

Original Research Article

Effects of Modifying Agents on the Dyeability of Cotton Fabric using Malachite Green Dye

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Abstract

Changes in thermodynamic parameters as a result of modifying agents on dye uptake of cotton fabric using malachite green (MG) dye was investigated in this study. Five modifying agents {Acetic acid (CH_3COOH), hydrated Sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), Sodium Chloride (NaCl), Ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) and Hydrogen peroxide (H_2O_2)} were used on cotton fabric. The equilibrium exhaustions (%E) were determined before and after modification of the cotton fabric at different concentrations which were 88.24%, 80%, 77.14%, 65.10% and 30.88% for CH_3COOH , NaCl , $(\text{NH}_4)_2\text{SO}_4$, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and H_2O_2 respectively. The results also showed a correlation between the standard affinity ($-\Delta\mu^0$) of dye on cotton fabric and the equilibrium exhaustion. The values of entropy (ΔS^0) and enthalpy (ΔH^0) change revealed the feasibility (spontaneity) and exothermic nature of the reaction. The optimum parameters were attained in acidic solution (CH_3COOH) at the highest temperature (70°C) of dyeing as it showed the highest % efficiency of 88.24%. This work established that modification of cotton fabric with modifying agents is one of the best route to improve the affinity between dye and fabric as it reduces stress, amount of dyes wasted in dyeing, time required to achieve satisfactory results leading to a cost effective environmental friendly approach in the field of cotton dyeing.

Keywords: Exhaustion; Modifying agents; Malachite green; Cotton; Thermodynamics parameters.



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1.0 Introduction

Owing to the vast growth in textile industry, modification of individual fiber types has been developed to broaden uses. Modified fibers can be produced by chemical alteration of the polymer fiber or fabric or by the use of non-reacting additives. Improved dye-ability is usually effected by use of a suitable comonomer (Sundrarajan *et al.*, 2012, Salah and El-Badry 2012, Shahin 2015). These chemicals add value to the cotton fabric by transforming the cotton fabric handle to match the customer perception. (Kamel *et al.*, 2007, 2009, El-Molla *et al.*, 2011, Fang *et al.*, 2013, Wang and Liu 2014).

Cellulosic fiber possesses inherent attractive bulk properties but surface modifications are used to diversify its end uses (Baltazar *et al.*, 2007, Termerman and Leys 2007 Mahbulul and Khan 2013, Wang and Liu 2014, Shahin 2015). The dyeing of cellulose fibers with cationic dyes (for instance Malachite green dye) suffers from two major disadvantages; one is poor dye uptake and the other is unsatisfactory dye fixation. Due to poor dye uptake, the exhaustion of unmodified cotton fabric on cationic dye is limited (lesser) and time-consuming than the one obtained for modified cotton fabric. Consequently, the effluents become more concentrated with dye and their discharge to the receiving bodies becomes problematic to human health. In the case of poor dye fixation, the contributing factor is the presence of inactive hydrolyzed dye. In order to overcome this problem, modification of cotton before dyeing was studied so as to ensure increase dye uptake on cotton fabric. Modification of cotton is emerging as an effective tool to solve environmental problems associated with dyeing of cotton

The purpose of physical and chemical procedures for modification of cellulose fibers is to increase reactive dye exhaustion and fixation degree and saving electrolytes. The pretreatment to improve functionality and dyeing ability of cellulose fibers, using cationic agents, has attracted attention recently (Hasani *et al.*, 2009, Liu *et al.*, 2007, Hyde *et al.*, 2007, Mahbulul and Khan 2013, Wang and Liu 2014, Mansour *et al.*, 2014, Fang *et al.*, 2015.). The reason for such treatment is improvement of cationic activities of cellulose fibers and reduction of electrostatic repulsion of negative ions resulting in a positive effect on absorption of anionic dyes and poly electrolytes. Recently, Xie *et al.*, (2007, 2008) reported the chemical, structural and morphological changes of cotton after treatment with triazine derivatives containing cationic and anionic groups and the effects of the treatment on dyeing with reactive dyes. Epoxy compounds (Xie *et al.*, 2008), chlorotriazine type quaternary compounds (Ma *et al.*, 2005), N-methylolacrylamide (Tutak and Ozdmir 2011), choline chloride (Michel *et al.*, 2002), chloroacetic acid etc. are the monomers commonly used in modification of cotton fiber. Due to the smaller molecular size, these compounds present good penetrability in fiber, and the exhaustion and fixation of reactive dyes on the modified fiber have improved. A number of changes are identified on modified cotton: formation of new molecular

structures containing cationic and anionic groups, very low reduction of crystallinity degree, and modification of surface

morphology. Modified cotton was dyed with reactive dyes and a higher exhaustion and fixation degree of reactive dyes was achieved as a result of reaction with new groups. The increased yield of reactive dye on cotton fabrics treated with commercial cationic agent is explained by positive surface charge of cationized cotton fiber (Tutak and Ozdmir 2011, Wang and Liu 2014).

