ASSESSMENT OF DYEING AND SOME FASTNESS PROPERTIES OF NANOCRYSTALLINE CELLULOSE EXTRACTED FROM CORN COB

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ABSTRACT

The dyeing of nanocrystalline (NCC) cellulose powder extracted from corn cob (Saleh, 2015) was carried out using Reactive (Procion Violet H-3R), Disperse (Foron YellowS.E 2GL) and Direct (Solophenyl Yellow) dyes. The percentage exhaustion in each case was calculated to determine which of the dyes exhausted best. The fastness of the dyed NCC powder to washing, chlorination and light were also investigated to determine which of the dyes has the best fastness properties and which of the dyes is suitable for application in a particular area. Based on the exhaustion and fastness results, the disperse dye with overall excellent properties was chosen as the best dye for nanocrystalline cellulose dyeing. Fabrics were dyed alongside to serve as a control.

Keywords: *Nanocrystalline cellulose powder, dyeing, exhaustion, optical density, stripping,ISO, washing,active chlorine, blue cards, grey scale*

INTRODUCTION

Nanocrystalline cellulose (NCC) is a kind of renewable natural resource. It is typically rod-shaped monocrystalline cellulose with tens to hundreds of nanometres in length and 1 – 100 nm in diameter (Ruiz *et al.*, 2000).

Nanocrystalline cellulose (NCC) is an emerging renewable nano material that holds promise in many different applications, such as foods, pharmaceuticals, personal care etc. Its properties and many potential forms allow many uses which in addition to the afore mentioned are: iridescent magnetic films, improved construction products, biocomposite for bone replacement, paint additives, reinforced composites, recyclable interior and structural components for the transportation industry (Coffey *et al.*, 1995;De Souza and Borsali, 2004).

Nanocrystalline cellulose is a refined form of cellulose, it can be extracted from virtually all cellulose-based materials. The extraction principle is that of finding a way of dissolving the amorphous regions in cellulose, leaving behind the pure crystalline material. A number of processes were reported to be successful in achieving this including: acid hydrolysis, enzymolysis and chlorine oxidation degradation.

NCC has received a lot of recognition in recent years owing to its promising properties which include: high strength, very good optical properties and biodegradability. These properties give NCC its widespread application in areas such as: biocomposites, advanced building materials, iridescent or magnetic films, nanostructured foams, switchable optical films, cosmetics etc. Therefore, the successful application of colour to NCC (originally white) will go a long way in improving its aesthetic properties and applications.

MATERIALS AND METHODS

Materials

All chemicals and reagents used in this work were of analytical grade. The dyes used are commercial dyes and obtained from the Department of Textile Science and Technology, Ahmadu Bello University, Zaria, Nigeria. Fabrics were dyed alongside the powder to serve as control. The stock solution used for each of the dye was 1%, depth of shade 3%, and the material to liquor ratio 1:20. The calculation of the dye bath volume was carried using:

$$\frac{weight\ of\ NCC\ powder \times percentage\ shade}{concentration\ of\ stock\ solution} \text{ ---- (1)}$$

Dyeing with Direct dye

The dye was added in a well-dissolved condition to the dye bath containing a wetting agent. Common salt (20% owf) was then added. The NCC powder was then added into the dye bath at a temperature of 40 – 50ºC. The temperature of the bath was raised to the boil over a period of 30 minutes and dyeing was continued at this temperature for 60 minutes. Thereafter, the powder was then filtered, rinsed with distilled water and dried. The direct dye used was Solophenyl Yellow PFL which is a bright yellow dye with the chemical structure (Nkeonye, 1987);

Dyeing with Reactive dye

The NCC powder was introduced into a neutral dye bath at 20 - 40ºC, equilibrated over a period of 20 minutes, common salt was then added and dyeing was continued for 30 minutes at a temperature of 60ºC. 2% caustic soda (NaOH) was added at this juncture to effect fixation and dyeing was continued for another 20 minutes after which the NCC was filtered, rinsed and dried (Nkeonye, 1987). The reactive dye used was Procion Violet H-3R with the chemical structure:

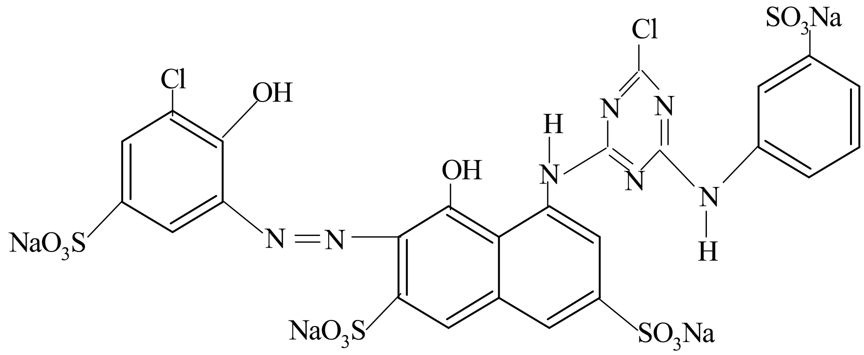

Figure 1: Procion Violet H-3R

Dyeing with Disperse dye

High temperature method of disperse dyeing was adopted. The NCC was introduced into a dye liquor containing 5 g/l dispersing agent at a temperature of 60ºC. The temperature was raised to not less than 100ºC and dyeing was continued for 90 minutes. The NCC was filtered, rinsed with distilled water, filtered and dried (Nkeonye, 1987). The disperse dye used was Foron Yellow S.E – 2GL with the chemical structure:

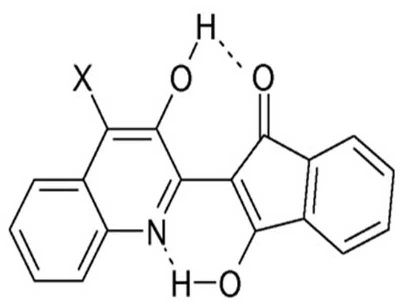

Figure 2: Foron Yellow S.E 2GL

SOAPING

After each dyeing process, the dyed NCC was treated in a bath containing 5g/l soap solution at 90ºC for 20 minutes followed by rinsing, filtering and drying. This was intended to get rid of unabsorbed dyes.

DETERMINATION OF PERCENTAGE EXHAUSTION

The percentage exhaustion of each of the dyes used was determined by measuring the optical densities of dye solutions before and after dyeing. In the case of the disperse dye, optical densities were obtained by taking 3 ml of the prepared dyebath into a beaker, the water was then allowed to evaporate and 2 ml of absolute ethanol added, stirred well and then the optical density measured as OD_1. After dyeing, 3 ml of the used dye liquor was measured into a beaker and the water allowed to evaporate, 2 ml of absolute ethanol was then added into the beaker and stirred, the optical density was then measured as OD_2.These values where then used in the formula:

$$Exhaustion\ (\%) = \frac{OD_1 - OD_2}{OD_1} \times 100\% \text{ ---- (2)}$$

where: OD_1 is optical density of dye solution before dyeing

OD_2 is optical density of the dye solution after dyeing.

DETERMINATION OF PERCENTAGE FIXATION

The percentage fixation is the amount of the total dye in dye bath that has been retained by the material being dyed. It is expressed as a percentage and was calculated using the formula

$$Fixation\ (\%) = \frac{OD_1 - OD_2 - OD_3}{OD_1 - OD_2} \times 100\% \text{ ---- (3)}$$

where: OD_1 and OD_2 remain optical densities before and after dyeing respectively

OD_3 is the optical density after soaping.

COLOUR FASTNESS TESTS

After dyeing, the dyed fabrics and the NCC powder were subjected to colour fastness tests to investigate how well the dyed powder can withstand certain agencies. It is worth mentioning here that: the fastness tests were only conducted in relation to the end use of the NCC. Thus, fastness to washing, light and chlorinated water were conducted.

Washing fastness (ISO test No. 1)

The dyed NCC powder was introduced into the wash bath containing 5g/l soap solution at a temperature of 40ºC using liquor ratio of 50:1. Washing was carried out for 30 minutes after which the NCC was filtered, rinsed and dried. The grey scales were then used to assess change in colour in comparison with the untreated sample.

Light fastness (ISO B01: 1994)

The dyed NCC and the blue standards were exposed together inside the digital light fastness tester. Exposure was stopped when blue standard 7 has faded to grade 4 (the contrast between the exposed and unexposed NCC was equal to grade 3 on the grey scale for assessing change in colour). The setup is shown below:

Figure 4: Determination of light fastness of Sample and fabrics

Fastness to chlorinated water (ISO 105 – E03)

This test was intended to assess the resistance of coloured NCC to concentrations of active chlorine such as used in the treatment of water for swimming baths. The NCC was introduced into a still container containing a solution of sodium hypochlorite (20mg/l active chlorine) at a pH of 8. The container was closed and agitated for 1 hour in the dark at 27 ± 2ºC (room temperature). The specimen was filtered, rinsed and dried after which change in colour was accessed using the grey scales for assessing change in colour.

RESULTS AND DISCUSSION

RESULTS

Percentage Exhaustion and Fixation of Dyes

The percentage fixation of the reactive dye on NCC and fabric were calculated as 64.79% and 76.36% respectively. Percentages of exhaustion were calculated for each of the dyes. The results are shown below:

Table 1: Dye exhaustion on NCC and fabrics

S/N	Dyes	NCC Powder			Fabric		
		OD_1 (mg/l)	OD_2 (mg/l)	Exhaustion (%)	OD_1 (mg/l)	OD_2 (mg/l)	Exhaustion (%)
1.	Foron Yellow S.E-2GL	1.33	0.62	53.38	1.33	0.58	56.39
2.	Procion Violet H-3R	1.56	0.50	67.94	1.56	0.52	66.66
3.	Solophenyl Yellow	1.42	0.66	53.52	1.42	0.71	50.00

COLOUR FASTNESS RESULTS

The results for the colour fastness to washing, light and chlorinated water are shown in Table 2.

