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Modification of cellulosic material for rapid dyeability with malachite green dye

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ABSTRACT

Chemical modification of cellulose fibre is one of the efficient ways to improve the dye uptake and increase the dyeability properties of the fibre. The challenge with dyeing cellulose fibres is poor dye uptake and unsatisfactory dye fixation. The major scope of this study is to determine the optimum dyeing conditions that will guarantee the dye fastness onto the cotton fabric. Four modifying agents (sodium chloride (NaCl), ammonium sulphate ($(NH_4)_2SO_4$), hydrated sodium carbonate (Na_2CO_3•$10H_2O$), and acetic acid (CH_3COOH)) in aqueous form were employed in the treatment of the cotton fabrics in a slacked condition. The study examined changes in thermodynamic parameters due to dyeing modified cotton fabric with malachite green (MG) dye. The equilibrium percentage dye exhaustions (%E), which is a measure of dye uptake by the fabrics were determined prior to and post-modification of the cellulose at varying concentrations and temperatures. The optimum values of %E obtained for the modification agents viz: CH_3COOH, $NH_4)_2SO_4$, NaCl, and Na_2CO_3•$10H_2O$ were: 89.71%, 88.57%, 85.71%, and 68.70% at concentration 2% v/v and temperature of 70 °C. The%E of modified cotton fabric dyed with malachite green was optimum in acidic conditions (i.e.CH_3COOH with%E of 89.71%) followed by $(NH_4)_2SO_{4;}$ 88.57%, which undergoes hydrolysis in an aqueous solution. This was then followed by $NaCl_{aq}$ (i.e. a neutral solution) and Na_2CO_3•$10H_2O$ (i.e. an alkaline solution). However, all modifying agents used enhanced the dye uptake. The values of partition coefficient (K) were in the order of 1307.73 L.tkg^{-1}, 1162.34 L.tkg^{-1}, 899.69 L.tkg^{-1}, and 329.23 L.tkg^{-1}, respectively at 70 °C; while the values for standard affinities ($-\Delta\mu^{\theta}$) were 20,463.94 kJ.mol^{-1}, 20,127.85 kJ.mol^{-1}, 19,397.40 kJ.mol^{-1}, and 16,530.65 kJ.mol^{-1}. This implies a correlation between the equilibrium exhaustion and standard affinity of dyed modified cotton fabric. The values of entropy change (ΔS^{θ}) are 175.53 J.mol^{-1}K^{-1}, 141.29 J.mol^{-1}K^{-1}, 148.16 J.mol^{-1}K^{-1}, 81.023 J.mol^{-1}K^{-1} and 255.10 J.mol^{-1}K^{-1} for the four modifying agents, respectively, which implies that the reaction is feasible (spontaneous) whereas ΔH^{θ} are -39,729 kJ.mol^{-1}, -28,144 kJ.mol^{-1}, -31,531 kJ.mol^{-1}, -11,669 kJ.mol^{-1} and -73,928 kJ.mol^{-1}, respectively. The negative values of ΔH^{θ} suggested that the reactions were exothermic. This study established that modifying agents on cotton fabric is one of

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the finest ways to improve the affinity between dye and fabric, thereby significantly reducing the time, cost, and stress required to achieve an optimal result in the dyeing process.

Introduction

Dyes are intensely coloured compounds used for the colouration of various substances, including textile materials, paper, leather, hair, food, drugs, cosmetics, waxes, grease, petroleum products, plastics, etc. Dyes are retained in these substrates by physical absorption of salts, metal complex formation, mechanical retention, or covalent bonds formation [1]. There are several applications of dyes, including colouration of natural and synthetic fibres (for example, silk, cotton, wool and linen, polyester nylon). However, most of these applications result in the discharge of dangerous effluent into the environment, thereby rendering the ecosystem unsafe. Considering the availability, affordability, and colour effectiveness of most dyes, primarily due to limited sustainable alternatives, these dyes are continuously employed for dyeing purposes [2]. Therefore, this calls for attention since they are not prohibited for usage. Seeking an alternative option to limit the amounts of this effluent discharged into the environment is a viable approach. There is an urgent need to find a solution to the volume applied to the fabric materials. Significant usage of these dyes in textile or fabric applications can be alleviated by ensuring the modification of the substrates for maximum uptake and stickiness/fixation to the fabrics (substrates). This, in turn, would limit the concentrations/volumes that are discharged into the environment such that the remaining concentration released into the environment can be within the acceptable/permissible limit.

In recent times, the malachite green dye (supporting information (SI) Figure SI 1a) has become one of the most utilized dyes for cellulose fibres [3–5]. This showcases its importance in the dye manufacturing industry [6,7]. Primary reasons for the prominence this dye has gained; are due to its variety of hue, brilliancy, ease of use, better fastness properties and applicability [8–12]. However, there are lingering challenges associated with its use, these include an increased volume of wastewater discharged, low dye utilization or uptake by the fabrics, and a huge amount of electrolyte is used [7,13-15]. Another major challenge is that charge repulsion causes the exhaustion of the dye bath, thus making it limited [16].

One of the materials that are usually dyed with malachite green dye is cellulosic materials, for instance, cotton fabric (Figure SI 1b). Cellulose is essentially a polymer, and its molecule is composed of a large number of repeating units of glucose attached end to end [17,18]. However, unsatisfactory dye fixation and poor dye uptake are the two significant drawbacks that the dyeing of cellulose fibres with dyes still experiences. Poor dye uptake is related to the existence of the charge barrier effects between the fibre surface and dyes. The negative charge on the fabric repels the dye ions, and therefore, the exhaustion of the dye bath is limited [16]. Inactive hydrolysed dye remains a major contributing factor in poor dye fixation. To overcome these problems necessitates structural or surface modification of the fabric prior to dyeing to create additional functionalities or porosity for enhancing its potentiality for higher dye uptake.

