces a severe environmental impact in a watercourse, as they are non-biodegradable, toxic and visible. Further, they transform into carcinogenic, teratogenic, and even mutagenic agents and create a serious threat to human health and marine organisms (Sansuk et al. 2016). As in the textile industry, the wastewater is contaminated with dyestuffs, inorganic salts and other chemicals (Han et al. 2017), the release of extremely contaminated wastewater into aquatic environments causes deleterious consequences to the aquatic ecosystems and public health and decreases the measure of accessible water. The unceasing exposure of colouring matter and their intermediates are responsible carcinogens and, to a lesser extent sensitizers and allergens (Horng and Huang 1993). Malachite green (MG) and congo red (CR) dyes, cationic and anionic respectively, are water-soluble dyes and are consistently used in the textile and paper industries (Rao 1995; Bekci et al. 2008; Ahmad and Kumar 2010; Kolya and Tripathi 2013). The effective treatment and retrieval of the severely polluted water before returning to the biological system have become a significant
issue. Therefore, efficient methods of separation and removal of water contaminants are required to cope with hazardous situations (Sansuk et al. 2016; Han et al. 2017). In principle, diverse methods are utilized for the decolouration viz. coagulation, biodegradation, chemical degradation, and photodegradation (Bouaziz et al. 2017). Further, reducing the turbidity of industrial and municipal wastewater by coagulation–flocculation treatment is a well-known process. The polymers with anionic and cationic amalgamation have been used in the coagulation–flocculation process to reduce the coagulant dosages, the volume of sludge and the ionic load of the wastewater, and further, to reduce the overall costs (Larsson and Wall 1998; Ovenden and Xiao 2002; Yan et al. 2009a, b; Sirvio¨ et al. 2011). Generally, synthetic polymers viz., polyacrylamides, polyacrylic acids, and polystyrene sulfonic acids and their derivatives are used in coagulation–flocculation treatment. These polymers are not readily biodegradable and behave as neurotoxic and carcinogenic (Suopaja¨rvi et al. 2013, 2014). Alternatively, starch, guar gum, chitin, pectin, and algin, and their derivatives have been studied for the treatment of wastewater as dye adsorbent and flocculants due to their biodegradable nature and safe to human beings (Wang et al. 2013).

The galactomannan obtained from the seeds of C. tora Linn. a ruderal species (Family: Leguminosae; subfamily: Caesalpiniaceae (Pawar and D’mello 2011; Sharma et al. 2020a, 2020b), is of developing interest because of its non-toxicity, safety, biodegradability, biocompatibility, renewability, and sustainability (Thombare et al. 2016). It possesses a main chain comprised of (1 → 4)-β-D-mannopyranose (Man) units which are attached to (1 → 6)-α-D-galactopyranose (Gal) units with the M/G ratio of 5:1 (Hallagan et al. 1997). C. tora gum has owned its limitations due to its unique structure and performance in its native form. The functional properties of the galactomannans significantly affect the degree of their application. The incorporation of new functional moieties onto the galactomannans intensifies inherent properties, such as polarity and hydrophilicity. The new functional moieties enhance the interaction of the gum with various compounds. Quaternization and carboxymethylation are well-known derivatization processes for imparting the new functional properties to the galactomannans. Quaternization and carboxymethylation of polysaccharides viz. cellulose, starch, chitosan, and galactomannans, are regarded as a safe strategy to synthesize functional polysaccharides having unique characteristics like high water solubility, solution clarity, stability in aqueous systems, antibacterial activity, conditioning property in hair styling products and improvement in biological activities by changing their molecular structure, dye adsorbent and as a flocculant in wastewater treatment (Heinze and Koschella 2005; Dodi et al. 2011; Narayanan et al. 2014; Novac et al. 2014; Rahul et al. 2014; Thombare et al. 2016; Huang et al. 2016; Xu et al. 2019).

The objective of the present study is to synthesize a water-soluble hybrid novel amphoteric derivative (CMQCTG) of C. tora gum (CTG), comprising anionic and cationic groups. The derivative was investigated for the adsorption of cationic (MG) and anionic (CR) dyes from aqueous solutions and as a flocculant. For this purpose, a systematic Taguchi L9 design was planned and executed to perform the experiments. The synthesized amphoteric derivative was characterized by NMR (1H, 13C, DEPT-135 and 2D HSQC), FTIR, FESEM, X-ray diffraction, and TG analysis.

