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Dye Selectivity and Colour Fastness Assessment of Dyed MicrocrystallineCellulose Extracted From Cornstalks

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Abstract: *Microcrystalline cellulose (MCC) was extracted from cellulose obtained from cornstalks by sulphuric acid hydrolysis method. The exhaustion dyeing of microcrystalline cellulose with selected commercial dyes; Procion Violet H-3R (reactive), Solophenyl Yellow PFL (direct), and Foron Yellow S.E-2GL (disperse) was carried out and their substantivity were studied from their percentage exhaustions. The percentage exhaustion (% E) of 17.9%, 65.5%, and 75% were obtained for reactive, direct, and disperse dyes, respectively. The fastness properties of dyed microcrystalline cellulose to light, wash, and chlorinated water were investigated. The colour fastness result of the dyed microcrystalline cellulose to chlorinated water was very good for Solophenyl Yellow PFL but fair to wash and light fastness. Procion Violet H-3R displayed good fastness to light than others. Foron Yellow S.E- 2GL exhibited very good fastness to wash test than Procion violet H-3R and Solophenyl Yellow PFL which have good and fair fastness, respectively. And based on these findings, the colour fastness tests that were conducted have revealed that any of the three dyes could be used for MCC colouration depending on the area of use.*

Keywords: *Cornstalks,Microcrystalline Cellulose (MCC), Procion Violet H-3R, Solophenyl Yellow PFL, Foron Yellow S.E- 2GL.*

I. Introduction

Corn stalk is one of the post-harvest residues of maize cultivation which is made up of lignified tissue. This stalk is an interesting lignocellulosic biomass which composes of lignin, cellulose and hemicellulose, as potential sources of biomaterials. Corn stalk is considered as biodegradable agricultural wastes, which contain high quantities of organic matter therefore, an efficient utilization of such agricultural wastes is of great importance not only for minimizing the environmental impact, but also for obtaining a higher profit (Nuruddin*et al*., 2011).Microcrystalline cellulose (MCC) can be obtained from any material that is high in cellulose ranging from pure cellulose, commercial grade wood cellulose to lignocellulosic materials. Microcrystalline cellulose is a purified form of cellulose, obtained from the natural polymer after a severe acid hydrolysis treatment in which the amorphous regions are preferentially attacked and transformed into a crystalline residue (Vieira Ferreira*et al*., 1995).The hydrolysis of cellulose to obtain microcrystalline cellulose can also be accomplished using enzymes or microorganisms. Although enzymatic methods are more desirable because glucose, a useful by-product, is produced, these methods are more expensive and create products having a lower crystallinity. Thus, acid hydrolysis is the conventional method of choice for manufacturing microcrystalline cellulose (Hanna *et al*., 2001). MCCis used in various fields such as pharmacy, cosmetics, food industry, and plastics processing industry. In the powder form, it is used, as a filler and binder in medical tablets and food tablets for dietary purposes. In the gel form, microcrystalline cellulose is used as viscosity regulator, a suspending agent, emulsifier in different pastes, creams, etc. (Laka and Chernyavskaya, 2007). It has also been reported elsewherethat microcellulose fibres from corn stalk could find applications inindustrial sectors like the paper, textile and as reinforcements for compositesused in the automotive and construction industries(Weirnick*et al*., 2002).Colouration generally imparts beauty and improve aesthetic properties of materials, thus to the best of our knowledge determination of substantivity of commercial dyes and their colour fastness properties on MCC has never been done.

II. Materials And Methods

2.1 Raw materials

The cornstalks were collected from Samaru College of Agriculture, Ahmadu University, Zaria Nigeria. In the dried form, outer covering of the stalks was peeled off to obtain the soft inner lignocellulose stalk. A bleached cellulose fabric pieces which serves as control during colouration were also obtained. The chemicals used are of analytical grade and the commercial dyes are reactive (Procion Violet H-3R), direct (Solophenyl Yellow PFL), and disperse (Foron Yellow S.E-2GL).