Recently, the chemical modification of cotton fabrics has been considered an alternative option to enhance the dyeability of fabric [19,13]. The point behind the cationization of cotton is to increase the neutral substantivity of anionic dyes for cotton by introducing positively charged sites on the cotton [20–22]. Pretreatment of cotton using compounds such as glycidyl trimethyl ammonium chloride and polyamide epichlorohydrin resin with and without thiourea or ethylenediamine to increase the dyeability for anionic dyes have already been reported [19]. Therefore, creating numerous porosities on cotton fabrics to increase the surface area, active sites and accessibility to the dye molecules is an effective way to increase maximum dye uptake of the fabric and decrease the concentration of dye residues discharged into the surrounding after the process. This will enable disposal/discharge of lesser hazard effects that reach the surrounding ecosystem, thereby decreasing the consequential pollution to both water bodies, humans, aquatic habitat and microorganisms [6,12,13,23,24].

Several researchers have reported the purpose of modification on different fabrics over the past decades. For example, Bello et al. [25] reported the kinetics and thermodynamics studies of an acid dye on modified Nylon 6 fabrics. Nylon 6 woven fabric obtained locally was modified by different agents such as urea, thiourea, diethylamine, propylamine. The fabric modification improved the dyeing process thermodynamically by reducing the conventional dyeing temperature of nylon 6 fabrics. The dyeing rate was observed to have increased massively, although, on a few occasions, the dyeing exhaustion did not show any major changes in the kinetic study. Conversely, the thermodynamic parameter experienced changes (K, $\Delta\mu^{\theta}$, ΔH^{θ} and ΔS^{θ} of the treated nylon 6 with urea (0.3 $moldm^{-3}$) showing a great increase in K, $\Delta\mu^{\theta}$ and ΔH^{θ}). The observed changes in the thermodynamic parameters imply that urea and other related compounds used to modify the fabric can likely develop lower temperature dyeing. Another author Renuga et al. [26] studied the surface modification and application of functionalized polymer nanofibers and concluded that one of the finest techniques for contemporary textile finishing processes is surface functionalization of synthetic fibres for various applications, especially related to the improvement of the dyeability of fabrics.

Modification of polyester for medical uses has been investigated [27–29]. The study of Martin et al. [27] concluded that the excimer laser modification process has a high industrial prospect given that it does not involve any of the required solvents for the wet chemical process, and it is also eco-friendly. Additionally, the dyeing properties inherent in the dyes are enhanced via post-laser treatment, providing another choice for dyeing polyamide materials. The work of Salah [30] revealed that cotton/nylon has the utmost colour measurement values of 75:25%. The process employed in dyeing cotton/nylon blended fabric to a solid shade in one bath was noted to save time and is cost-effective. Sundrarajan et al. [31] reported that the modified fabrics showed improved dye uptake than unmodified fabric. Compared to sulfonation modification, the cross-linking modification was observed to have been incredibly effective.

Typically, modification of cotton fabric remains an important tool to alleviate the associated problem of dyeing of cotton, thereby enabling easy diffusion of the dye molecule into the fibre. Dyes are important integral components of the textile industry, and chemical modification of cellulose fibres is regularly applied to correct the deficiencies of the fibres. There is enough justification and innovation to embark on cellulose fabric modification before dyeing due to the following reasons: (i) the textiles consume thousands of tonnes of dyes annually, of which over 90% are imported at huge cost leading to depletion of the country's foreign exchange [2], (ii) the importation of dyes reduces our potential to produce internally and generate employment (iii) the sales of textile materials largely depend on their colour (dyes). (iv) a large amount of dye, much time and effort, are required to achieve satisfactory results with deeper shade when embarking on dyeing of unmodified cotton. The study in this area is not available in the literature, thus establishing the novelty of the current study.

The present study aims at ascertaining the optimal conditions that ensure the dye fastness onto the cotton fabric using various modification reagents. The first step in this work is the surface modification of cotton fabric, and this is considered the best way to obtain modern textile treatments using different modifying agents to create the cationic sites and thereby improve the dyeability of the dyes. The dyes were applied to modified cotton and their usage properties were determined. This work also studied the effects of various experimental parameters using exhaustion method including the effect of time, temperature, and effects of different modifying agents on the cotton fabric, effect of malachite green dye on the modified cotton fabric and study of thermodynamic parameters governing the dyeing process (including partition coefficient (K), enthalpy change (ΔH^{θ}), entropy (ΔS^{θ}) and standard affinity ($\Delta \mu^{\theta}$)).

Materials and methods

Cellulose (cotton) fabric modification

Cotton fabric obtained from Oja-Igbo market in Ogbomoso, Nigeria, was utilized in this study. A 100 mg weight cotton was cut from the bulk fabric for a set of concentrations and a modifying agent. In a slacked condition and for an estimated period of 30 min, the cotton was treated with an aqueous solution of acetic acid, ammonium sulphate, sodium chloride and hydrated sodium carbonate at two different concentrations (1 and 2% v/v) that were measured out of stock into the distilled water in 10 mL modification bath. The cotton fabric was then immersed into it, covered with aluminium foil paper to maintain a constant volume throughout the modification period and allowed to sit and soak for 40 min. Finally, the modified fabric was removed and rinsed five times with distilled water and kept for further use. The above procedures were repeated for each modifying agents and concentration at a time. All chemicals used were purchased from Sigma-Aldrich and used without further treatment.

Preparation of standard dyes solution

Preparation of 1% w/v of MG dye solution involves dissolving 1 g of MG dye in distilled water, made up to 100 cm^3 mark in a volumetric flask [32]. Other solutions were prepared via the standard dye solution, and a series of five solutions in a dyebath was prepared.