Experimental section

Materials

C. tora gum was procured from M/s Goodrich Cereals Haryana, India. The quaternizing reagent 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC, 60 wt. % aqueous), and deuterium oxide (99.9 atom % D) were procured from Sigma-Aldrich, St. Louis, Missouri, USA. Monochloroacetic acid (MCA, 99% pure), sodium hydroxide, isopropanol, methanol, and acetic acid (AR grade) were purchased from Merck India Ltd., Mumbai, India. Malachite green (C.I. No. 4200), Congo red (C.I. No. 22120) dye, and Kaolin extra pure were purchased from Loba Chemie Pvt. Ltd.
Methods

Synthesis of carboxymethyl and quaternized Cassia tora gum (CMQCTG)

*C. tora* gum (CTG, 100 mesh, 0.03075 mol) was dispersed in an aqueous isopropanol solution (isopropanol:water, 80:20, v/v) and alkalized by 0.15 mol sodium hydroxide (NaOH). The reaction flask was kept on a magnetic stirrer for continuous stirring at a temperature 50 °C. After 10 min, MCA (0.0396 mol) was added in parts and continuously stirred for 60 min. The pH was monitored during the reaction. To this reaction mixture having pH 12.9, a quaternary ammonium reagent (CHPTAC 0.00478–0.0319 mol) was added and the reaction mixture was further stirred for 240 min (Sharma et al. 2020a). Intriguingly, the pH depends upon the addition of the varying amounts of CHPTAC, therefore, the pH of the reaction mixture was monitored during and after the completion of each reaction. The reaction product was filtered under vacuum after designated reaction time and dispersed in distilled water. An aqueous acetic acid (5%, v/v) was added dropwise to neutralize the reaction mixture. The neutralized reaction mixture was subjected to precipitation with methanol. The precipitated product was separated by centrifugation (15,000 rpm for 12 min) followed by washing with 80% aqueous methanol (3 × 20 mL) and finally with pure methanol. The purified dual derivative (CMQCTG) was dried in an oven at 60 °C for 6 h.

Preparation of Malachite green (MG) and Congo red (CR) solution for optimizing adsorption capacity of CMQCTG

The stock solutions of MG and CR (100 ppm) were prepared by dissolving 0.1 g of dye into 1 L distilled water (Koyla and Tripathy 2013). Calibration curves for MG and CR (5 to 25 ppm) were prepared to determine the concentration of residual dyes in the experiments. The concentration of the dyes in the experimental solutions was determined by UV–VIS spectrophotometer (Chemito-2700) at λ max 617 and 495 nm respectively. Analysis was carried out using the CMQCTG as a cationic and anionic adsorbent. Taguchi L’9 array, a statistical design of experiment was used for optimizing the MG and CR removal. The operating variables viz. degree of substitution (DS), amount of adsorbent, temperature, and contact time were the four factors with three sub-levels for the optimization process. For dye experiments, CMQCTG, (cationic DS, 0.023, 0.123, & 0.197; anionic DS, 0.52) with different dose amounts (10, 25, & 50 mg) was added to a 30 mL of dye solution (25 ppm) in a 100 mL beaker. The dye solution was stirred for a stipulated time (60, 120, & 190 min) and temperature (25, 35, & 45 °C). The solution was allowed to settle for five minutes. The supernatant liquid at the half-height of the beaker was taken for analysis by UV–VIS spectrophotometer. The percentage of dye adsorbed was calculated using the formula given in Eq. no 1.

\[
\text{Adsorption\%} = \left( \frac{C_o - C_e}{C_o} \right) \times 100
\]

where *C*o is the initial dye concentration and *C*e is the final concentration obtained after adding the adsorbent.

Flocculation Test

Flocculation performance of the CMQCTG was carried out using Coagulation-Flocculation jar tests (Bratby 1980). Kaolin was dispersed in five 250 mL beakers containing water (1%, w/v). The CMQCTG (10–50 ppm) was added to the beakers. Immediately after the addition of the CMQCTG, all the suspensions were stirred using magnetic bars at a constant speed of 100 rpm for 2 min, followed by a slow agitation of 50 rpm for 5 min (flocculating time). The flocs were then allowed to settle down for 2 min (sedimentation time). At the end of the settling period, the absorbance of supernatant liquid at the half-height of the clarified layer was measured using a UV–VIS spectrophotometer (Chemito-2700) at 670 nm.

Characterization of CMQCTG

Elemental analyses

The nitrogen content of the CMQCTG samples was determined by the Kjeldahl method.
Determination of degree of substitution (DS)

The DS for the quaternization of CMQCTG samples was determined based on an increase in nitrogen content using the following formula (Heinze et al. 2004):

\[
DS = \frac{162.2 \times \% \text{Nitrogen}}{1401 - 151.6 \times \% \text{Nitrogen}}
\]

where 162.2 denote the molecular weight of the anhydroglucose unit, 1401 is 100 times the atomic weight of nitrogen, and 151.6 is the molecular weight of the epoxypolytrimethylammonium chloride (EPTMAC) group added.