In the dyeing process a solution of the dye is made, and the material to be dyed, called the substrate, is put in the solution. Coloured matter from the solution is transferred to the substrate by the process of adsorption; the removal of the dye from the solution is called exhaustion. This is a general description of all dyeing processes. In some cases, dyeing assistants are added to the dye solution to facilitate the interaction of a particular type of dye with the substrate, these are called modifying agents.

Malachite green (MG) is most commonly used for the dyeing of cotton, silk, paper, leather and also in manufacturing of paints and printing inks. Malachite green is widely used in distilleries for colouring purposes (Khattry *et al.*, 1999, Igwe *et al.*, 2008; Gharbani *et al.*, 2008; Goyal *et al.*, 2008; Shah *et al.*, 2009; Zvinowanda *et al.*, 2009, Mahbulul and Khan 2013). Malachite green dye is basically a cationic dye. It has properties that make it difficult to remove from aqueous solutions and also toxic to major microorganisms (Papinutti *et al.*, 2006). Its discharged into receiving streams will affect the aquatic life and causes detrimental effects in liver, gill, kidney, intestine, gonads and pituitary gonadotrophic cells (Srivastava *et al.*, 2004). Therefore, the treatment of effluent containing such dye is of interest due to its esthetic impacts on receiving waters.

The aim of this research work is to ascertain the optimum parameters that will ensure the fastness of the dye on cotton fabrics using different modifying agents especially the common reagents that are readily available but often used for other purposes (such as buffer, leveling agents, etc) in the dyeing industries. To the best of our knowledge, nobody has ever reported the utilization of Acetic acid (CH_3COOH), hydrated Sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), Sodium Chloride (NaCl), Ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) and Hydrogen peroxide (H_2O_2) as modifying agents for cotton fabrics in order to achieve salt free dyeing when using Malachite green dyes.

2.0 Materials and Method

2.1 Chemicals

All chemicals used were of analytical grade. Modifying agents were Acetic acid (CH_3COOH), Hydrated sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), Sodium Chloride (NaCl), Ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) and Hydrogen peroxide (H_2O_2). The cationic dye (Malachite green) was selected in the present study.

2.2 Modification of Cotton

Cotton fabric obtained from a market in Ogbomosho, Oyo State Nigeria was used in the investigation. The modification process was carried out as follows. Cotton was treated with aqueous

solution of acetic acid (CH₃COOH), hydrated sodium carbonate (Na₂CO₃·10H₂O), Sodium Chloride (NaCl), ammonium sulphate (NH₄)₂SO₄ and Hydrogen peroxide (H₂O₂) at different concentrations for a fixed time period of 40 minutes in a slack condition as reported previously (Bello et al., 2002, Bello et al., 2014). 1% v/v solution of each modifying agents were measured into a modification bath and make up to 10 cm³. Each stripe of 0.1g cotton fabric was inserted into it, covered with aluminum foil paper in order to keep the volume constant throughout the period of modification and cotton fabric was allowed soak on its own for a period of 40 minutes.

2.3 Preparation of Standard Dyes Solution

The Malachite green dye, IUPAC name 4-[[4-dimethylamino)-phenyl](phenyl)methylidene]- N, N –dimethylcyclohexa-2,5-diene-1-iminium Chloride (C₂₃H₂₅N₂Cl) with molecular weight 364.911g/mol was obtained from S.D fine Chemical, Limited, Mumbai, India. An accurately weighed quantity of 1% w/v dye solution was prepared by dissolving 1g of malachite green dye in distilled water and made up to 100cm³ in a standard volumetric flask (Bello et al., 2002; Bello et al., 2009). All other solutions series of four or five in a dye-bath with 0.1g of cotton fabric inserted in each of them. These are then placed in hot water bath with the open end of each dye-bath covered with aluminum foil paper in order to keep the volume of the dye constant throughout the dyeing period. The dyeing was carried out at varying temperatures (323K, 333K and 343K) with different batch of dye-bath at the same concentration for the minimum of 1 hour for each bath. After dyeing, the cotton fabric was then removed immediately from the dye-bath and the solution was allowed to cool after which the absorbance A_T was taken.

2.6 Measurement of Absorbance

The absorbance of the standard solution of the dyes (1%) were scanned between 400-700nm to determined their λ_{max} using UV-VIS spectrophotometer (Bello et al., 2009, 2014). Distilled water gotten from Aquamat model V4.60 water distillation apparatus was used as blank to calibrate the spectrophotometer to zero absorbance. The absorbance of each sample were taken

2.7 Estimation of Percentage Exhaustion (% E)

Exhaustion was the total amount of dye taken up by cotton fabrics, which was measured by sampling the dye bath at the beginning and the end of the dyeing process. This was done by removing a dye-bath away from the water bath and the cotton fabric also withdrawn from the bath. The dye-bath was cooled and the residual dye solution was filtered after dyeing and optical density measured at maximum wavelength corresponding to maximum, absorbance namely λ_{max}= 619 nm (experimentally obtained). The optical density of the original dye-bath solution before dyeing was also measured. From these two measurements, the percentage dye bath exhaustion of the dyed cotton fabric (i.e. cotton) was calculated using the equation (Kawee and Papapida 1998; Bello et al., 2002; Bello et al., 2009, Bello et al., 2014).

were prepared from the standard solutions of the dyes.