Preparation of dye bath

A 1% v/v dye solution was prepared following the previous procedure [32]. Modified cotton fabric was dyed by using the conventional methods and at 1% depth in each case [32]. The fabric to liquor ratio was 1:150 for various equilibrium exhaustion periods of the dyeing [32]. The recipes for the dyebath of 1:150 for the fabric to liquor ratio include 1% w/v dye stock solution, 0.1 cm^3 dye volume, 100 mg fabric and 14. 8 cm^3 distilled water.

Dyeing of cellulose (cotton) fabric

The dye batch technique, which is usually used to dye all types of textile fibres, is determined by the fibre; it contains and its physical properties. The preparation of dyebath solution was done in triplicates and occasionally in quadruple or quinary sequence in a dyebath, and 100 mg of cotton fabric was put in each of them. In this study, five solutions of dyebath were prepared, and modified cotton fabric was inserted into each dye bath. The dyebath was then placed in a 30 min preheated (hot) water bath with an opened end of each dyebath sealed with aluminium (foil) paper throughout dyeing. The dyeing of the fabric was performed at 50 °C, 60 °C and 70 °C for 1 h and a different batch of the dyebath were used for each dyebath at the same concentration. Once the dyeing is completed, the dyed modified cotton fabric was removed at 5 min intervals, and the solutions were allowed to cool to room temperature and then measured the absorbance.

Measurement of absorbance

To determine the absorbance (A_T), the UV–VIS spectrophotometer (model Aquamate V4.60) was calibrated to zero absorbance using distilled water which also served as blank. Using this spectrophotometer, the absorbance of the standard solution of the MG dye (1%) was scanned between 400 and 700 nm to determine the maximum wavelength (λ_{max}), and then the absorbance of the samples was recorded.

Estimation of percentage exhaustion (% E)

The total amounts of dye uptakes determine the exhaustion by the fabric. It was measured through the sampling of the dyebath at the start and end of the dyeing process. The dyebath was removed from the water bath, and the dyed fabric was also withdrawn from the dyebath. After dyeing and upon cooling down of the dyebath to room temperature, the residual solutions of the dyes were filtered, and the optical densities were measured at wavelengths corresponding to the λ_{max}= 619 nm (obtained experimentally). It should be noted that the optical density of the original dyebath solution was also recorded before dyeing. The percentage dye exhaustion of the dyed fabric was estimated using Eq. (1).

$$\%E = \frac{A_0 - A_t}{A_0} \times 100 \tag{1}$$

Where A_0 = the absorbance at time zero (i. e. before dyeing), A_t = the absorbance at time t, (i. e. after dying) [32–34]

Determination of partition coefficient (K)

Partition coefficient, K (L/kg) was defined as the ratio of the dye amounts absorbed by the cotton fabric to that of dye amounts in the dyebath at equilibrium [25,35]. It is expressed as

$$K = \frac{[D]_f}{[D]_b} \tag{2}$$

where $[D]_f$ and $[D]_b$ are dye concentration in the fibre (g/kg) and dye concentration in the residual dyebath (g/l) at equilibrium and at dyeing temperature, T, (Eqs. (2) - (6). K and %E are related by the following equations [35].

$$K = \frac{\text{liquor ratio}}{Q} \times \%E \tag{3}$$

$$\text{Liquor ratio} = \frac{\text{dye bath}}{\text{fibre}} = \frac{15l}{0.11\text{g}} = 150lg^{-1} \tag{4}$$

$$Q = 100 - \%E \tag{5}$$

where Q is the amount of dye left in the solution at the equilibrium exhaustion and%E is the percentage equilibrium exhaustion. Here, the liquor ratio used is 150:1 liquor to the fabric. Therefore, 150:1 liquor ratio, K, now becomes

$$K = \frac{150 \ \times \%E}{100 - \%E} \tag{6}$$

Estimation of thermodynamic parameters

Standard affinity (-$\Delta\mu^\theta$)

It is the measure of the driving force in a dyeing process. Dyeing of cotton with MG dye corresponds to the partition mechanisms, and hence the standard affinity (-$\Delta\mu^\theta$) of dyeing cotton fabric was calculated using:

$$-\Delta\mu^\theta = \frac{\text{RTln}[D_f]}{V \times [D_s]} = \text{RTln}K_v \tag{7}$$

where R is the universal gas constant (kJ K^{-1} mol^{-1}); T, the dyeing temperature (K); $[D_f]$, the dye concentration in the fibre (g/100 g of the fabric); $[D_s]$, the dye concentration in the solution (g/L); and v, the colcine term represents the effective volume of water in the substance [32–34]

Table 1
Dyeing parameters of MG dye on cotton fabric.

Modifying agents	% E			K (L kg^{-1})			$\Delta\mu^0$ (kJ mol^{-1})		
	50 °C	60 °C	70 °C	50 °C	60 °C	70 °C	50 °C	60 °C	70 °C
Unmodified cotton	10.11	12.80	12.90	16.87	19.30	22.22	7.6×10^3	8.2×10^3	8.8×10^3
CH_3COOH	82.35	83.82	89.71	699.86	777.07	1307.73	17,591.81	18,426.25	20,463.94
NaCl	75.71	77.14	85.71	467.54	506.17	899.69	16,508.58	17,239.47	19,397.40
$(NH_4)_2SO_4$	80.00	82.57	88.57	600.00	710.59	1162.34	17,178.46	18,178.64	20,127.85
$Na_2CO_3{\bullet}10H_2O$	61.14	63.40	68.70	238.60	259.84	329.23	14,702.12	15,393.39	16,530.65

Enthalpy change (ΔH^{θ}) of dyeing

The ΔH^{θ} and ΔS^{θ} were calculated using the relation:

$$-\Delta\mu^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta} \tag{8}$$

The enthalpy change ΔH^{θ} in the dyeing process is obtained from the empirical plot that shows the relationship between $-\Delta\mu^{\theta}/T$ and $1/T$ using Eq. (8).

$$\Delta H^{\theta} = \frac{\delta\left(-\Delta\mu^{\theta}/T\right)}{\delta(1/T)} \tag{9}$$

$$\frac{\Delta H^{\theta}}{T} = \frac{-\Delta\mu^{\theta}}{T} + C \tag{10}$$

Where ΔH^{θ} =the heat of adsorption (kJmol^{-1}); $-\Delta\mu^{\theta}$ = standard affinity (kJmol^{-1}); and C = integral constant [32–34].