The DS for the carboxymethyl products was determined according to a reported method with minor modifications (ASTM D 1439-15, 2015). CMQCTG (500 mg) was converted into acid form by treating with 0.1 M aqueous methanolic HCl (methanol:water::90:10, 50 mL) in a 250 mL beaker with continuous stirring for 2 h. The solution was filtered and washed under suction using a G-4 sintered glass funnel with aqueous methanol (methanol:water::90:10, 8–20 mL) and finally with pure methanol. The resulting sample was dried in the oven at 100–110 °C for 1 h and kept in a vacuum desiccator. The desiccated sample (250 mg) was dispersed in double-distilled water (100 mL) and treated with alkaline solution (10 mL, 0.1 M NaOH) in a 250 mL conical flask. The flask was kept for stirring at 70–80 °C until a clear solution (20–30 min) was obtained. The solution at this stage was titrated with 0.1 M HCl using phenolphthalein as an indicator. The degree of etherification (G) was calculated as follows:

\[
A = \frac{(BC - DE)}{F}
\]

where \(A\) = milliequivalents of acid consumed per gram of sample, \(B\) = NaOH solution added, mL, \(C\) = molarity of NaOH solution added, \(D\) = HCl required for titration of excess NaOH, mL, \(E\) = molarity of HCl, \(F\) = weight of CMCTG, g

\[
G = \frac{0.162A}{(1 - 0.0584A)}
\]

where \(A\) denotes the milliequivalents of acid consumed per gram of sample, 162 is the gram molecular mass of anhydroglucose unit of CTG, and 58 is the net increase in molecular mass of anhydroglucose unit for each carboxymethyl group substituted.

Infrared spectroscopy

FT-IR spectra were recorded on a Fourier transform infrared (FT-IR) spectrophotometer (Perkin Elmer-Spectrum II). Samples (2–3 mg) were blended with spectroscopic KBr powder (100 mg), and pellets were prepared for recording the spectrum. All spectra were acquired with an average of 16 scans with a resolution of 4 cm\(^{-1}\) within a frequency range of 400–4000 cm\(^{-1}\).

\(^1\)H, \(^13\)C, DEPT-135 and 2D NMR (HSQC) spectroscopy

The NMR spectra of CTG and CMQCTG were acquired using a 500 MHz Bruker spectrometer at 25 °C. The samples were hydrolysed before recording the spectra. CTG (0.5 g) was treated with an aqueous sulfuric acid solution (20%, 50 mL), and stirred for 30 min at 50 °C. After cooling in a water bath, the reaction mixture was neutralized by saturated sodium bicarbonate solution and dialyzed against deionized water for 48 h. The dialysate was filtered and freeze-dried. The freeze-dried sample (60 mg) was dissolved in 1 mL D\(_2\)O for NMR spectral analysis (Sharma et al. 2020a). Spectral recordings were performed at 303.3 K using parameters- \(^1\)H-NMR spectrum: 500.17 MHz, 32 scans, 2.2282 s data acquisition time, 1 s relaxation delay time; \(^13\)C-NMR: 125.77 MHz, 1024 scans, 0.8847 s data acquisition time, 2 s relaxation delay time; DEPT-135: 512 scans, 0.8847 s data acquisition time, 2 s relaxation delay time; HSQC: 2 scans, 0.1946 s data acquisition time and 1.500 s relaxation delay time.

Thermogravimetric analysis

Thermogravimetric analysis was carried out using ~3 mg of sample in a DTG-60 unit (Shimadzu, Japan) under a nitrogen atmosphere with a flow rate of 40 mL / min. The scan was carried out at a heating rate of 10 °C / min from 0 °C to 800 °C.
X-ray diffraction (XRD) analysis

XRD patterns of powdered samples were acquired using a Bruker D8 Advance (Germany) diffractometer (30 kV, 30 mA) equipped with Cu Kα radiation at a wavelength of (\(\lambda = 1.5418 \text{ Å}\)). The relative intensity was recorded in the scattering range (2\(\theta\)) of 0–90\(°\) at the scanning rate of 2\(°\)/min.

Field emission scanning electron microscopy (FESEM)

The field emission scanning electron microscopy was used to study the morphology of CTG and CMQCTG using instrument MIRA3 TESCAN, USA. The sample was mounted on a circular aluminium stub with double sticky tape, coated with gold, and the images of samples were captured with an accelerating potential difference of 10 kV at a working distance of 5 mm.

