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# Kinetics of Dyeing Cotton Fabric with Some Dye Extracts from Plants

**[1]Gumel S.M., [1]Ibrahim B.M. and *[2]Galadima A.**

*[1]Department of Pure and Industrial Chemistry,*
*Bayero University, P.M.B.3011 Kano, Nigeria.*
*[2]Surface Chemistry and Catalysis Research Group,*
*University of Aberdeen, AB24 3UE, Aberdeen, United Kingdom.*
*[*]Corresponding Author's E-mail: agaladima@abdn.ac.uk, ahmadgldm@yahoo.com*

**Abstract**

Colouring matters extracted from the leaves of Henna and Pods of Roselle (Zobo) were employed to dye a 5 g cotton fabric at 50 and 70 $^0$C. Half time ($t_{1/2}$) of dyeing and the dyeing activation energy ($E_D$) were determined at these temperatures for each extract using spectroscopic and kinetic methods respectively. The $t_{1/2}$ values were found to be 43 and 28(Henna) and 30 and 23 (Roselle) minutes at 50 and 90 $^0$C respectively. Coupling these with the respective $E_D$ values (2.495 and 1.540 kcalmol$^{-1}$), it could be established that, the fabric have higher affinity towards the Roselle extract at both temperatures.

**Keywords:** Natural-dyes, dyeing-time, activation-energy, cotton

## Introduction

Nowadays, synthetic dyes are replacing natural dyes in almost all applications due to their remarkable properties, easy processibility and affordability. However, in the dyeing process, a large amount of chemicals generated from these dyes polluted the effluent. Owing to the increasing awareness of ecological and economical restrictions imposed on the textile industry, the development of dyes that are environmentally friendly will be in great demand in the future. Natural dyes have become a part of human life since time of immemorial (1). The Alchemy of colours started its use from an early time (2). Use of natural dyes in colouration of textile materials and other purpose is just one of the consequences of increased environmental awareness (3). Natural dyes exhibit better biodegradability and generally have a better compatibility with the environment. Also they possess lower toxicity and allergic reactions than synthetic dyes (4). Today, in the world of growing environmental consciousness, natural colourants have attracted the attention of everyone.

Henna (*Lawsonia inermis*) leaves is an ancient dye, evidence being the Egyptian mummies found in the tombs that had their nails dyed with henna. In the present times, it is used in many countries for dyeing hair, eyebrows and fingernails during religion festivals and marriages etc. For use as colouring material, henna powder is pasted with water and applied to the part to be dyed. For dyeing hair, it is applied as a pack; it acts as a substantive dye for keratin and imparts an orange red colour. It is harmless and causes no irritation of skin (5). Roselle (*Hibiscus Sabdariffa*) is specie of plant belonging to the family malvaceae which is composed of about 150 or more species of Herbs, shrubs and trees. The pod, 1-2inches long and 0.75inch broad, red to black red in colour is the part of the plant from which colourant can be extracted. The plant is popular among the Hausas in northern Nigeria and beyond, chiefly for its medicinal uses, especially in the treatment of hypertension and as local soft drink.

Dyeing processes are considered to be the processes of coloring textile fibres with either natural or synthetic dyes. In most cases the material to be dyed is brought into contact with a transfer medium containing the dye. The most common medium is water in which the dye may be dissolved or dispersed; during dyeing the dye molecules pass from this medium into the fibre.

The whole dyeing process can be divided into three stages (6,7)

a. The transfer of dye from the bulk of solution to the fibre surface;
b. The sorption of dye at the fibre surface;
c. The diffusion of dye in to the fibre.

Any one of these processes may control or influence the rate of dyeing; the laboratory conditions are usually adjusted so that stage (c) becomes the rate-determining step (7). The diffusion of dye in a fibre is governed by Fick's law

$$ds/dt = -Ddc/dx \quad (1)$$

where ds/dt is the mass of dye diffusing across a unit area during the time dt (the diffusion flux), c is the concentration of dye at a point x from the surface, and D is the diffusion coefficient which is usually considered to be only temperature dependent. This dependence is written as an Arrhenius-type equation, i.e.

$$D = D_0 exp^{-E/RT} \quad (2)$$

where $D_O$ is a constant, $R$ = 1.987 cal $mol^{-1}$ $K^{-1}$ is the gas constant, $T$ is the temperature (K), and $E$ is the activation energy of the diffusion (cal $mol^{-1}$). The whole dyeing process can be schematically written as follows

$$Dye + Fibre \rightarrow Dyed\ fibre \quad (3)$$

Equation (3) describes a quasi-chemical reaction and, therefore, its kinetics can be analysed by chemical kinetic methods. The study of the kinetics of reaction (3) should take into account that the reaction is heterogeneous and, thus, it is described by the kinetics of heterogeneous processes.