Entropy of dyeing (ΔS^{0})

This is the rate of disorderliness of the reaction system. ΔS^{θ} was determined from Eq. (8)

$$\frac{-\Delta\mu^{\theta}}{T} = \frac{-\Delta H^{\theta}}{T} + \Delta S^{\theta} \tag{11}$$

A plot of $\frac{\Delta\mu^{\theta}}{T}$ against T^{-1} gives a straight-line graph where ΔH^{θ} is the slope and ΔS^{θ} is the intercept of the graph [32–34]

Results and discussion

Effects of modifying agents on cellulose (cotton) fabric

Table 1 presents the datasets of dyeing parameters of MG on the modified cotton fabric with a 2% v/v solution of modifying agents compared to the unmodified cotton fabric. An increase in percentage exhaustion was noticed as the temperature increased in both modified and unmodified cotton fabric. The dye of cotton without modification demonstrated lower uptakes during the exhaustion dyeing process (Table 1). Lower%E suggests the difficulty of dye molecules to penetrate the cotton fabric due to the insufficient active (attacking) sites on the unmodified cotton fibre, thereby hindering ease diffusion of the MG dye. Conversely, upon modifying the fabric with the respective modifying agents as presented in Table 1, there was a significant increase in the dye uptakes by the fabric.

Table 1 and Fig. 1 present the results of different modifying agents and the corresponding dyeing parameter values (including%E, K, $\Delta\mu$) using two different concentrations. The higher values of K noticed can be attributed to the high volume of dye-bath (150:1). This resulted in rapid migration rates of dye molecules onto the fibre and consequently a higher dye uptake by the cotton fabric leading to good colour fastness. Bello et al. [25] reported that K values could be employed to forecast the dye fastness property onto the fibre. This was observed to be due to the rapid mobility of dye ions with the temperatures, thus a rise in the numbers of dye molecules that interacted with the surface-active sites. Therefore, modifying fabric (cotton in this case) led to significant enhancement in the dye uptakes by the fibre, hence improving the dye exhaustion. This study observed that the 2% v/v demonstrated the highest%E with the CH_3COOH.

Effects of time and temperature on dye exhaustion

Fig. 1 also presents the influence of time on the%E of MG dye uptake by modified cotton at different times and temperatures. One of the essential qualities or characteristics that denote the exhaustion of MG dye on the modified cotton fabric is