Results and discussions

The synthesis of amphoteric derivative proceeds consecutively via Williamson’s ether synthesis (Scheme 1) (Su et al. 2019). The substitution of sodium carboxymethyl and quaternary ammonium moiety onto CTG was achieved by etherification, where the alkoxide ion reacts with the MCA and subsequently with the EPTAC (2,3-epoxypropyltrimethylammonium chloride), produced in situ from CHPTAC leading to the formation of the amphoteric product (CMQCTG) comprising carboxymethyl and quaternary ammonium groups. The maximal degree of substitution is achieved only when all the hydroxyl groups are etherified. However, during the reaction, sodium glycolate and 2,3-dihydroxy propyltrimethylammonium chloride are also formed as by-products simultaneously that affect the DS (Su et al. 2019; Sharma et al. 2020a).

The effect of CHPTAC concentration (0.00478–0.0319 mol) on the cationization of anionic CTG was studied in terms of the effect on DS and pH of reaction medium (Table 1). A distinct pattern was observed for the pH versus CHPTAC concentration (Fig. 1). As the concentration of CHPTAC increases from 0.00478 to 0.0319 mol, the pH of the reaction medium decreases (12.9 to 12.2). A maximum of 0.2 DS for quaternization was achieved using 0.0319 mol of CHPTAC concentration at different reaction parameters studied. The increase in the cationic DS on increasing the CHPTAC concentration may be due to the increased accessibility of the reactive groups (EPTAC) to the available alkoxide ions generated onto the galactomannan. Further, a decrease in pH on increasing the concentration of CHPTAC may be due to the utilization of available alkali by the CHPTAC. Subsequently, the formation of EPTAC occurs as an active species.

Characterization

Spectroscopic analysis was carried out for the structural screening of CMQCTG. 1D and 2D NMR spectra (Fig. 2) were recorded to confirm the incorporation of carboxymethyl substituent and quaternary ammonium groups onto CTG. In \(^1\)H-NMR spectra, corresponding to \(\alpha\)- and \(\beta\)- anomeric protons of galactose and mannose units, signals were observed in the region from 4.8 to 5.3 ppm (Bigand et al. 2011; Tako et al. 2018). The \(^1\)H-NMR spectrum of CTG (Fig. 2a) and CMQCTG (Fig. 2b) showed characteristic chemical shifts clustered between 3.3 ppm to 4.25 ppm for ring protons of mannose and galactose units. The occurrence of a new signal of protons at 3.07 ppm in the CMQCTG spectrum attributed to methyl protons (C-d, -\(\text{CH}_2\text{N(CH}_3)_3\)) of quaternary ammonium groups and another downfield signal at 4.3 ppm was assigned to the methylene protons (-O-\(\text{CH}_2\text{COO}^-\)) of the carboxymethoxy substituents (Dodi et al. 2011).

These two additional peaks in \(^1\)H-NMR of CMQCTG confirm the presence of quaternary ammonium and carboxymethyl groups. The \(^13\)C-NMR spectrum of CMQCTG (Fig. 2d) showed three additional peaks in comparison to CTG (Fig. 2c). The prominent peak observed at 54.22 ppm was assigned to quaternary ammonium methyl carbons (-\(\text{CH}_2\)-N(\(\text{CH}_3)_3\), C-d), and the peak at 68.09 ppm was attributed to carboxymethyl methylene carbon (-O-\(\text{CH}_2\text{COO}^-\), C-X). The extreme downfield peak observed at 178.07 ppm was assigned to the carboxyl (\(-\text{COO}^−\)) group at the C-Y position. Further, the negative peaks appeared at 68.12 ppm and 60.53 ppm in DEPT-135 NMR (Figs. 2e and f), corroborates the presence of \(\text{CH}_2\) groups on the carboxymethyl substituents (C-X) and carbon at the C-6 (\(\text{CH}_2\)) position, respectively. In addition, the correlation peaks (absence of signals in Fig. 2g) of carbon and
hydrogen (Fig. 2h) for C-7 at 4.3 and 68.09 ppm and C-d at 3.07 and 54.22 respectively confirm the presence of carboxymethyl and quaternary ammonium substituents in the amphoteric derivative.