2.4 Preparation of Dye Bath

A 1% w/v dye solution was prepared as stated previously. 0.100 g of bleached cotton fabric was dyed in each case to 1% depth by conventional methods (Bello et al., 2002 Bello et al., 2014). The liquor to cotton fabric ratio was 150:1 for different period of equilibrium exhaustion of the dye (Bello et al., 2002). The recipe for the dye bath of 150:1 liquor to cotton fabric ratio is as given below:

Dye Stock Solution 1% w/v:

Volume of the dye = 0.1 cm³, Mass of cotton fabric = 0.100 g,
Water = 14.8 cm³, Total = 15.0 cm³

2.5. Dyeing

Basically, all types of textiles fibers are dyed using batch method of dyeing. These methods are dictated primarily by the physical properties of the textiles and the types of fiber it contains. Dye bath of the solution was prepared in triplicate and sometimes in ut

$$\% E = \frac{A_o - A_t}{A_o} \times 100 \quad 1$$

Where A_o is absorbance at time zero (i. e. before dyeing), A_t is absorbance at time t, (i. e. after dyeing).

2.8 Determination of Partition Coefficient (K)

Partition Co-efficient (K) is the ratio of the amount of dye absorbed by the cotton fabric to the amount of dye in the dye-bath at equilibrium (Bello et al., 2002; Bello et al., 2009). It is expressed mathematically as;

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

where [D]_f is the concentration of dye in the fiber (g/kg) when equilibrium is attained at dyeing temperature, T. [D]_b is the concentration of dye in the residual bath dye (g/l) when equilibrium is attained at dyeing temperature T.

Partition Co-efficient (K) and percentage exhaustion are related by the equation (Bello et al., 2002, 2009).

$$K = \frac{\text{LiquorRatio}}{Q} \times \% E \quad 3$$

$$\text{LiquorRatio} = \frac{\text{volume of dye bath}}{\text{mass of fiber}} = \frac{15l}{0.1g} = 150l g^{-1} \quad 4$$

$$Q = 100 - \% E \quad 5$$

where Q is the amount of dye left in the solution at the equilibrium exhaustion and % E is the percentage equilibrium exhaustion. In this case, the liquor ratio used is 150:1 liquor to fabric. The above recipe was used throughout this work. For 150:1 liquor ratio, K now becomes (Bello et al., 2002; 2009);

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

2.9 Estimation of Thermodynamic Parameters.

2.9.1. Standard Affinity ($-\Delta\mu^\theta$)

It is the measure of the driving force in any dyeing process. Dyeing of cotton with the malachite green (MG) dye corresponds to the partition mechanism, and hence the standard affinity ($-\Delta\mu^\theta$) of the dyes for cotton fabric was calculated using the following equation (Bello et al., 2002; Bello et al., 2009)

$$-\Delta\mu^\theta = RT \ln \frac{[D_f]}{(V \times [D_s])} = RT \ln K_v \quad 7$$

where R in the universal gas constant in ($\text{kJ K}^{-1} \text{mol}^{-1}$); T, the temperature of dyeing in Kelvin (K); $[D_f]$, the concentration of dye in the fiber ($\text{g}/100\text{g}$ of the cotton fabric); $[D_s]$, the concentration of dye in solution (g/L); v, the colcine term represents the effective volume of water in the substance and K is the Partition co-efficient (L/kg).

2.9.2. Enthalpy Change (ΔH^θ) of Dyeing

The ΔH^θ and ΔS^θ were calculated using the following equation;

$$-\Delta\mu^\theta = \Delta H^\theta - T\Delta S \quad 8$$

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

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

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

where ΔH is Heat of Adsorption (kJ mol^{-1}); $-\Delta\mu^\theta$ is Standard Affinity (kJ mol^{-1}); T, Absolute Temperature (K); and C, Integral Constant.

2.9.3. Entropy of dyeing (ΔS^θ)

This is the rate of disorderliness of the reaction system. ΔS^θ was determined by using the relation below; Dividing equation (3.8) through by $-T$

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

A plot of $\Delta\mu^\theta/T$ against T^{-1} gives a straight line graph where ΔH^θ is the slope of the graph and ΔS^θ is the intercept of the graph.

3.0 Results and Discussion

3.1 Dyeing Without Modification

Table 2 showed the results of % E, K, and $\Delta\mu^\theta$ of cotton dyed with malachite green at different temperature without modification. Fig. 1 revealed the Percentage Equilibrium Exhaustion (% E) of cotton fabric dye without the use of any modifying agent and the equilibrium were reached at different time for different temperature.

For example, dyeing process at 323 K, 333 K, 343 K, 353 K, 363 K and 373 K have the % E are 10.11%, 12.80%, 12.90%, 18.50% 18.60% and 18.60% respectively. was that the penetration of dye molecule onto cotton fabric was small which could be as result of insufficient attacking sites between the unmodified cotton fabric and the Malachite Green dye. The thermodynamic parameters obtained were: partition coefficient (K): 16.87 L kg^{-1} , 19.30 L kg^{-1} , 22.22 L kg^{-1} , 34.05 L kg^{-1} , 34.28 L kg^{-1} and 34.28 L kg^{-1} respectively while standard affinities ($\Delta\mu^\theta$) were 7.6x10³ kJ mol^{-1} , 8.2x10³ kJ mol^{-1} , 8.8x10³ kJ mol^{-1} , 1.06x10⁴ kJ mol^{-1} , 1.07x10⁴ kJ mol^{-1} , 1.09x10⁴ kJ mol^{-1} respectively.