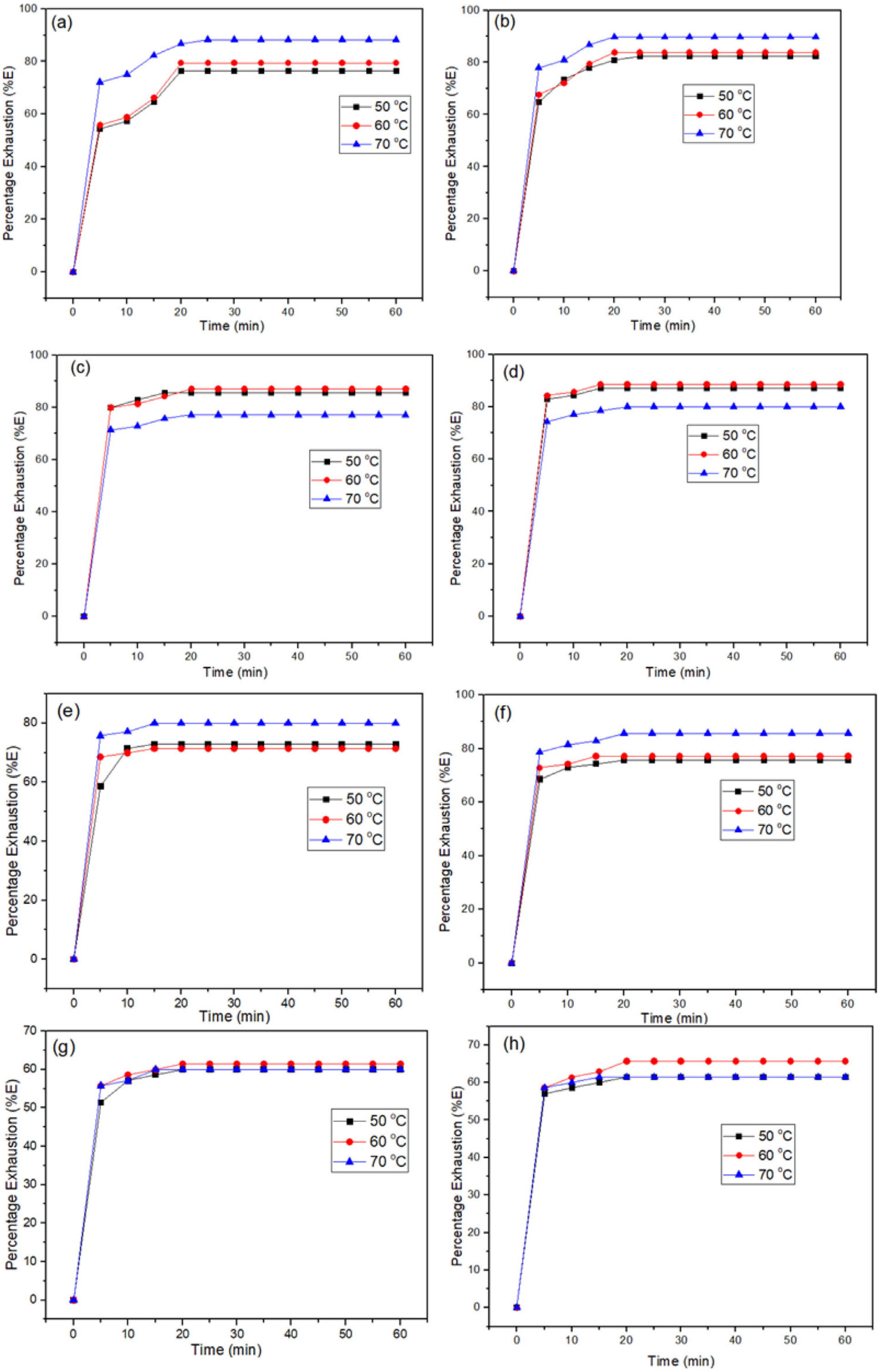

Fig. 1. Effect of modifying agents on cotton fabric dyed with MG dye for 1% v/v and 2% v/v concentration of modifying agents (a and b), (c and d), (e and f), and (g and h), respectively for CH_3COOH, $(NH_4)_2SO_4$, NaCl and $Na_2CO_3\bullet10H_2O$.

Table 2
Effect of concentration of modifying agents on cotton fibre dyed with MG dye at 50 °C, 60 °C and 70 °C.

Modifying agents	1% v/v modification				2% v/v modification			
	%E	K (Ltkg^{-1})	$\Delta\mu^{\theta}$(kJmol^{-1})	$\Delta\mu^{\theta}$/T (kJmol^{-1}K^{-1})	%E	K (Ltkg^{-1})	$\Delta\mu^{\theta}$(kJmol^{-1})	$\Delta\mu^{\theta}$/T (kJmol^{-1}K^{-1})
50 °C								
CH_3COOH	76.47	487.48	16,620.77	51.46	82.35	699.86	17,591.81	54.46
NaCl	72.86	402.69	16,107.61	49.87	75.71	467.54	16,508.58	51.11
$(NH_4)_2SO_4$	85.71	899.67	18,266.36	56.55	87.14	1016.41	18,593.94	57.57
Na_2CO_3•$10H_2O$	60.00	225.00	14,544.52	45.03	61.14	238.60	14,702.12	45.52
60 °C								
CH_3COOH	79.41	578.51	17,609.31	52.88	83.82	777.07	18,426.25	55.33
NaCl	74.28	433.23	16,808.23	50.48	77.14	506.17	17,239.47	51.77
$(NH_4)_2SO_4$	87.14	1016.41	19,169.61	57.57	88.57	1162.34	19,541.03	58.68
Na_2CO_3•$10H_2O$	61.4	238.60	15,157.30	45.52	65.70	287.32	15,671.69	47.06
70 °C								
CH_3COOH	88.24	1125.51	20,036.03	58.41	89.71	1307.73	20,463.94	59.66
NaCl	80.00	600.00	18,242.14	53.18	85.71	899.69	19,397.40	56.55
$(NH_4)_2SO_4$	87.14	1016.41	19,745.27	57.57	88.57	1162.34	20,127.85	58.68
Na_2CO_3•$10H_2O$	65.10	279.80	15,718.85	45.83	68.70	329.23	16,530.65	48.19

the determination of the equilibrium time. According to Fig. 1, dye exhaustion increases with time up to about 18 min and attained equilibrium afterwards at all temperatures. Once the equilibrium is reached for all modifying agents, the longer reaction times showed no influence, suggesting that all the open pores by the modifying agents have been filled up and the fabric no longer take any more dye more since all the vacant spaces have been occupied. Thus, suggesting the stability of%E as time increases.

Increasing the temperature of the dyeing process resulted in an expected increase in the value of standard affinities for all modifying agents (Table 1). This suggests that increasing temperature progressively increases the partition coefficient, which is the ratio of the amounts of dye molecules absorbed by the cotton in the dyebath at equilibrium with an increase in temperature.

The partition coefficient is related to the equilibrium exhaustions of the dyes, thereby implying that a satisfactory hue would be achieved in dyeing fabric at a higher temperature. Increasing kinetic energy of the system, viscosity reduction and increasing the swelling of the substrates with subsequent accessibilities remain critical factors responsible for enhanced dye affinities [35,33,19]. It can be established that the highest%E was obtained at the higher temperature and that the increase in dyeing reaction time and the temperature has effects on the fabric dyeing,%E and also favoured the dye uptake by the modified cotton until equilibrium [25,35]. Therefore, as presented in Fig. 2, a continuous progression in percent exhaustion can be noticed as time increases, suggesting that the cotton fabric absorbed greater amounts of MG dye for a long time until when the equilibrium was reached. The penetration of dyes onto the polymer at a longer time can be attributed to the deeper shade on the fibre thereby, resulting in a higher%E [31].