2.2 Delignification of cornstalks

A 5g quantity of cornstalks were placed in a three-neck flask containing a magnet and securely clamped on a magnetic stirrer hot plate. The delignification was carried out in a reflux setup at boiling temperature with 90% (v/v) formic acid, stalk-to-liquor ratio, 1:30, for 2hrs.The hot plate rotor drives the magnet and the stalks were continuously stirred while water passes through the condenser to cool the reaction. The formic acid at boil temperature dissolved the stalks to a dark brown colour pulp. On completion of the reaction time, the lignocellulosic pulp was washed thoroughly in hot distilled water and filtered in a Buchner funnel. The formic acid treated residue was further delignified by treatment with peroxyformic acid (prepared by mixing 90% formic acid with 4% H_2O_2), at 80^oC in a thermostatic water bath to dissolve the residual lignin and hemicelluloses in the pulp. After 2hrs, the mass was washed by adding water and filtered in a Buchner funnel. The cellulose obtained from this treatment was dried gently in oven at 50^oC for 1hr.30min.

2.3 Extraction of microcrystalline cellulose

Microcrystalline cellulose was extracted by acid hydrolysisof cellulose isolated from cornstalks, under the following conditions: 50% w/w sulphuric acid solution for 2hours at 40 °C, using mass-to-liquor ratio 1:8, under constant stirring. Hydrolysis was stopped by adding large volume of distilled water to the reaction mixture. The resulting mixture was washed with cold water, repeatedly centrifuged to recover the microcrystalline cellulose, and subsequently neutralised with 1% sodium hydroxide. It was finally rinsed thoroughly in water and repeatedly centrifuged, filtered and dried gently in oven at 50^oC for 1hr.30min.

2.4 Bleaching of microcrystalline cellulose

Bleaching was carried out at 80^oC for 1hr in thermostatic water bath in the following recipe; 10% microcrystalline cellulose, 4% hydrogen peroxide on oven dry (o.d) microcrystalline cellulose, 1% sodium silicate and magnesium sulphate were used to stabilise the bleaching process at pH 11 by addition of required amount of sodium hydroxide. This procedure was repeated once to producea bleached, product which was then properly rinsed with distilled water, centrifuged and filtered.

2.5 Percentage yield

The yields of all products obtained aftereach chemical treatment was calculated, and expressed in percentage, as the ratio of weight of product, w_2, to its theoretical weight, w_1.

$$\%Yield = \frac{w_2}{w_1} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

2.6 Determination of particle size of microcrystalline cellulose

The micro-cellulose particles, obtained were milled in a laboratory mortar with pestle to produce the crystalline powder. The average particle size of the microcrystalline cellulose was carried out using Zetasizer Nano-S. 1mg of MCC powder per 10ml of water was prepared and the resulting suspension was transferred into a disposable cuvette using 0.22 micrometer filter unit. The cuvette containing the sample was placed into the analysis stage of the equipment for analysis.

2.7 Dyeing of microcrystalline cellulose and cellulosic fabric

The dyeing of the microcrystalline cellulose and cellulosic fabric which served as control samples was carried out to 3% shade.

2.7.1 Dyeing with reactive dye

At dye-baths temperature 30^oC, a 0.5g microcrystalline cellulose and 0.5g cellulose fabric were introduced to attain equilibrium for a period of 20minutes. Sodium chloride 20% (o.w.f) was added to each dye bath and dyeing was continued for another 20minutes to assist the exhaustion of dye. Sodium hydroxide (0.3%) was introduced for fixation and dyeing was carried out for further 20minutes at 60^oC. The dyed samples were then rinsed soaped at the boil for 30mins, rinsed in distilled water and dried (Nkeonye, 1987).

2.7.2 Dyeing with direct dye

The dye was added in well dissolved condition to the dye bath, 20% sodium chloride was then added. A 0.5g microcrystalline cellulose and 0.5g cellulose fabric were introduced into the dye liquor at 40^oC, the temperature of the bath was raised over a period of 30min to the boil and dyeing was continued at this temperature for 60min (Nkeonye, 1987). Thereafter, the samples were rinsed thoroughly and dried.

2.7.3 Dyeingwith disperse dye

A 0.5g each of microcrystalline cellulose and fabric was entered into a separatedyebathcontaining 5g/l soap solution (dispersing agent) at 60°C.The temperature was raised to the boil and dyeing was performed at this temperature, for 90minutes. The dyed samples were soaped, rinsed with distilled water to remove any surface deposit of dye and dried.