3.2. Effects of Modifying Agents on Cotton Fabric

It was observed during exhaustion dyeing process that the dyeing uptake of cotton fabric without modification was low. However, when the fabric was modified, the dye uptake of modified cotton fabric was observed increased significantly. Tables 3 and Figures 2 show the results obtained at different concentration of modifying agents and % E, K, $\Delta\mu$ values with different modification reagents concentrations. The high values of K may probably due to higher volume of dye bath (150:1) which led to faster rate of migration of dye molecules to the fiber hence high uptake of the dyes molecules by the cotton fabric. It has been reported that the values of K can be used to predict the fastness properties of dyes to the fibers (Bello et al., 2002).

Consequently, the dyeing behaviour of cotton as rendered by the reaction of various modifying agents and result reflect an increase in the mobility of the large dye ions with temperature and thus an increase in the number of molecules interacting with the active sites at the surface. Hence, the application of modification agents on the fibers therefore enhanced a rapid dye uptake by the fiber thereby improved dye exhaustion. It can also be deduced here that CH_3COOH gave the highest % E with respect to 1% v/v. This observation is similar to many other works reported in the literature (Kawee and Papapida, 1998; Bello et al., 2002; Zhang, 2005; Bello et al., 2013, Bello et al., 2014).

Table 1: Dyeing parameters (% E, K and $\Delta\mu^0$) of MG dye onto cotton fabric without modifying agent

Modifying agents	% E			K (L kg ⁻¹)			$\Delta\mu^0$ (kJ mol ⁻¹)		
	323 K	333 K	343 K	323 K	333 K	343 K	323 K	333 K	343 K
Unmodified	10.11	12.80	12.90	16.87	19.30	22.22	0.0076	0.0082	0.0088
CH ₃ COOH	76.47	79.41	88.24	487.48	578.51	1125.51	16620.77	17609.31	20036.03
NaCl	72.86	74.28	80.00	402.69	433.23	600.00	16107.61	16808.23	18242.14
(NH ₄) ₂ SO ₄	85.71	87.14	77.14	899.67	1016.41	506.17	18266.36	19169.61	17757.17
Na ₂ CO ₃ .10H ₂ O	60.00	61.4	65.10	225.00	238.60	279.79	14544.52	15157.30	16066.69
H ₂ O ₂	23.53	27.94	30.88	46.16	58.16	67.01	10290.57	11249.21	11991.12

Keys: % E is Percentage Exhaustion, K (L kg⁻¹) is Partition Coefficient, K and $\Delta\mu^0$ (kJ mol⁻¹) is Standard Affinities.

3.3 Effects of Temperature on Dyeing

It is evidently clear from the results illustrated graphically in Figure 3 that temperature change affects dyeing and the percentage dye exhaustion. For instance, when cotton is modified with 1% v/v CH₃COOH; at 323 K the % E is 76.47% while at 333 K it is 79.41%. The same progression goes for NaCl, (NH₄)₂SO₄, Na₂CO₃.10H₂O and H₂O₂ for temperature at 323 K and 333 K.

Similarly, when the temperature is increased to 343 K the % exhaustion equilibrium of the dyes 88.24%, 80%, 77.14%, 65.10% and 30.88% for CH₃COOH, NaCl, (NH₄)₂SO₄,

Na₂CO₃.10H₂O and H₂O₂. Therefore, CH₃COOH show highest % exhaustion while dye H₂O₂ gave the lowest percentage exhaustion of 30.88% at the highest temperature which therefore corresponds to what is reported in the literatures (Bello *et al.*, 2002; 2009). The modifying agents and dye applied to cotton fiber showed high exhaustion at the highest temperature. This is so, because, there is greater segmental mobility of the fiber polymer chains at higher temperatures and this causes penetration of dye molecules into the cotton fiber.

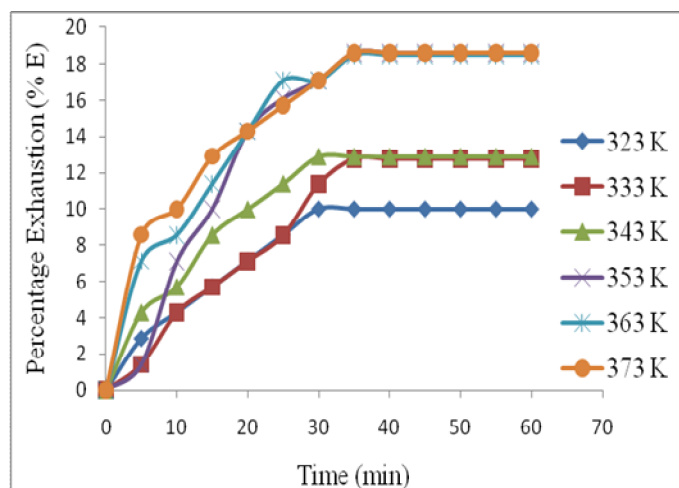


Fig. 1: A Plot of Percentage Equilibrium Exhaustion (% E) Against Time for Dyeing at Different Temperatures (Without Modification).