Effect of concentration of modifying agents on dyed cellulose (cotton) fabric

Table 2 revealed the results of percentage exhaustion (% E), partition coefficient (K) and standard affinities ($\Delta\mu^{\theta}$) of modified cotton dyed with malachite green dye at different concentrations of modifying agents and temperatures Table 2. presents a comprehensive representation of optimum percentage exhaustion reflecting the effects of different concentrations of modifying agents on the dyeability of cotton fabric**.**

According to Table 2, it was observed that as concentration increases, there is an increase in MG dye uptake, thereby accompanied by an increase in percentage equilibrium exhaustion (% E) while keeping the temperature constant. For instance, for NaCl; the% E increases from 80% to 85.71%, while for $(NH_4)_2SO_4$; it increases from 87.14% to 88.57%, Na_2CO_3•$10H_2O$; 65.10% to 68.70%, and CH_3COOH; 88.24% to 89.71% by keeping the temperature constant at 70 °C (i.e. 343 K), which means that there is a significant increased % E as the concentration of the modifying agents increases, thereby progressively increase the partition coefficient (K) and the standard affinity. Comparable observations were reported by the previous studies [25,33,32,35].

Effect of exhaustion on cellulose (cotton) dyed with MG dye

According to the result presented in Tables 1-2, it can be observed that modification of cotton led to significant enhancement in dyeing exhaustion. This can be further explained schematically as presented in Fig. 3 (a-b). This enhancement may be attributed to the surface, structural and morphological changes in cotton fabric by the modifying agent, suggesting that the barrier effects associated with dyeing cotton were diminished [32]. This thereby results in stronger ionic bonds between the dye and modified cotton (cellulose) than the hydrogen bond or Van der Waal forces that linked the dye with the unmodified cellulose (Fig. 3) [32,35].

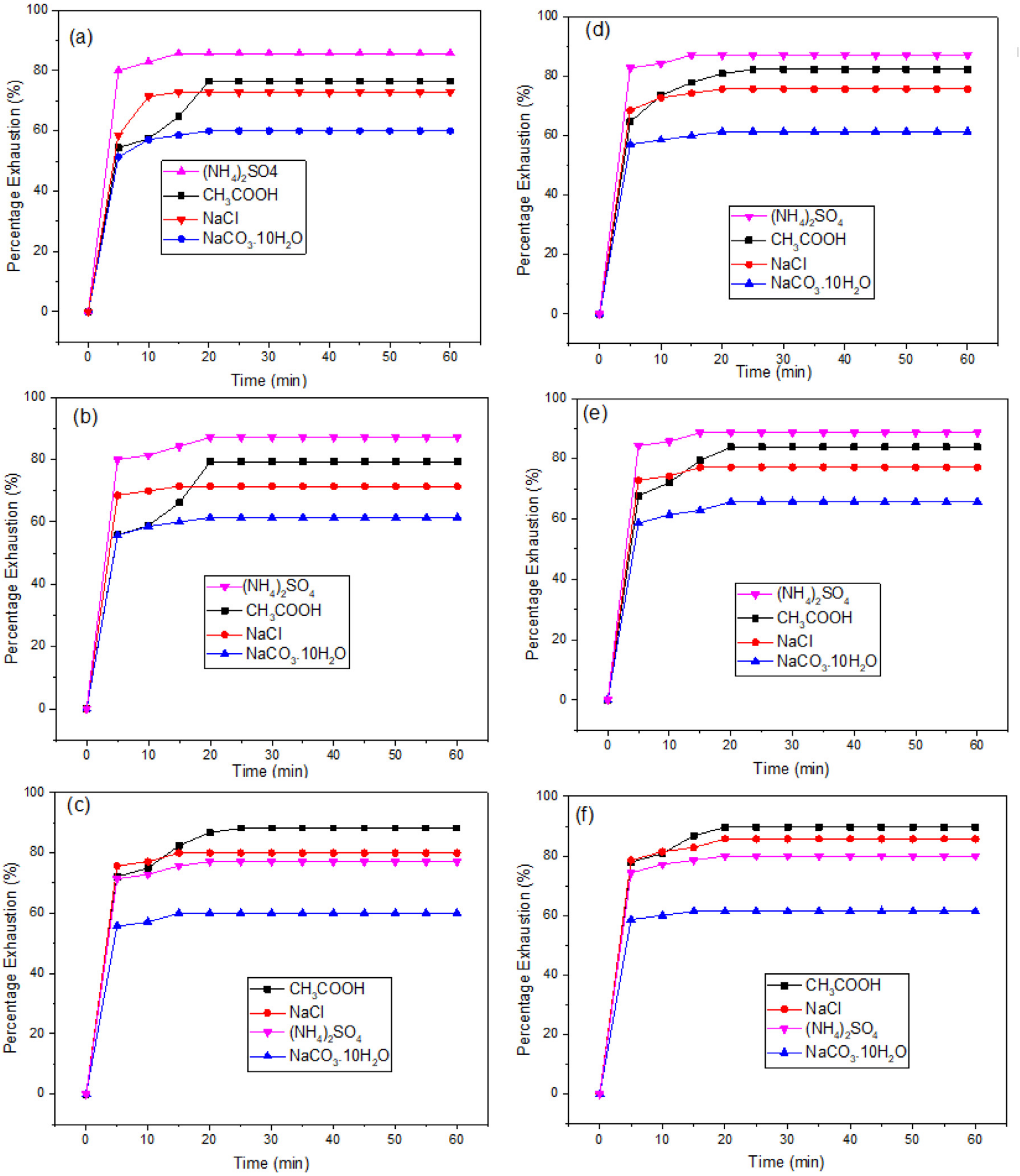

Fig. 2. Effect of time on dyeing exhaustion of cotton modification with CH_3COOH, NaCl, $NaCO_3$•$10H_2O$ and $(NH_4)_2SO_4$ at (a,d) 50 °C, (b,e) (60 °C) and (c,f) (70 °C) for 1% v/v (a-c) and 2% v/v (d-f).

