Inhibitive Effect of NaCl and Citric Acid on the Colour Yield of Acid Dye on Nylon Fabric

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Abstract
Nylon 6 fabric was dyed with C.I. Acid Yellow 23 at a temperature 50˚C using sodium chloride (NaCl) and citric acid as auxiliaries. The adsorption kinetic mechanism was studied using two models. Results of the UV-Vis spectroscopy indicated that colour yield of C.I. Acid Yellow 23 reduced when more than 1% (acid) and 5% (salt) concentration were used respectively for dyeing. NaCl however had the most inhibitive effect on the dye colour yield. The adsorption kinetics mechanism result fitted the pseudo-second-order-kinetic model with R² of 0.993.

Keywords
Nylon 6, Acid Dye, Sodium Chloride, Citric Acid, Exhaustion, Colour Yield, Adsorption Kinetic

1. Introduction
Dyeing involves the uniform covering of a whole material with one colour with some degree of fastness achieved. A dye must have affinity for a fibre before it can colour the fibre with the required colour yield. Colour yield is the depth of colour obtained when a standard weight of colourant is applied to a substrate within specified conditions [1]. The colour yield of any particular dye depends on the exhaustion of the dye during dyeing. Exhaustion is the rate of transferring the dye from solution to the fibre and where dye-fibre affinity does not exist (or is minimal) the dye will not colour the fibre adequately and the required dye colour yield will not be achieved. Several factors that can affect dye exhaustion and hence colour yield of any particular dye includes but not limited to temperature of the dye solution, dyeing period, dye bath assistants, pH of dye bath, type of material being dyed, dyeing process and the geometry of both fiber and dye mo-
molecule. Colour yield of a dye also depend on the dye’s diffusion rate, which is the process in which dye adsorbed on the surface of the textile fibre passes into the interior of the fibre. Other factors include the attractive power of the dye to the fibre (substantivity) and levelness quality of the dye [2].

Dye adsorption, fixation, substantivity and diffusion can be greatly affected by the structure and chemical composition of both dye and fiber. Hence the use of particular dyes for particular fibres to achieve the good dyeing results. Attachment of a dye molecule to fibre is one of absorption, adsorption or chemical reaction either of which can be achieved via ionic forces, hydrogen bonding, Van der Waals forces or covalent chemical linkages [3].

Application of acid dyes on nylon fabric is done within strongly acidic to neutral pH conditions (3 - 7.5). Acidification of the dye bath is done to increase the level of cationisation of the fibre in order to improve its dye uptake. Under such condition, dyes with high molecular weight and high affinity would adsorb too rapidly on the fibre hence a levelling agent will be required. Acetic acid or a buffer system containing formic acid and ammonium sulphate is usually used for such acidification. However at high concentrations acetic acid is toxic hence citric acid a weak organic acid has been considered its replacement [4]. This paper highlights the effect of two dye assistants used in the exhaust dyeing of nylon fabric with an acid dye.

The unique chemistry of nylon makes it possible to easily dye nylon using same acid dyes commonly used on wool and other animal fibres [5]. The dyeing efficiency of nylon fibre is enhanced due to the end groups -COOH (carboxylic) and -NH2 (amide) which exhibit polar and hydrophilic characteristics [6].

2. Materials and Methods

2.1. Materials

The following materials were used for the research work; Nylon 6 fabric, C.I Acid Yellow 23, Citric acid (C6H8O7), Sodium Chloride (NaCl), and Water. All the chemicals used were of analytical grade and bought from Pac Besh Scientific Co (Nig.) located in Owerri, Imo State. All tests were carried out at the laboratory of the Department of Polymer and Textile Engineering, Federal University of Technology, Owerri (FUTO).

2.2. Methods

2.2.1. Preparation of Dye Stock Solution

Stock dye concentration of 0.4% was prepared by dissolving 1 g in 250 ml of warm distilled water in a 500 ml beaker. The exhaust dyeing method was used to dye the nylon 6 fabric.

2.2.2. Preparation of Dye Bath

The dye bath solution is a mixture dye solution and auxiliaries (Figure 1). Different w/w% concentration of the two auxiliaries (citric acid and sodium chloride)
used were prepared and stored as stock solution. After preparation of the stock solutions, the required quantities of dye solution or auxiliaries to be used for dyeing were calculated using Equation (1) [7]:

\[
\text{Stock solution required (ml)} = \frac{W \times P}{C}
\]  \hspace{1cm} (1)

where \(W\) is Weight (g) of sample to be dyed, \(P\) is the Percentage of dye or auxiliary to be used and \(C\) is the Concentration (%) of dye or auxiliary stock solution.