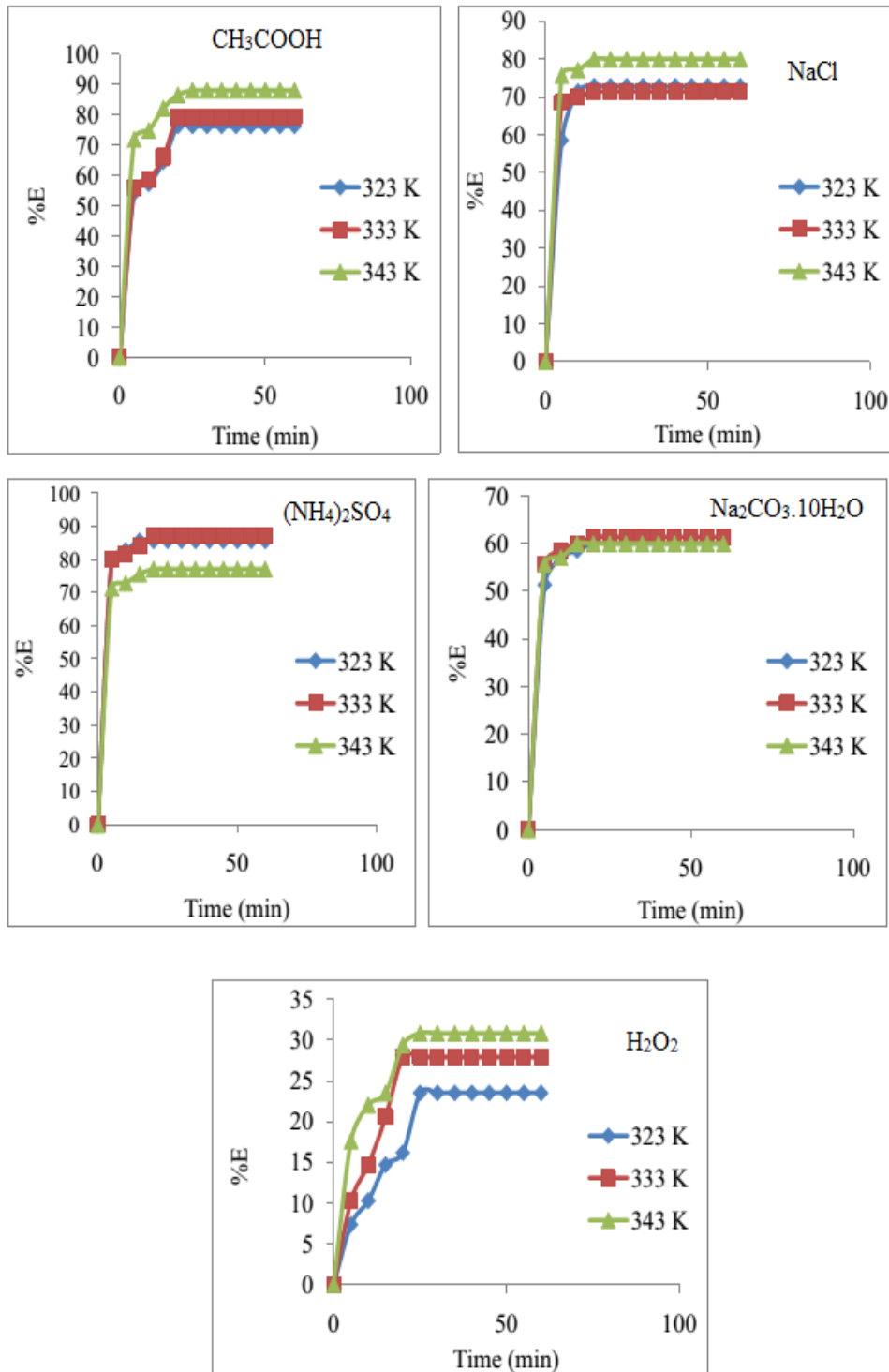


Fig. 2: Effect of different Modifying Agents on Dyed Cotton Fabric at Different Temperature of Dyeing With Modification