FT-IR spectra were recorded to elucidate the structure of CTG and CMQCTG (Fig. 3a). The broad band in the range 3600 to 3000 cm\(^{-1}\) was attributed to the O–H stretching frequency, and it is due to the inter and intramolecular hydrogen bonding of the hydroxyl
groups. The band that appeared at 2919.6 cm\(^{-1}\) was assigned to the characteristic symmetrical stretching vibrations, due to the CH\(_2\) groups (Yuen et al. 2009). In native CTG, the band at 1641.3 cm\(^{-1}\) was attributed to the scissoring of two O–H bonds of absorbed water molecules (Liu et al. 2012; Mudgil et al. 2012). The band appeared at 1025.8 cm\(^{-1}\) was due to the -C–O–C- stretching frequency of the ether bond in the ring. The two other absorption bands at 814.6 cm\(^{-1}\) and 875.5 cm\(^{-1}\) can be assigned to a \(\alpha\)-D-galactopyranose and \(\beta\)-D-mannopyranose units of the anomeric region, respectively (Figueiro et al. 2004; Prado et al. 2005; Yuen et al. 2009). These characteristic peaks were also observed in the amphoteric derivative. In addition, four new absorption bands are observed in the case of CMQCTG. A new band at 1475.7 cm\(^{-1}\) can be assigned for C-N stretching frequency of quaternary ammonium groups, band at 1599.6 cm\(^{-1}\) can be assigned for –COO\(^{-}\) asymmetric stretching frequency; (Pi-Xin et al. 2009; Banerjee et al. 2013) and another band at 1428.7 cm\(^{-1}\) and 1325.2 cm\(^{-1}\) were attributed to a symmetric stretch of –COO\(^{-}\) groups (Gong et al. 2012).

A wide-angle X-ray diffractogram of native gum (Fig. 3b) showed the presence of diffraction peaks at 20\(^\circ\) and 38\(^\circ\) 20 suggesting a semi-crystalline structure (Prajapati et al. 2013; Dos Santos et al. 2015). By contrast, in the XRD of CMQCTG, the diffraction intensity has reduced and the peak shape transformed from broad to a sharp peak, which indicates an increase in crystallinity. A sharp peak at 20\(^\circ\) 20 might be due to the intermolecular and intramolecular interactions in the galactomannan chains due to the presence of cationic quaternary ammonium and anionic carboxymethyl groups, which leads to more ordered conformation.

The TG & DTG chromatograms are presented in Fig. 3c and d, which provides vital information about the thermal stability of polymeric material. The thermophysical information is of great use for industrial applications of the polymer. The CTG & CMQCTG showed two-stage weight losses up to 800 \(^\circ\)C. The first weight loss is due to the moisture content up to 125 \(^\circ\)C. The second weight loss is due to the decomposition of polysaccharides and, water is the main product of decomposition, below 350 \(^\circ\)C. The CTG began to decompose at 250 \(^\circ\)C and underwent a 65% weight loss at 380 \(^\circ\)C. The studies indicate that the maximum degradation occurred within the range, 240–410 \(^\circ\)C and the peak as indicated by the DTG (DTG max) (Fig. 3d) was at 335 \(^\circ\)C. Further heating from 450 to 800 \(^\circ\)C resulted in carbonization and ash formation. In the case of CMQCTG, maximum degradation occurs within the range of 220 to 390 \(^\circ\)C with 45% of mass loss and the peak indicated by DTG (DTG max) was at 315 \(^\circ\)C. There is a small difference in the final decomposition temperature for CTG & CMQCTG, but the percentage mass loss for CTG is greater than the CMQCTG. The lesser percentage mass loss in the case of CMQCTG (45%) in comparison to CTG (65%) indicating the better thermal stability of amphoteric derivative. The initial decomposition temperature of CMQCTG is lower than the initial decomposition temperature of the CTG. This effect may be due to substituting hydroxyl groups with carboxymethyl and quaternized ammonium groups.
groups that result in better thermal stability of CMQCTG (Li et al. 2010). The surface morphology of CTG and CMQCTG were studied using FESEM. The micrographs showed the presence of smooth and well-defined particles of various sizes in CTG (Fig. 4) whereas, the surface morphology of CMQCTG altered markedly due to the insertion of cationic and anionic moiety onto CTG.

Figure 4 shows the surface of CMQCTG, which is completely disintegrated into a porous and highly rough surface devoid of well-defined edges. The incorporation of cationic and anionic moieties disintegrates the particle shape and size, consequently increasing the surface roughness. In addition, the changes in the surface morphology of the CTG may also be due to the effect of the alkaline medium during the modification of the derivative, which is explicable for the disruption of the crystalline structure of the molecule. The chemical analysis and thorough spectroscopic studies showed that CTG was successfully derivatized into an amphoteric derivative.

Adsorption study of malachite green and congo red dyes by amphoteric derivative

The removal of Malachite Green (MG) and Congo red (CR) dyes were performed considering four factors viz. cationic DS, adsorbent amount, temperature, and contact time, for the optimization process. The effect of each parameter was assessed using Taguchi’s experimental design comprising a total of 9 experiments (Table 2) in terms of response values as percentage and signal to noise (S/N) ratios.