Modification treatment has a slightly damaging effect on the surface scale-like structure of cotton as compared to the unmodified cotton counterparts; the scale edge is slightly eroded; it is considered that the destruction of the surface improved the absorption (uptake) of dye molecules by the cotton fibres during dipping and diffusion of dye molecules into the cotton fibres (Fig. 3b). The implication is that modification increases the pore surface, thereby enhancing the adsorption uptake, which promotes the permeation of the dye molecules into the modified cotton fibre. This improves the extent of reaction between the malachite green dye and cotton fibre. For example, the fabric modified with CH_3COOH, Na_2CO_3•$10H_2O$, NaCl, and $(NH_4)_2SO_4$, there is a significant binding force (ionic attraction) which is evident between the dye molecules and cellulose hydroxyl group, thereby strongly attract malachite green dye, allowing the cotton to be dyed and ensured a good dye uptake. Therefore, fabric modification can be considered an important criterion for improving the dye uptake unto sub-

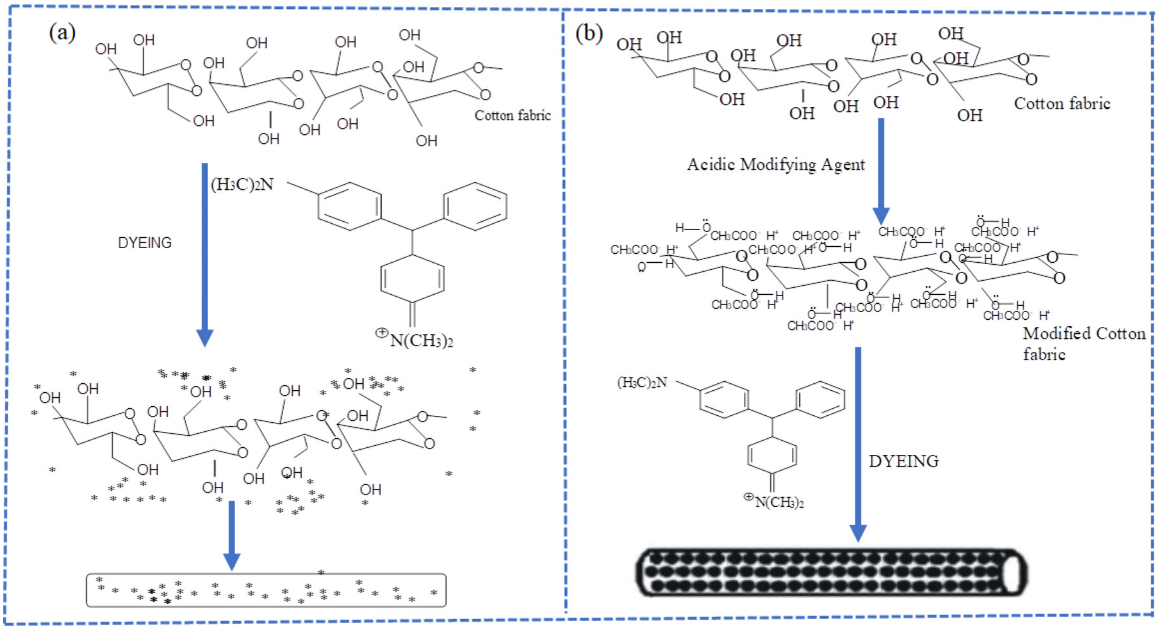

Fig. 3. Schematic dyeability process of (a) unmodified and (b) modified cellulose (cotton) fabric with malachite green dye.

strate and reducing the effluent loads. This improvement could be related to the higher affinity toward malachite green dye. The values of the partition coefficient (K) were in the order of 1307.73 L kg^{-1}, 1162.34 L kg^{-1}, 899.69 L kg^{-1}, 329.23 L kg^{-1} at 70 °C (Table 2). The values for standard affinities ($-\Delta\mu^{\theta}$) were 20,463.94 kJ mol^{-1}, 20,127.85 kJ mol^{-1}, 19,397.40 kJ mol^{-1}, 16,530.65 kJ mol^{-1}, for CH_3COOH, $(NH_4)_2SO_4$, NaCl, and $Na_2CO_3{\bullet}10H_2O$, respectively. The implication of the standard affinities and partition coefficient (K) is that there is a correlation between standard affinity of a dye on fabric and the equilibrium exhaustion and that such dye combines somewhat more easily with the fabric.

As a result, the reaction probability between the dye and cotton fibres is increased, resulting in an improved dye uptake of the dyed cotton samples. The poor or low% E of unmodified cotton fabric (Table 1) observed may be due to the poor or insufficient of interaction between the MG dyes and active site (hydroxyl group of cellulose) on the unmodified cotton fabric resulting in a reduction in the efficiency of the reaction with the cellulose substrate. This agreed well with the works of [19,33,35].

Typically, modification with $(NH_4)_2SO_4$, CH_3COOH, NaCl, and $Na_2CO_3{\bullet}10H_2O$ (Table 2) showed that % E improved in acidic media with CH_3COOH demonstrated 89.71% followed by $(NH_4)_2SO_4$ with 88.57%, which could undergo hydrolysis in aqueous media to promote the breaking of cellulosic chain, reduce the fibre packing thereby improving the dye uptakes. The trend was followed by the $NaCl_{aq}$ (with 85.71%), which is a neutral solution and apparently with a lower %E of 68.70 under $Na_2CO_3{\bullet}10H_2O$ (alkaline media). It can be explained here that the bonding forces between the hydroxyl groups in cotton and nucleophilic groups in the dyes enforced the electrostatic attractions between the dyes and the cationic sites, thus resulting in higher %E. The trends can be attributed to suppressing negative charges on the surface of cotton fibre, thereby permitting the dye to diffuse into the fibre. In addition, since dye fixation onto the cellulosic fibre requires alkaline dyeing condition(s) to activate the cellulose hydroxyl groups to allow interaction with the dye, some dyes can inevitably experience competing for hydrolysis reactions with the hydroxide nucleophile(s), thereby leading to further improvement in dye uptakes by the fibre [32,36-38].