Nylon 6 fabric (1 g) will be dyed to a 2% depth using 4% citric acid (owf), 20% sodium chloride (owf) and liquor ratio of 100:1.

2.2.3. Dyeing with Different Salt Concentration
The already calculated volume of the respective auxiliaries and dye stock for 5% salt concentration was pipetted into 1000 ml beaker. The dye bath was then made up to 100 ml (Figure 1). 1 g of Nylon 6 fabric was dyed for 10 mins at 50˚C with the dye bath stirred at intervals of 3 min using a glass stirrer. The fabric was removed after 10 mins, from the dye bath and dried.

This procedure was also used for dyeing with 10%, 15%, 20%, 25% and 30% salt concentrations. Temperature, time and acid concentration remained constant at 50˚C, 10 min and 1% respectively.

2.2.4. Dyeing with Different Acid Concentration
The same procedure for the variation of salt test was followed using the already calculated volume of acid at the different acid concentrations. Salt concentration was however kept constant at 5%. Temperature and time was also constant at 50˚C and 10 mins respectively. The pH of dye bath during dyeing was maintained at 5.

2.2.5. Absorbance Measurement
The measurement of absorbance was done using a spectrophotometer. The absorbance of the dye bath solution before and after dyeing was measured with a spectrophotometer using a wavelength of maximum absorbance of 570 nm. The
results were also used to calculate the percent dye uptake (or dye bath exhaustion) at each concentration of the variables tested using the equation

\[
\text{% dye uptake} = \frac{\text{absorbance before dyeing} - \text{absorbance after dyeing}}{\text{Absorbance before dyeing}} \times 100 \quad (2)
\]

2.2.6. Kinetics of Adsorption Studies
The absorption kinetics was studied by varying time of dyeing with interval of 5 min until absorption equilibrium was achieved. Temperature, Acid and salt concentrations were kept constant at 50˚C, 1% and 5% respectively. The adsorption process mechanism was studied using the pseudo-first order and the pseudo-second order kinetic models.

3. Results and Discussion
The spectrophotometer absorbance value of dye effluent solution shows the direct proportion of dye particles left in the dye bath after dyeing. Absorbance values are also used to calculate the % dye uptake by the fibre.

1) Effect of Salt
From Table 1 the absence of salt or increase in salt concentration beyond 5% in the dye bath greatly affected the acid dye exhaustion as shown by their high absorbance readings. Percent dye uptake decreased as the salt concentration increased beyond 5%. Effect of salt can also be seen in Figure 2. At 0% salt concentration, the absorbance value was high; an indication that much of the dye molecules were not exhausted and therefore remained in the dye bath after the dyeing time. According to Beer-Lamberts law, absorbance is directly proportional to concentration at all wavelengths, hence high absorbance value is an indication of high concentration of dye molecules in the dye bath.

Acid dyes dissociate into a coloured anion [sulphonate group (SO$_3^-$)] and metal cation (Na$^+$) in an aqueous solution as illustrated in Equation (3) [8].

\[
\text{acids dye} + \text{water} \rightarrow \text{coloured anion} + \text{metal cation}
\]

\[
\text{X–SO}_3^-\text{Na} \rightarrow \text{X–SO}_3^- + \text{Na}^+
\]

Table 1. Percent Dye uptake after dyeing at varied concentration of auxiliaries.