The S/N ratio was used to assess the quality characteristics of the product (Yang and Tarng, 1998; Tutar et al. 2014; Li et al. 2016). The highest S/N ratio signifies the optimum level for each factor and contributes to the maximum percentage. The S/N ratios were calculated using Eq. 5 for each of the 9 trials, and the values are shown in Figs. 5 and 6.

\[
\frac{S}{N} \text{ ratio} = -10 \log \left( \frac{1}{n} \sum_{i=1}^{n} y_i^2 \right)
\]  

(5)
Where \( y_1, y_2, y_3, \ldots, y_n \) are the responses of the quality characteristics for a trial condition repeated \( n \) times.

Dyes comprising a positive and negative charge and their adsorption on the dual derivative are based on the ion exchange mechanism (Bouaziz et al. 2017) and, indulge by the electrostatic attraction between amphoteric groups and the cationic and anionic dye molecules, \((MG)^+\) and \((CR)^-\). The carboxylic groups of the carboxymethyl substituents (COO\(^-\)) present on CMQCTG binds to the positively charged malachite green molecules. In the case of anionic dye (CR\(^-\)), an electrostatic force of attraction among the negatively charged surface of CR and positively charged quaternary ammonium groups function and results in the removal of dye from water by settling / precipitation on the surface.

**Effect of amphoteric derivative on adsorption capacity of dyes**

The \( S/N \) ratio was studied on the amphoteric derivatives vs dyes. The ratio obtained is directly proportional to the adsorption percentage of dyes. In the present study, the anionic DS (0.5) was kept constant, and the cationic DS was varied (0.012, 0.123, & 0.197). At constant anionic charge and increasing the cationic charge, initially, a slight decrease in adsorption of dye was found, followed by an increase in adsorption. The increase in adsorption percentage at high cationic DS may be due to the coexistence of hydrogen bond interaction between the modified gum and dye molecules on the CMQCTG, the concentration of CMQCTG and also due to the cationic and anionic interaction of gum, and MG surface, however,
the S/N ratio increases with an increase in cationic DS constantly leading to an increase in adsorption of anionic CR dye. The product with cationic DS (0.197) showed maximum adsorption of the dyes as determined by the ‘Taguchi’ design in terms of S/N ratio for both MG & CR dye (Figs. 5 and 6).

### Table 2 Matrix layout of Taguchi L'9 and the adsorption percentage of MG and CR

| Run | Factor | Cationic DS | Dose amount (mg) | Temperature (°C) | Time (min) | % MG | % CR |
|-----|--------|-------------|------------------|------------------|------------|------|------|
| 1   | 0.197  | 50          | 35               | 60               |            | 63.20| 16.88|
| 2   | 0.123  | 10          | 35               | 120              |            | 51.20| 7.00 |
| 3   | 0.023  | 25          | 35               | 90               |            | 50.60| 4.56 |
| 4   | 0.023  | 10          | 25               | 60               |            | 53.40| 3.32 |
| 5   | 0.197  | 10          | 45               | 90               |            | 48.80| 10.48|
| 6   | 0.123  | 50          | 25               | 90               |            | 60.00| 4.56 |
| 7   | 0.023  | 50          | 45               | 120              |            | 72.60| 3.76 |
| 8   | 0.123  | 25          | 45               | 60               |            | 56.60| 3.12 |
| 9   | 0.197  | 25          | 25               | 120              |            | 66.00| 12.80|

**Fig. 4** FESEM image of CTG and CMQCTG
Fig. 5 Effect of parameters on Malachite Green dyes with respect to S/N ratio

Fig. 6 Effect of parameters on Congo Red dyes with respect to S/N ratio
Effect of the amount of amphoteric derivative on adsorption capacity

The study of MG and CR on the CMQCTG was performed at a dose of 10 to 50 mg in the dye solution (25 ppm) for the S/N ratio as obtained from the Taguchi L’9 statistical design. The results shown in Fig. 5 and 6 reveal that on increasing the amount of CMQCTG, the adsorption of dyes (MG and CR) increases. The increase in adsorption may be due to the presence of more active sites on the amphoteric derivative. Consequently, better adsorption of dyes takes place. A dose of 50 mg of absorbent showed maximum adsorption of the dyes.