2.7.4 Determination of dye exhaustion

The percentage exhaustion (% E) ofeach dyes used wasdetermined by measuring the optical densities of dye solutions before and after dyeing. In the case of disperse dye, optical densities were obtained by taking 3 ml of the prepared dyebath into a beaker, evaporated to dryness by gently heating and 2 ml of absolute ethanol was then added. The mixture was well stirred and then the optical density measured as OD_1. After dyeing, 3 ml of the used dye liquor was taken into a beaker and evaporated to dryness 2 ml of absolute ethanol was then added. The mixture was well stirred and the optical density measured as OD_2. The percentage exhaustion was calculated using the following relationship:

$$\%\mathrm{E} = \frac{OD_1 - OD_2}{OD_1} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where OD_1 and OD_2 are optical densities (absorbance) of the dyes before and after dyeing, respectively obtained from colorimetric measurements.

2.7.5 Determination of dye fixation for reactive dyeing

Dye soaping to remove unfixed dyes was carried out on 0.5g dyed MCC and 0.5g dyed cellulosic fabric by boiling each in 10ml of 5g/l soap solution for 20minutes. Then the mixture was filtered and solution allowed to cool and made up to the required volume. The absorbance were taken and denoted as OD_3. The percentage fixation (% F) of the reactive dyed microcrystalline powders was calculated using the following relationship:

$$\text{Fixation } (\%\ \mathrm{F}) = \frac{\Delta - OD_3}{\Delta} \times 100 \ldots\ldots\ldots\ldots\ldots 3$$

Where Δ is the difference in optical densities before and after dyeing, OD_3 is optical density after soaping.

2.8 Colour fastness test for dyed mccand cellulosic fabrics

The colour fastness tests of dyed microcrystalline cellulose and fabrics were carried out using ISO Standard for testing textiles. Fastness to washing, light, and chlorinated water was carried out.

2.8.1 Colour fastness to washing (ISO Test No. 1)

The ISO wash fastness test No.1 was adopted to evaluate the colour fastness of the dyed MCC and cellulosic fabrics to washing. Each dyed samples was subjected to washing, in a test tubes securely clamped on top of a thermostatic water bath, using swift soap. Washing was carried out with 5g/l soap solution, L: R 50:1 at temperature of 40°C for 30min (Nkeonye, 1987). The washed samples were then extracted, thoroughly rinsed and dried. The change in colour of the tested specimens was assessed with the Grey Scale for assessing change in colour.

2.8.2 Light fastness using SUNTEST CPS+ solar simulator (ISO B02: 1994)

The light fastness test was conducted using SUNTEST CPS+ solar simulator. The dyed microcrystalline celluloses were placed in a specimen cell tray which had been conditioned with starch adhesive film to hold the specimens in order to withstand the fanning mechanism of the machine. The specimens were exposed alongside with the blue wool standards for 24hours, at 60% relative humidity. The test was terminated on fading that was equal to grade 4 on a Grey Scale for assessing change in colour on a reference blue wool no.6. The rating obtained using the eight-blue wool standards are presented in Table: 3.

2.8.3 Colour fastness to chlorinated water (ISO 105-E03)

The test was carried out to access resistance of the dyed MCC and fabrics to concentration of active chlorine. The materials were treated in a solution of sodium hypochlorite containing 20mg of active chlorine per litre of distilled water (Nkeonye, 1987). The treatments, of required quantity of each dyed powder, with NaOCl solution were performed in boiling tubes based on material-to-liquor ratio 1:50 for 60mins in darkness at a room temperature. The test tubes were covered and occasionally agitated over the experimental period to ensure even reaction. The treated specimens were properly rinsed with distilled water, filtered and dried. And the change in colour was accessed using the Grey scale for assessing change in colour.

III. Results And Discussion

3.1 Percentage yield

The yields were calculated, based on relationship given in Equation 1, after the cornstalks were treated with formic acid and peroxyformic to produce cellulose from which microcrystalline cellulose was extracted and bleached as shown in Table 1.

Table 1: The weights obtained from delignification of cornstalks up to extraction of MCC

	Cornstalk (g)	**Cellulose (g)**	**Unbleached MCC (g)**	**Bleached MCC (g)**
	5	2.53	2.41	1.40
	5	2.45	2.25	1.36
	5	2.48	2.28	1.46
Average	5	2.49	2.31	1.41
Yield (%)		49.7	92.7	60.9

As shown in Table 1, the yield of cellulose obtained in the treatments of cornstalks with formic acid 90% v/v and peroxyformic acid was 49.7%. However, the value of the yield obtained also affirmed that formic acid and peroxyformic acids appeared as potential chemical agents for the removal of lignin and hemicellulose from lignocellulose biomass, in line with Jahan*et al.*(2009) opinion. The loss in yield of the final product to 60.9% may be attributed to removal of inherent impurities present in MCC. In addition, it can be attributed that peroxide bleach is an effective bleaching agent for cellulose pulp and microcrystalline cellulose bleaching.