The time taken for a fibre to absorb 50% of the dye it will absorb at equilibrium is referred to as time of half dyeing. It provides an indirect measure of rate of diffusion and is useful for comparing dyeing behavior of dyes under identical conditions (8). The Activation energy of dyeing is the total energy that is consumed for a particular dyeing process and is usually obtained from rate of dyeing measurement.

The aim of this study is to determine the $t_{1/2}$ and $E_D$ values of dyeing a cotton fabric with extracts from Henna leaves (*Lawsonia inermis*) and the pods of Roselle (Zobo, *hibiscus sabdariffa*). These parameters could provide explanatory information on the effects of dyeing chemistry and the affinity of the fabric towards the extracts.

## Experimental

### Materials and Reagents

Sun dried Pods of Roselle and Henna Leaves were purchased from Rimi market in Kano, Nigeria. They were freed from dirt particles, grounded in to powder and stored in labelled sample bottles under laboratory conditions for 2 days prior to dye extraction. All the Glass wares used were pyrex type and were thoroughly washed with detergents, rinsed with distilled water and dried in oven at 110 $^0$C before used. Spectroscopic studies were carried out with the aid of Aquarius Cecil CE7400 UV-Visible Spectrophotometer.

### Extraction of the colouring matter

The extraction was carried out in bulk by percolating 100 g each of the powdered sample in 1000 $cm^3$ distilled water for seven days with occasional stirring. The mixtures were then filtered and the filterate was concentrated using rotary evaporator. The extracts were further dried in an open beaker until all the water was evaporated.

### Dyeing

Two separate 1% solution of the Henna extract were prepared each in a 500cm3 beaker using distilled water. In to each of the beakers was introduced a 5g pre-treated cotton fabric and dyed at 50$^o$C and 90$^o$C, respectively, and both were dyed for one hour. The same procedure was repeated for Roselle extract (9).

### Determination of Time of half Dyeing ($t_{1/2}$) and Activation energy of dyeing ($E_D$)

A dye solution was used for dyeing cotton fibre at 50 and 90$^o$C. From each dye bath above, 5$cm^3$ of the dye solution was collected after 0, 5, 10, 30 and 60minutes from the start of the dyeing and absorbance were taken. The concentration of the dye solutions were estimated spectrophotometrically from their absorption spectra (9,10).

For each dyeing temperature, a plot of percentage exhaustion against time of dyeing was made, and $t_{1/2}$ values were extrapolated from the graphs.

The activation energy of dyeing "$E_D$" was calculated from the equation

$$E_D = 2.3R\,(\log t'_{1/2} - \log t''_{1/2}) \,/\, {}^{1}/T_1 - 1/T_2$$

Where $t'_{1/2}$ and $t''_{1/2}$ are the times of half dyeing at absolute temperatures $T_1$ and $T_2$ respectively

The same procedure was repeated for Hibiscus Sabdariffa extract (9,10).

## Results and Discussion

### Preliminary Analysis of the Extracts

The dried and purified colouring matter extracted from Henna and Roselle were analysed for their percentage yield, colour, solubility and $\lambda_{max.}$ The results obtained are shown in Table 1 below.

**Table1:** Analysis of the Extracts.

| Extract | % Yield | Colour | Solubility in water | $\lambda_{max}$ (nm) |
|---|---|---|---|---|
| Henna | 29.3 | Dark brown | Soluble | 421.5 |
| Roselle | 37.8 | Red | Soluble | 460.5 |

Both plants produced extracts with appreciable solubility in water, with Roselle producing higher yield of extract that absorbed radiation at a longer wavelength. The two extracts dyed cotton fabric brown and red colour for Henna and Zobo respectively. The dye uptake increases with increasing dyeing time and temperature. The dye is firstly adsorbed on the surface of the fibre. Equilibrium is then established between adsorbed and diffused dye inside the pores. The affinity of the dye to the fibre increases with increasing temperature (Table 2).