<table>
<thead>
<tr>
<th>(w/w%) Salt concentration</th>
<th>Absorbance after dyeing at varied salt conc. and 1% acid conc.</th>
<th>% dye uptake at varied salt conc. and 1% acid conc.</th>
<th>(w/w%) Acid concentration</th>
<th>Absorbance after dyeing at varied acid conc. and 5% salt conc.</th>
<th>% dye uptake at varied acid conc. and 5% salt conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.738</td>
<td>15</td>
<td></td>
<td>0.687</td>
<td>20.1</td>
</tr>
<tr>
<td>5</td>
<td>0.476</td>
<td>41.2</td>
<td>1</td>
<td>0.476</td>
<td>41.2</td>
</tr>
<tr>
<td>10</td>
<td>0.613</td>
<td>27.5</td>
<td>2</td>
<td>0.562</td>
<td>32.8</td>
</tr>
<tr>
<td>15</td>
<td>0.681</td>
<td>20.7</td>
<td>3</td>
<td>0.649</td>
<td>23.9</td>
</tr>
<tr>
<td>20</td>
<td>0.706</td>
<td>18.2</td>
<td>4</td>
<td>0.637</td>
<td>25.1</td>
</tr>
<tr>
<td>25</td>
<td>0.733</td>
<td>15.5</td>
<td>5</td>
<td>0.673</td>
<td>21.5</td>
</tr>
<tr>
<td>30</td>
<td>0.769</td>
<td>11.9</td>
<td>6</td>
<td>0.674</td>
<td>21.4</td>
</tr>
</tbody>
</table>

Absorbance value before dyeing is 0.888.
Figure 2. Effect of salt concentration on the Absorbance of Acid dye on nylon fabric.

where X dye chromophore.

The coloured dye anion colours the fabric by reacting with the cationic nylon fibre shown in Equation (4) [9];

\[
\text{X}^- + \text{SO}_3^- \text{H}_3\text{N}^+ \text{H}^- \text{N}^+ \text{H}^+ \text{CO}^- \text{R} \text{COOH} \rightarrow \text{O}_3\text{S}^- \text{X}
\]  

(4)

Salt serves as an electrolyte, moving dye molecules quickly toward the textile material during the dyeing process [10]. Such action leads to exhaustion of dye molecules. An electrolyte also fixes dye stuff to the textile material especially cellulose [11]. Its absence therefore means that the coloured acid dye anions was not able to transport quickly to interact with the nylon fibre within the dyeing interval.

Similarly, sodium chloride an electrolyte releases Na' and Cl' as free ions in an aqueous medium. Increase in salt concentration above what is required increases the concentration of both the chloride anion and the sodium cation in the dye bath. This leads to some possible reactions; (1) interaction of excess chloride anion (Cl') with cationic sites on the nylon fibre, neutralizing them and consequently reducing dye substantivity (2) neutralization of the coloured dye anions by the excess electrolyte cations affecting the dye substantivity and inhibiting there interaction with the nylon fibre cations. The increase in absorbance values and reduction in percent dye uptake are indications that more dye molecules were left in the dye bath after dyeing. Hence at 30% salt concentration the dye uptake was lower and absorbance values higher than at 0% salt concentration. Increase in salt concentration therefore inhibits dye exhaustion and consequently colour yield on a nylon 6 fabric.

2) Effect of Acid

As shown in Table 1 and Figure 3 the effect of citric acid on acid dye colour yield on nylon fabric is similar to that of salt. The interaction of acid dye with nylon fibre is majorly ionic. Hydrogen bond and/or Van dar-waals forces also come into play in certain cases [12]. Nylon a polyamide gives out cationic sites such as -H,N' (ammonium ions) in an acidic medium. This is due to the presence of amide -NH groups on its chain as presented in Equation (5) [10];
Cationic nylon fibre

The earlier submission that nylon gives out cationic sites in acidic medium implies that in the absence of citric acid in the dye bath nylon fibre there will be inadequate or no cationic sites on the nylon fabric to interact with acid dye anions in the dye bath to yield the required colour depth. Several acid dye molecules will therefore be left in the dye bath after dyeing, leading to the high absorbance value recorded in Table 1 at 0% acid concentration. There is also a gradual increase in the absorbance values between 2% to 6% acid concentration.

It should be noted that Citric acid has three carboxylic (-COOH) groups which releases cationic hydrogen in an aqueous medium as shown in Equation (6) [13]:

\[
\text{Citric acid} \rightarrow \text{Citrate group} + 3\text{H}^+ 
\]

It can also be deduced from Equation (6) and Figure 4 that increase in the citric acid concentration beyond what is required of and in proportion to other auxiliaries will yield excess cationic hydrogen (-H⁺) which is capable to neutralize some of the coloured anion of the dye thereby reducing the attractive power of the dye to the fibre. This in turn leaves more dye molecules in the dye bath after dyeing. Increase in the concentration of citric acid therefore diminished acid dye colour yield on nylon fabric because it affected dye substantivity. The mechanism of nylon fabric dyeing with acid dye in an acidic medium is illustrated in Figure 4 [14].