TABLE 2: Colour fastness rating of dyed NCC and control fabrics

S/N	Dyes	NCC Powder			Fabric		
		Wash fastness	Light fastness	Chlorinated water	Wash fastness	Light fastness	Chlorinated water
1.	Foron Yellow S.E-2GL	3 – 4	6	2	4	6 – 7	2
2.	Procion Violet H-3R	3	6	2	3	6	2
3.	Solophenyl Yellow	2	5	3	2	5	2 - 3

DISCUSSION

Percentage Exhaustion

From Table 1 above, the reactive dye (Procion Violet H-3R) has the best exhaustion, followed by the direct dye (Solophenyl Yellow) andthe Disperse dye (Foron Yellow S.E 2GL). The high exhaustion of the reactive dye is as expected because, although the material is highly crystalline, it is still purely cellulose and therefore possesses good affinity for reactive dyes. The dyeing of NCC with reactive dye is achieved through covalent bonding between the dye reactive group and the OH groups of the NCC.

The exhaustion of the disperse dye is also reasonably good and resulted from the hydrophobic forces existing between the highly hydrophobic fibres and the hydrophobic dye molecule. However, the dyeing method used also has influence on the exhaustion of the dye, which means an even better exhaustion is possible when carrier dyeing is used. The small molecular size of disperse dyes is also an additional advantage to the dyeing of crystalline materials.

The dyeing of NCC with direct dyes is achieved mostly through van der Waals forces of attraction and hydrogen bonding between the dye molecules and the NCC. Direct dyes are known to have high affinity for cellulose.

Colour Fastness

Washing

FromTable 2, we can see that the NCC sample dyed with direct dye (Solophenyl Yellow PFL) shows poor fastness to washing (rating of 2). This is typical of direct dyes. However, poor fastness to washing in direct dyed material is often reduced using after treatment process like treatment with cationic fixing agents, formaldehyde, metallic and diazonium salts (Nkeonye, 1987).

The reactive dyed NCC shows better fastness to washing with rating of 3. This fairly good fastness can be attributed to the covalent bond that exists between the dye reactive groups and the cellulose. The covalent bond is thought to be a very strong attraction and therefore difficult to be broken by ordinary washing.

The Disperse dyed NCC shows the best washing fastness among the three. This can simply be attributed to the compactness of the NCC and once the disperse dye molecules find their way in, they become locked in and very difficult to come off.

Light

From Table 2 also, reactive and disperse dyed NCC have very close rating in light fastness. Light fastness is affected by a number of factors e.g. the intensity and spectral composition of the light used for exposure, the spectral properties of the dyed fibre, the natureof bond between the dye and the fibre, the dye concentration in the fibre, the dye reactivity, the state of the dye in the fibre and physical and chemical constitution of the fibre (Thiagarajan and Nalankilli, 2010). That is to say, the close fastness of the two to dyes can be better understood if those factors have been critically looked into. However, disperse dyes are known to have slightly better light fastness than reactive dyes.

The direct dyed NCC shows lesser fastness rating than the two dyes. Also, direct dyes are known to have moderate to good fastness to light.

Chlorinated water

The Disperse and reactive dyed NCC show poor fastness to chlorinated water. This is because the chlorine has bleaching effect on the dyes. However, the direct dyed NCC shows excellent fastness to chlorinated water. This is because the decolouration effect of the chlorine is on the bond between the fibre and the dye and not on the dye molecule itself. This was confirmed by treating each of the dye solutions with sodium hypochlorite (20mg/l available chlorine) in the absence of light. After 60 minutes, coloured solutions remained unchanged, confirming that the bleaching effect was not directly on the dye molecules.

Conclusion

The dyeing of NCC was successfully achieved using disperse, reactive and direct dyes. The work successfully pointed out that: the dual property of NCC of being crystalline and at the same time cellulosic, allows for both hydrophilic and hydrophobic dyes to be used.Therefore, it can be concluded that:

- NCC fibres/powder can be dyed using any of the three classes of dye used.
- The choice of dye will depend on the end use of the NCC being dyed. Thus:
- If NCC is to be used where there is frequent washing or cleaning, disperse or reactive dyed NCC suits best.
- If NCC is to be used where there is constant exposure to light, as in outdoor applications then Disperse dye is most suitable.
- Where there is contact with chlorinated water as in composites walls of swimming pools, the direct dyed NCC is the better choice.

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