## Estimation of Percent Exhaustion

The percent Exhaustion was estimated from the relation:

$$Ao - A/_{Ao} * 100$$

Where Ao = initial concentration of the dye bath
A = Concentration after time T

The percent exhaustions were found to increase with time and temperature (Table 2). This may be explained in terms of free volume theory. The rate of dyeing depends on the existence of sufficient number of holes between the fibre which are large enough to accommodate dye molecules and that a direct relationship exist between the available number of holes and the dyeing temperature (11, 12, 13). The values for the percent exhaustions were generally excellent which implies high affinity of the dye extracts to cotton fabric.

**Table2:** Extent of Exhaustion for each dye at different temperatures.

| Dyeing time (minutes) | Dyeing temperature ($^oC$) | Absorbance | | % Exhaustion | |
|---|---|---|---|---|---|
| | | Henna Dye | Roselle Dye | Henna Dye | Roselle Dye |
| 0 | 50 | 2.448 | 1.450 | 0.00 | 0.00 |
| | 90 | 2.448 | 1.450 | 0.00 | 0.00 |
| 5 | 50 | 2.210 | 1.100 | 12.05 | 18.70 |
| | 90 | 2.130 | 1.00 | 16.86 | 28.16 |
| 10 | 50 | 1.982 | 0.813 | 22.89 | 35.48 |
| | 90 | 1.815 | 0.718 | 25.50 | 35.48 |
| 30 | 50 | 1.362 | 0.581 | 40.96 | 49.67 |
| | 90 | 1.150 | 0.483 | 51.80 | 60.00 |
| 60 | 50 | 0.782 | 0.313 | 63.85 | 63.10 |
| | 90 | 0.536 | 0.108 | 70.08 | 76.77 |
| 90 | 50 | 0.777 | 0.260 | 63.85 | 67.00 |
| | 90 | 0.530 | 0.103 | 70.08 | 77.10 |

## Time of Half Dyeing

The time of half dyeing was obtained by extrapolation to 50% exhaustion. The values are presented on the Table 3 given below:

**Table 3:** $t_{1/2}$ values estimated in minutes.

| Dyeing System | $t_{1/2}$ (minutes) |
|---|---|
| Henna (50$^oC$) | 43 |
| Henna (90$^oC$) | 28 |
| Roselle (50$^oC$) | 30 |
| Roselle (90$^oC$) | 23 |

Determination of $t_{1/2}$ provides an indirect measure of the diffusion rate of dyes into the substrates. It seems to be a useful element for comparing the behavior of different dyes applied under identical conditions. Generally, Henna dyes are found to require more time to dye cotton fibre than Roselle dye. This could be as a result of the fact that Roselle dyes are more soluble in water and may possess groups that are more attractive to the cotton. This is seen from the percent exhaustion of the dyeing systems. It could also be observed that $t_{1/2}$ became smaller with increasing temperature. This is as anticipated since the rate of dyeing depends on the existence of sufficient number of holes between the fibre which are large enough to accommodate dye molecules and that a direct relationship exist between the available number of holes and the dyeing temperature as earlier on explained (11, 12, 13).

**Estimation of Activation Energy of Dyeing**

The activation energy of dyeing for the two extracts were determined from the relation

$$E_D = 2.3R \{\log t'_{1/2}(50^oC) - \log t''_{1/2}(90^oC)\} / {}^{1}/50^oC - 1/90^oC$$

The $E_D$ values are presented on Table 4 shown below.

**Table4:** $E_D$ values for the dye extracts.

| Dye Type | Activation Energy of Dyeing (Kcalmol$^{-1}$) |
|---|---|
| Henna Dye | 2.495 |
| Roselle Dye | 1.540 |

The Activation energy of dyeing cotton with Henna dye is higher than the energy required to dye same fibre with zobo dye. This could be as a result of the fact that dye from zobo possess groups that are more attractive to cotton fibre than dye from Henna, thus; making it more easier for the cotton to absorb zobo dye than Henna dye and therefore, more energy will be required in dyeing with Henna than Zobo.

## Conclusion

The colouring matters extracted from Henna and Roselle were found to dye cotton fabric. It was found that, the energy required to dye cotton fibre with Henna dye is greater than the energy required for dyeing with Roselle dye. In both cases the rate of dyeing increases with increase in temperature. This gives kinetics evidence on the higher affinity of the fabric towards the Roselle extract.

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