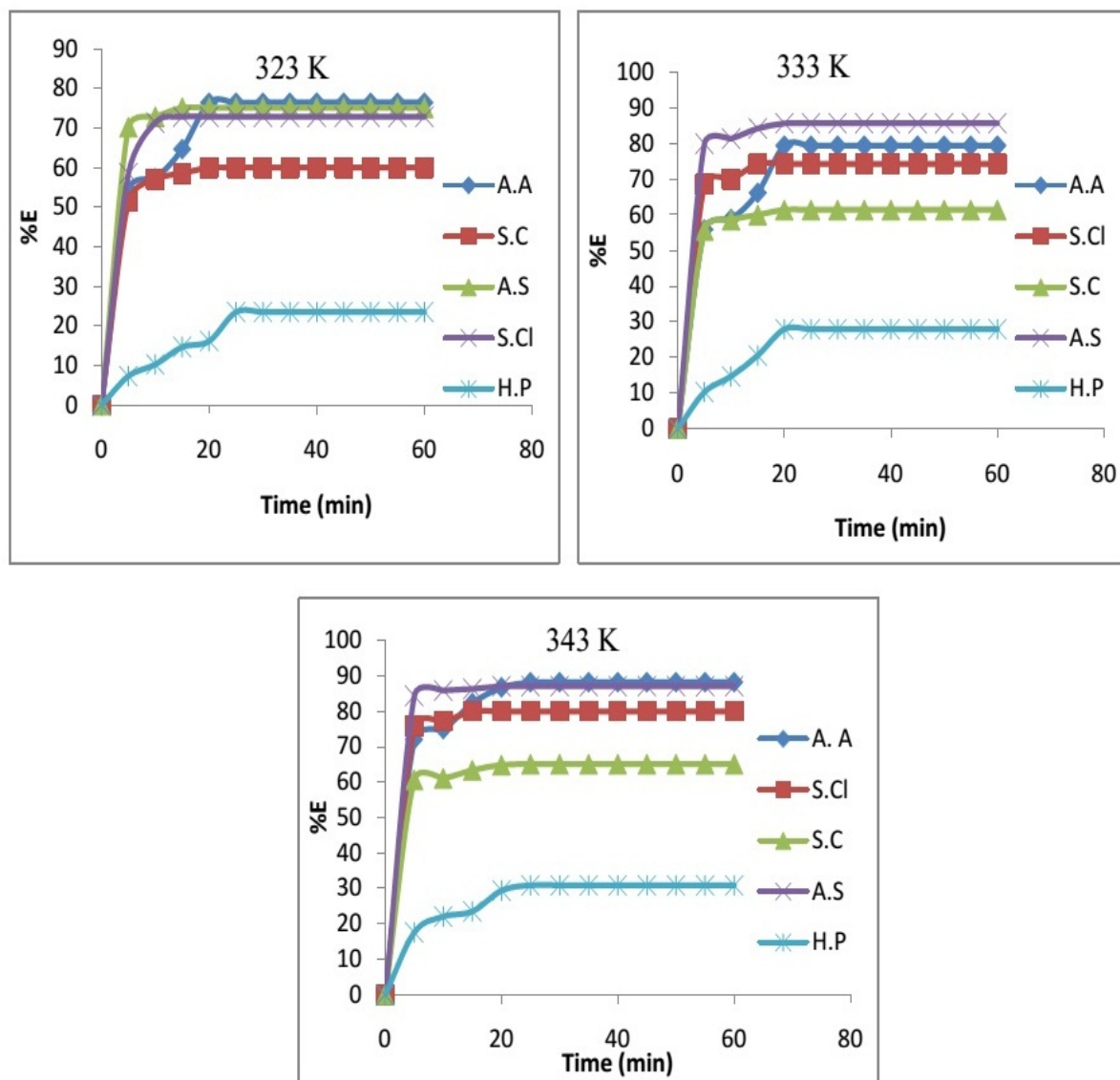


Fig. 3: Effect of time on dyeing exhaustion at 323 K for 1% v/v modification A.A, S.C, S.Cl, A.S, H.P

Key: A.A: Acetic acid, S.Cl: Sodium Chloride, S.C: Sodium Carbonate, A.S: Ammonium Sulphate, H.P: Hydrogen peroxide.

3.4 Effects of Time on Modified Cotton

Figure 3 showed the results of % E of modified cotton dyed with malachite green at different time and temperature. Determining of equilibrium time is one of the most characteristics which represent the exhaustion of MG dye on the modified cotton fabric. The Figures 3 indicates that the longer the dyeing time, the greater the amount of dye molecules absorbed by the fiber, until an equilibrium is attained, more dyes penetrate into the polymer at longer dyeing time resulting in high percentage exhaustion and deeper shade (Bello et al., 2014).

The dye exhaustion increases with increasing time to 15 minutes for three modifying agents ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$) and

equilibrium is attained within the 15 minutes whereas, it increases to 20 min and equilibrium is attained for only two modifying agents (CH_3COOH and NaCl) at 323 K and 25 mins for H_2O_2 before attaining equilibrium. Also at 333K, time increases to 20 mins and equilibrium is attained for both CH_3COOH , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$ and H_2O_2 but equilibrium is attained within 15 mins for NaCl . However, at the highest temperature (343 K), the time increases to 20 mins for only one modifying agent (i.e. $(\text{NH}_4)_2\text{SO}_4$), 25 mins for both CH_3COOH , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and H_2O_2 but 15 mins for NaCl . Longer time has no influence on dye exhaustion. This implies that the dye exhaustion reaches equilibrium for different temperatures.

This observation shows a good agreement with similar work by Burkinshaw and Gotsopoulos, (1999); Bello *et al* (2002); Adebayo *et al.*, (2010) and Bello *et al.*, (2009). As also shown in Figure 2, % E values obtained increases as the time increases and afterwards, the % E remains constant. The dyeing at the highest temperature gives a high % E value. Consequently, increase in time affects dyeing and dye exhaustion thus favours the uptake of dye by the modified fabric until the equilibrium is reached (Bello *et al.*, 2002; Zhang, 2005; Bello *et al.*, 2009; Sundrarajan *et al.*, 2012).