Effect of temperature on adsorption capacity

The adsorption study was carried out in the range of 25 to 45 °C, to examine the effect of temperature on the S/N ratio. Temperature is another significant factor that can reveal the adsorption is exothermic or endothermic (Argun et al. 2008). Generally, the adsorption capacity is decreased by increasing the temperature in an exothermic process. The probable reason is that on increasing the temperature, the adsorptive interactions between the dye molecules and the active sites of the adsorbents may be decreased due to the weakening of sorptive forces among the active sites on the CMQCTG and dye molecules, and adjacent dye molecules present on the sorbed phase in a physisorption system (Ofomaja and Ho, 2007). Conversely, if the adsorption process is increased by increasing the temperature, the process is endothermic. It may be due to the increase in the mobility of the dye molecules and active sites present on the adsorbents (Senthilkumar et al. 2006). The results are in good agreement in the case of MG adsorption, as shown in Fig. 5. On increasing the temperature to 35 °C, the S/N ratio is decreased in the case of MG, leading to a decrease in adsorption percentage and further increasing the temperature to 45 °C, the adsorption percentage is increased, which may be due to the increased mobility of the dye molecules and active sites present on the adsorbent, whereas, the maximum adsorption is observed at 35 °C in the case of CR, and thereafter it decreased. Therefore, at a temperature of 25 °C and 35 °C maximum adsorptions were observed for MG and CR dyes, respectively.

Effect of contact time on adsorption capacity

The effect of the dyes contact time on the CMQCTG was studied concerning the S/N ratio, using statistical design. The results reveal that on increasing the duration of time, the adsorption of dyes increased. Generally, it is a surface phenomenon, and at a prolonged time, the maximum dye adsorbed due to the active sites present on the adsorbent. The effect of the adsorption time was observed in terms of the S/N ratio, and at 90 min, not significant adsorption is obtained (Fig. 5). Further, as the time is increased from 90 to 120 min, a drastic increase in the S/N ratio was observed and is significant. However, the results are divergent at first sight, as shown in terms of the S/N ratio. The S/N ratio is a measure of the quality characteristics of the analysis of the results. It takes both the mean and the variability of the experimental results into account. In the present study, larger-the-better S/N characteristic was selected to obtain the maximum output among the stipulated factors and levels. The optimum level has been determined for each factor, which gives the highest positive effect on the mean. The S/N ratio has been analysed, by the category of the performance characteristics, as given in Eq. 5. Further, the L’9 array accommodates the effect of various parameters and generates the most reliable data correspond to the desired results among the stipulated factors and levels. The Matrix layout of the results and the S/N ratio is shown in Fig. 5 and Table 2. The results predict the best output of the experiments, irrespective of the factors and levels used in the design (Athreya and Venkatesh 2012). In addition, the overall quality of the test applications and the time of testing are maintained by identifying non-testable requirements during the experiments (Chiang and Hsieh 2009). Therefore, the results reveal, the optimized time for the maximum removal of MG & CR is 120 min (Figs. 5 and 6).

The experimental results (Figs. 5 and 6) suggest that the studied factors at the optimum levels strongly support the maximum removal of MG and CR. The optimized reaction parameters achieved for the adsorption of MG and CR are cationic DS 0.197, anionic DS 0.52, adsorbent amount 50 mg, temperature 25 °C (MG) and 35 °C (CR), and time 120 min respectively. A confirmatory experiment was conducted over the optimized reaction conditions for MG and CR. The results reveal that the maximum amounts
of dyes were adsorbed by CMQCTG (MG 73% and CR 17%) in comparison to the CTG. The adsorption capacity is associated with the cationic and anionic character of the CMQCTG. The results suggest the effectiveness of biopolymeric amphoteric derivatives for the removal of both cationic (MG) and anionic (CR) dyes from water.

Table 3 shows the dye removal capacity of the amphoteric derivative, synthesized from the Cassia gum and various other adsorbents, reported in the literature for malachite green, congo red, and other dyes from aqueous solutions. The dyes removal capacity of CMQCTG is 73% and 17% for the malachite green and congo red dyes, respectively. However, the zwitterionic cellulose shows a dye removal capacity of 76 to 99% for the malachite and congo red dyes (Haro et al. 2020; Laureano et al. 2019 and 2021). In addition, the other biopolymeric materials also exhibit the adsorption behaviour of the dye molecules, as shown in Table 3. Here in the present study, the amphoteric derivative possesses a positive and negative charge that has the capacity to remove the malachite and congo red dyes simultaneously. Intriguingly, this is the speciality of the dual derivatives to adsorb cationic and anionic dyes. In addition, the galactomannans are green biopolymeric materials and may be obtained from the Cassia tora (a ruderal species) seeds by a simple roasting process. The galactomannans so obtained may be utilized for the synthesis of dual derivatives for diverse applications.