3) Kinetics of Adsorption

The quantity of dye adsorbed by the fabric within the different time of dyeing \( q_t \) (mg/g) and at equilibrium \( q_e \) (mg/g) was calculated with Equations (7) and (8) [15]

\[
q_t = \frac{C_i - C_{eq} v}{w} \quad (7)
\]

\[
q_e = \frac{C_i - C_{eq} v}{w} \quad (8)
\]
where \( C_i \) (mg/ml) is the initial dye concentration, \( C_t \) (mg/ml) and \( C_e \) (mg/ml) are the dye concentrations at different time of dyeing and at equilibrium, \( w \) is the fabric weight in grams and \( v \) is the volume of the dye bath (ml). From Figure 5 we observe that equilibrium was reached after 30 minutes of dyeing with the highest dye uptake occurring within the first 5 minutes of dyeing. This shows that there is a high affinity between fiber and dye.

1) Pseudo-first-order-kinetic model

The fitting of the pseudo first-order-kinetic model was done using Langergren’s equation [16]

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

\( q_t \) (mg/g) and \( q_e \) (mg/g) are quantity of dye adsorbed at different time \( t \) (min) of dyeing and at equilibrium, \( k_1 \) is the rate constant of the pseudo first order kinetic model. Using Equation (9) a graph of \( \ln(q_e - q_t) \) versus \( t \) was plotted as shown in Figure 6 and was used to calculate \( R^2 \) the correlation coefficient. The \( R^2 \) value is 0.897 while the \( q_e \) and \( k_1 \) representing the intercept and slope are 25.8 mg/g and 1.173 respectively.

2) Pseudo-second-order-kinetic model

The pseudo second order kinetic model studied with the following equation [16]:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
\]

A graph of \( t/q_t \) versus \( t \) was plotted as shown in Figure 7, the slope and intercept were used to calculate \( k_2 \) (0.004) and \( q_e \) (500 mg/g). The calculated \( R^2 \) value is 0.993 which is higher and closer to 1 than that of the pseudo-first-order-kinetic model. This clearly shows that the adsorption mechanism of acid yellow 23 dye fits the pseudo-second-order-kinetic model more and hence can be described with it. This agrees with a similar work by Tayebi 1, H. et al. (2015) on dyeing of nylon 6 fabrics with acid dye [15]. Although the experimental \( q_{e,(exp)} \) for both models does not fit very well with the calculated \( q_e \) (2302 mg/g), the \( q_{e,(exp)} \) for the pseudo-second-order-kinetic model is much closer to the calculated \( q_{e,(cal)} \).

4. Conclusion

The effect of sodium chloride and citric acid on the colour yield of acid dye on nylon fabric depends on the concentration of both during dyeing. NaCl and Citric acid dye auxiliaries gave an inhibitive effect during dyeing of nylon 6 when

![Figure 4. Mechanism of nylon dyeing.](image-url)
Figure 5. Effect of time on adsorption of acid yellow 23 dye on nylon fabric.

Figure 6. Pseudo First Order kinetics for adsorption of acid yellow 23 dye on nylon 6 fabric.

Figure 7. Pseudo Second Order kinetics for adsorption of acid yellow 23 dye on nylon 6 fabric.

concentration more than 5% for NaCl and 1% for citric acid is used. For a two percent (2%) colour depth dyeing of nylon 6 fabric at 50°C dyeing temperature, 5% sodium chloride solution and 1% citric acid gave the best colour yield at 41% dye exhaustion. It possible to increase the % dye exhaustion beyond 41% by using salt concentration below 5% while keeping the acid concentration constant at 1%. High sodium chloride concentration ≥ 30% had more inhibitive effect on dye exhaustion than absence of Sodium Chloride. Citric acid also had same effect on nylon during dyeing but not as much as salt. Anything that affects dye
substantivity, absorption and/or exhaustion will definitely affect colour yield of such a dye. The adsorption mechanism of acid yellow 23 dye was studied using 5% sodium chloride and 1% acid concentration at 50°C dyeing temperature. The adsorption mechanism process fitted the pseudo-second-order-kinetic model.

**Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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[1] Percentage or Depth of Shade Dyeing Using Procion MX or Acid Dye (n.d.).


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