3.5 Effect of Exhaustion

The results of the dyeing exhaustion of the modified and unmodified cotton fabric are given in Table 1. It was observed that modified cotton fabric have improved exhaustion compared to the unmodified samples (Schemes 1 and 2). This may be due to the change in the surface morphological structure under modification condition which thus implies that the barrier effect in cotton dyeing is diminished. This can be explained by the fact that the ionic bonds formed between the dyes and the modified cellulose are much stronger than the hydrogen bonds and Van der Waals forces linking the dyes to unmodified cellulose (Kawee and Papapida 1998; Bello *et al.*, 2009; Bello *et al.*, 2014).

For cotton fabrics treated with CH_3COOH , $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, NaCl , $(\text{NH}_4)_2\text{SO}_4$, and H_2O_2 , it was observed that the percentage equilibrium exhaustion (% E) of cotton fabric dyed with Malachite green has improved dye uptake in acidic solution, for instance the % E at 343K for CH_3COOH is 88.24% followed by $(\text{NH}_4)_2\text{SO}_4$ (77.14%) which have ability to undergo hydrolysis in aqueous solution, thereby promotes breaking of the cellulosic chains, reducing the packing of the fibers and thus improves the dye uptake. This then followed closely by neutral solution (NaCl_{aq}) which is 80.00% and apparently with lower % E under alkaline conditions ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) which has 65.10%. H_2O_2 having the least % E (30.88%), due to redox reaction and absent of carbonyl electron withdrawing group unlike CH_3COOH . However, because the bonding force between the nucleophilic group in the dye molecule and the hydroxyl group in the cotton reinforces the electrostatic attraction between the dye and the cationic sites which therefore gave rise to higher percentage exhaustion (% E). The trend is $\text{CH}_3\text{COOH} > (\text{NH}_4)_2\text{SO}_4 > \text{NaCl} > \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} > \text{H}_2\text{O}_2$. The trend is so because the modifying agents suppressed the negative charge on the fiber surface and

then allowing reactive dye molecules to diffuse inside the fiber. Also since fixation of reactive dyes onto cellulose fibers requires alkaline dyeing conditions in order to activate the hydroxyl group of cellulose to be able to react with the dye, some of the reactive dye can inevitably undergo the competing hydrolysis reaction with hydroxide nucleophiles thereby resulting in an improved dye uptake by the fiber. This similar to the result obtained by Rattanaphani *et al.*, (2007); Bello *et al.*, (2009); Adebayo *et al.*, (2010), Bello *et al.*, (2013) and Bello *et al.*, (2014)

Figure 4 above show the relationship between $\Delta\mu^0/T$ ($\text{kJ mol}^{-1}\text{K}^{-1}$) and $1/T$ (K^{-1}) on enthalpy change for the modification of cotton fabric for some thermodynamic parameter ($-\Delta\mu^0/T$) values obtained from the application of MG dye on cotton fabric modified with different five modifying agents at three different consecutive temperatures (i.e. 323 K, 333 K and 343 K) using the mathematical relation stated in the previous above. The negative values of ΔH^0 imply that the reactions were exothermic (Table 4) and that more dye can be retained in the cotton fabric (i.e. dye molecules were strongly embedded within the fiber molecules.. Similar observations were reported by Bello *et al.*, 2002; Bello *et al.*, 2009 and Adebayo *et al.*, 2010.