**Table 3** Comparison of the removal of cationic and anionic dyes onto various adsorbents

| Adsorbents                                      | Maximum dye removal capacity (%) | Dye investigated          | References                     |
|------------------------------------------------|----------------------------------|---------------------------|--------------------------------|
| Amphoteric Cassia tora gum                      | 73                               | Malachite green           | Present work                   |
| Amphoteric Cassia tora gum                      | 17                               | Congo red                 | Present work                   |
| Luffia cylindrica fibres                        | 98                               | Methylene blue            | Cengiz and Cavas (2008)        |
| Almond gum                                      | 94.6                             | Malachite green           | Bouaziz et al. (2017)          |
| Grass waste                                     | 79.23                            | Methylene blue            | Hameed (2009)                  |
| Coffee husks                                    | 98                               | Malachite green           | Baek (2010)                    |
| Sun flower seed hull                            | 95.7                             | Methyl violet             | Hameed, (2008)                 |
| Untreated guava leaves                          | 88.7                             | Methylene blue            | Ponnusami et al. (2008)        |
| Solid waste of soda ash plant                   | 73                               | Reactive red 231          | Şener (2008)                   |
| Zwitterionic cellulose                          | 99                               | Congo red                 | Laureano et al. 2019           |
| Zwitterionic cellulose                          | 95/99                            | Congo red/Mordant blue    | Laureano et al. (2021)         |
| Zwitterionic cellulose                          | 76/88                            | Malachite green/crystal violet |                             |
| Zwitterionic cellulose                          | 90                               | Cotton blue               | Haro et al. (2020)             |
| Polyelectrolyte galactomannan-based hydrogels   | 89.9                             | Methylene blue            | Li et al. (2021)               |
| Starch-grafted                                  | 90                               | Acid Red 8                | Sadik et al. (2020)            |
| polY(N,N-dimethyl acrylamide)                  | 86                               | Methylene Blue            | Omer et al. (2020)             |
| Semi-interpenetrated PVA/PAMPS hydrogel         | 97/98                            | Azur II/Reactive Red      | Takam et al. (2017)            |

Flocculation characteristics

The flocculation results of the CMQCTG having cationic DS values (0.12, 0.197) and a control sample,
CTG (50 ppm) labelled as ‘0’, on the kaolin suspension are shown in Fig. 7. The output of the flocculation was measured as the absorbance of the supernatant liquid. The results reveal that the product having a DS (0.197) is a better flocculant in kaolin suspension than the product with lower DS (0.12) in all the concentrations. The effect was probably due to the electrostatic force of attraction between the cationic quaternary ammonium groups present on the CMQCTG and the negatively charged particles of the kaolin suspension via bridging and charge neutralization process (Cengiz and Cavas 2008). The present study shows that the absorbance increases on increasing the concentration of flocculant (10 to 50 ppm) in the solution, consequently affects the flocculation efficiency. The decrease in efficiency may be due to the charge neutralization process, which plays an important role during the kaolin clay flocculation by a cationic charged molecule. The Kaolin clay particles bear a negative charge on the surface that enables them to be suspended well in solution in the colloidal state. The addition of positively charged molecules to kaolin suspension facilitates the adsorption on the negatively charged surface of the kaolin via electrostatic attraction leading to charge neutralization progressively with increasing concentration. Therefore, adsorption % decreases on increasing the flocculant dose up to a certain extent and then increases. This phenomenon may be due to the mutual electrostatic repulsion of particles in a colloidal suspension, which prevents aggregation of colloidal particles in a suspension (Liaw et al. 1992; Hebeish et al. 2010). The CMQCTG having a high DS (0.197) shows better flocculation performance at a minimum concentration (10 ppm). The results reveal that the flocculation performance of CMQCTG is enhanced significantly by the substitution of cationic groups. Therefore the derivative may be used as an efficient flocculant in wastewater treatment.

Conclusion

A novel biopolymeric, amphoteric derivative of C. tora gum was synthesized under heterogeneous conditions using monochloroacetic acid and 3-chloro-2-hydroxypropyltrimethyl ammonium chloride. The derivative was thoroughly characterized by spectroscopic techniques and investigated for application in wastewater treatment for cationic (MG) and anionic (CR) dyes. The dye removal experiments were carried out using a systematic Taguch L’9 design. The results reveal that amphoteric derivatives (cationic DS, 0.52 and anionic DS 0.197) removed MG 73% and 17% CR efficiently under stipulated conditions. The flocculation results demonstrate that the derivative has good

![Fig. 7 Flocculation performance of CMQCTG](image)

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floculation efficiency at a minimum concentration of 10 ppm. Thus, it is deduced that the derivatized C. tora gum, an amphoteric derivative, is a promising candidate for the removal of cationic and anionic dyes and as a potential flocculant for wastewater treatment.

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Declarations

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