Thermodynamic studies

Fig. 4 presents the relationships between $\Delta\mu^{\theta}$/T (kJ $mol^{-1}K^{-1}$) and 1/ T (K^{-1}) on the enthalpy change (ΔH^{θ}) of the modified cotton fabric for the thermodynamic parameters studied. Using the Eqs. (7)-(11) described above, their values were obtained from three temperatures (i.e. 50 °C, 60 °C and 70 °C). The ΔH^{θ}, which is the heat of the reaction, and the entropy (ΔS^{θ}), i.e. the disorderliness of the system, were obtained by plotting the graph of $-\Delta\mu^{0}/T$ against T^{-1} as shown in Fig. 4. The straight-line graph was obtained where the intercept of the graph is ΔH^{θ} and the slope is ΔS^{θ} [25,33,39].

From Fig. 4, the slopes (ΔS^{θ}) for 2% v/v are 175.53, 148.16, 141.29, 81.023 and 255.10 $Jmol^{-1}K^{-1}$ for CH_3COOH, NaCl, $(NH_4)_2SO_4$, and $Na_2CO_3.10H_2O$, respectively (Table SI 1). Their intercepts (ΔH^{θ}) are −39,729, −31,531, −28,144, −11,669 and −73,928 kJ mol^{-1}, respectively. The negative values imply that there was an exothermic reaction and that more dyes were retained in the fabric suggesting a stronger embedded of dye molecules within the fabric molecules. This agreed with similar findings reported by other studies [40,33,35].

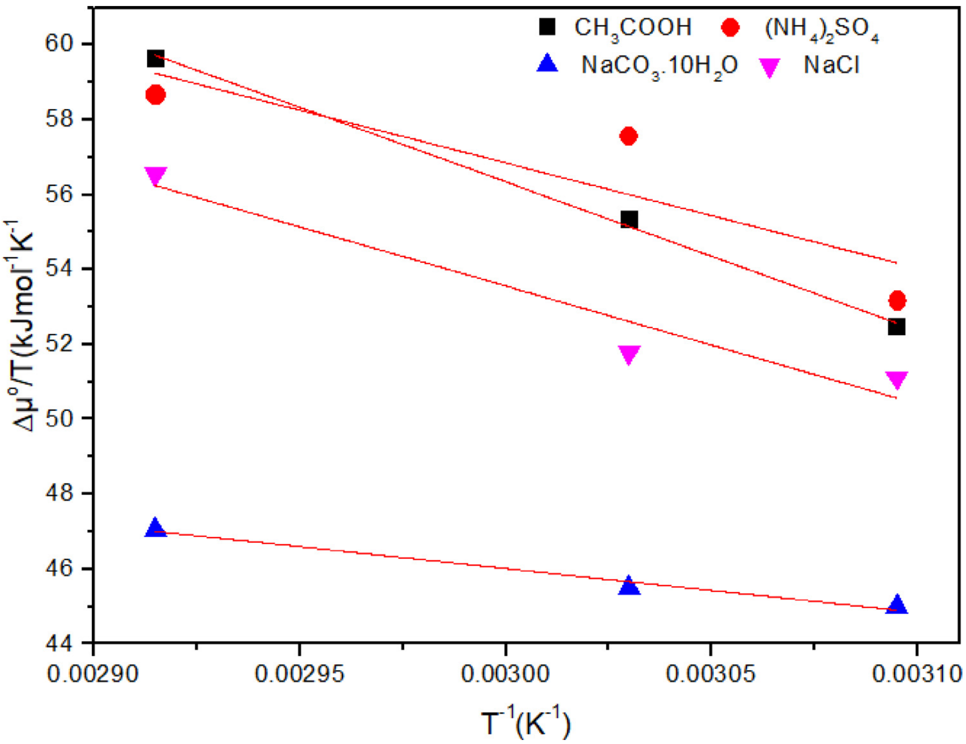

Fig. 4. Relationship between $\Delta\mu^{\theta}$/T (kJ mol^{-1}K^{-1}) and 1/T (K^{-1}) on enthalpy change for the modification of cotton fabric with the 2% v/v concentration of modifying agents.

Conclusion

The present study established that eco-friendly modification of cotton fabric with four modifying agents: sodium chloride, ammonium sulphate, hydrated sodium carbonate, and acetic acid is one of the best routes to enhance the affinities between dyes and fabrics. These reagents improved the dyeability of cotton fabric and uptake of MG dye. The optimum result was achieved with CH_3COOH with %E of 89.71%, followed by $NH_4)_2SO_4$ (88.60%), NaCl (85.71%) and Na_2CO_3•$10H_2O$ (68.70%). This study provides a modification technique that is an environmentally friendly approach and has a significant potential for industrial application as it reduced stress, the amounts of dyes to be used for satisfactory dyeing and the time required to obtain good dyeing results (performances). Therefore, it is a promising approach to improve the cationic activity of the cellulosic fibres and decrease the electrostatic repulsion of negative ions, thereby enabling the positive effects on dye absorption.

Authors' contributions

Kayode Adesina Adegoke: Conceptualization, data curation, formal analysis and investigation, methodology, validation, visualization, writing-original draft preparation, and writing- review and editing. Mujeeb Balogun Adeyemi: data visualization, and writing- review and editing. Isah Adewale Bello, and Olugbenga Solomon Bello: Conceptualization, data curation, validation, visualization and supervision. Nobanathi Wendy Maxakato: data curation, and validation. All authors read and approved the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Availability of data and materials

All data and materials used in this study are available within this article.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.sciaf.2022.e01138.

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