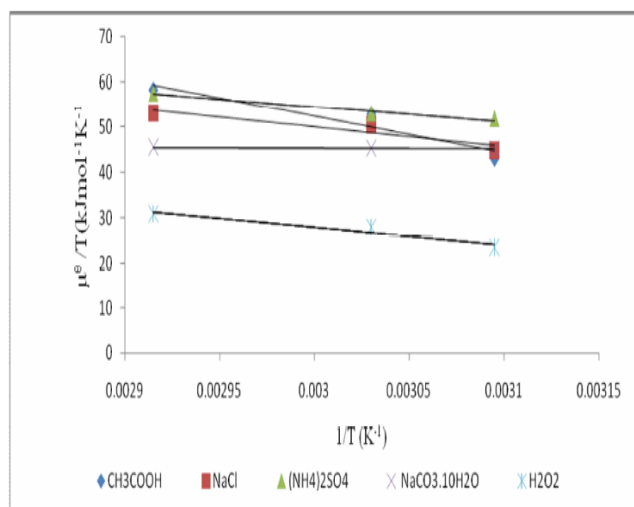
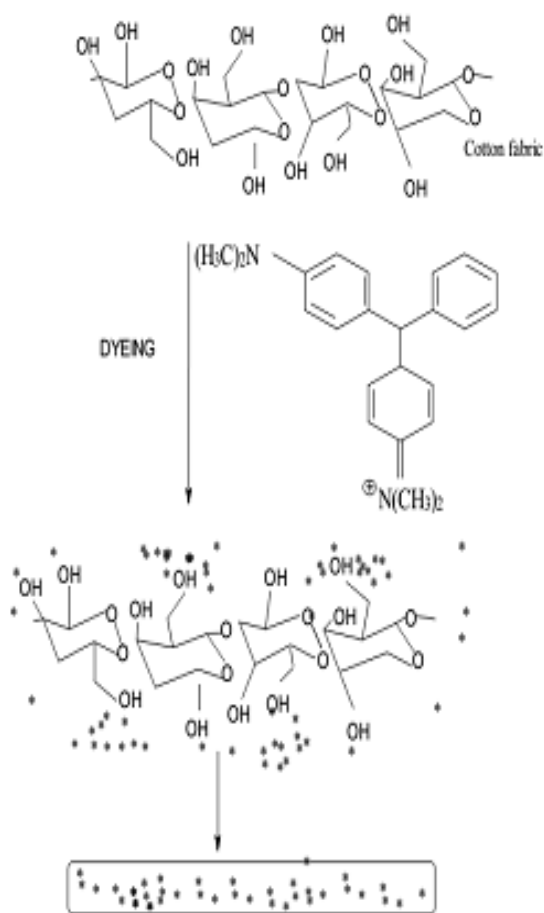
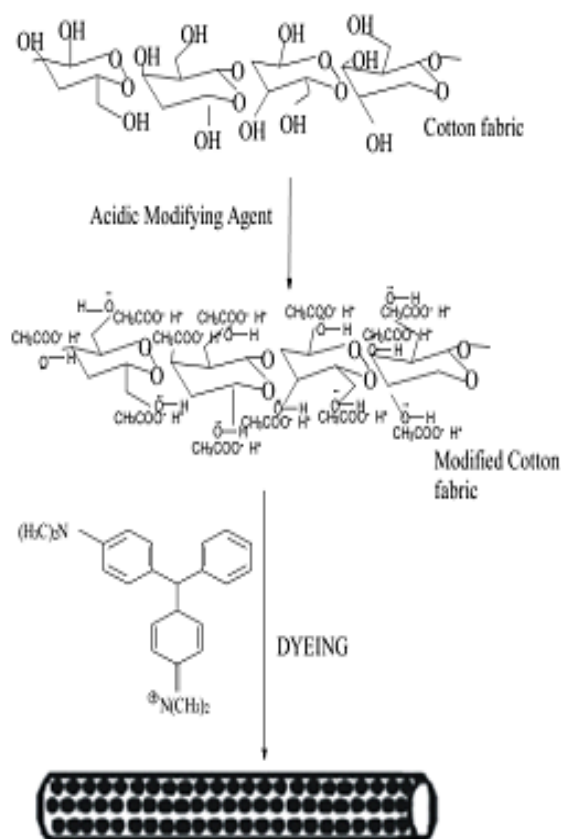


Fig. 4: Relationship between $\Delta\mu^0/T$ ($\text{kJ mol}^{-1}\text{K}^{-1}$) and $1/T$ (K^{-1}) on Enthalpy Change for the Modification of Cotton Fabric for 1% v/v.



Scheme 1: The Dyeing Process of MG on Cotton Fabric



Scheme 2: The Dyeing Process of MG on Modified Cotton Fabric

Table 5: Thermodynamic Parameters (ΔH^0 and ΔS^0) for Modifying Agents (for 1% v/v)

Modifying Agents	ΔH^0 of Dyeing (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)
CH ₃ COOH	-81283	296.36
NaCl	-43550	180.74
(NH ₄) ₂ SO ₄	-330.89	153.82
Na ₂ CO ₃ ·10H ₂ O	-2628.9	53.205
H ₂ O ₂	-39072	145.1

5.0 Conclusion

The dye uptake of cotton fabric improved after modification. The treatment time and modification power have a greater impact on the dye uptake of the fabric. The dye uptake of modified fabric increases with increasing time until equilibrium is established which means that the longer the time the greater the dye uptake of modified cotton fabric and also resulted into greater dyeability of modified fabric than unmodified one. The optimum temperature is 343 K with percentage Exhaustion (%E) of 88.24%, the dye

uptake of modified cotton fabric for the Malachite green dye increased with temperature. This may be a result of increase in the mobility of the large dye ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the cotton fabric enabling large dyes to penetrate further.

Modification of fabric was an essential criterion to improve the dye uptake and also to reduce the effluent load. If eco-friendly modification agents are used, it will protect the environment from pollution. Such modification agents were used in this study to improve the dyeability of cotton fabric using Malachite green (MG) dye and these are linked on the fabric thereby increased the dye uptake. Modification agents such as CH₃COOH, Na₂CO₃·10H₂O, NaCl, (NH₄)₂SO₄ and H₂O₂ will be the cost effective environmental friendly approach in the field of dyeing industry. Modification technique therefore has significant potential for industrial application.

5.0 Conflict Of Interest

All Authors have declared that there are no conflicts of interest.

Authors Contribution

Isah A. Bello and Olugbenga S. Solomon: conception, data analysis and interpretation, correction of the article for important intellectual content and final approval of the published version.

Kayode A. Adegoke: conception, design, data acquisition, data analysis and interpretation, writing and revision of the article.

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