3.2 Particle size distribution of microcrystalline cellulose

The particles sizes distribution of microcrystalline cellulose, obtained from Zetasizer Nano-S, was poly-modally distributed in range of 260.5-556 nm. However, the average diameter (z-average) was found to be 1094 nm with poly-dispersity index of 0.783.

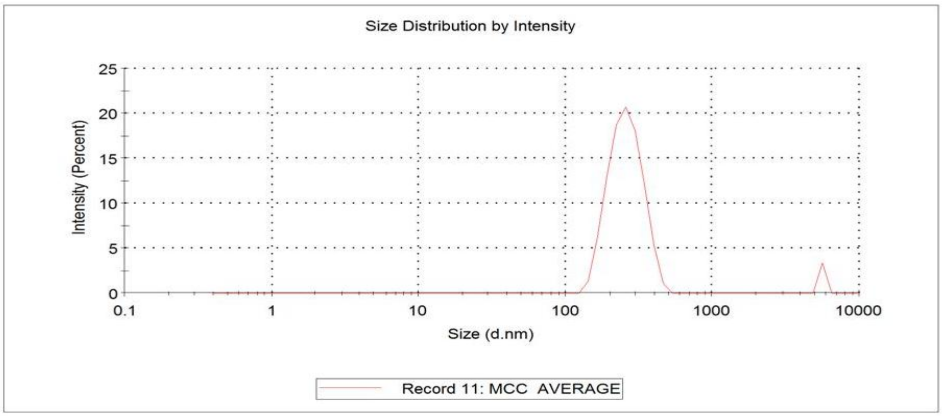

Figure 1: Particle size distribution curve for MCC

A material is considered as nanomaterial when the size of the elements, crystallites, grains, fibres etc. does not exceed 100 nm, at least in one dimension. This statement justifies the average particles size diameter of 1094 nm obtained for microcrystalline cellulose as a micro-material.

3.3 Dyes exhaustion and their substantivity for mcc and cellulose fabric

The percentage dyes exhaustion was estimated using the relationship in Equation 2, and the values obtained are summarised in Table 2, to assess the substantivity of the dyes for the samples. The dye fixation of reactive dye on MCC and the cellulose fabric was found to be 81% and 97%, respectively.

Table 2: Percentage Exhaustion and shades of dyeing

Dye Used	**MCC Powder**		**Cellulose fabric**	
	Exhaustion %	Shade	Exhaustion %	Shade
Procion Violet H-3R	17.9	Violet	57.7	Deep violet
Solophenyl Yellow PFL	65.5	Bright yellow	68.9	Bright yellow
Foron Yellow S.E-2GL	75	Yellow	23.5	Faint yellow

The disperse dye had a better exhaustion for microcrystalline cellulose even more than the cellulose fabric and over other dyes used. This can be ascribed to the structural compactness of MCCwhich enhances the penetration and retention of small molecular size disperse dyes within it microscopic structure where the necessary forces of attraction such van der Waals comes into play. The acid degradation of intra- and intermolecular hydrogen bonds between hydroxyl groups, and between hydroxyl groups and cyclic oxygen of cellulose chain during hydrolysisreduce the reactivity of the microcrystalline cellulose (Ganster and Fink 1999). This has likely affected its covalent bonding with reactive group in reactive dye therefore exhibiting a low exhaustion but this is not so for the cellulose fabric which exhibited good exhaustion as shown in Table 2. The direct dye exhaustion on microcrystalline cellulose and the fabric was reasonably good, owing to the role of sodium chloride used which facilitated the dyeing through reduction in the negative potential of the respective substrates(Perkns, 1996).

3.4 Fastnessproperties to wash, light and chlorinated water

All dyeing obtained on microcrystalline cellulose and cellulose fabrics were assessed for wash fastness test by adopting the ISO, standard procedure, light fastness using SUNTEST CPS+ solar simulator and their fastness to chlorinated water. The ratings were obtained using Grey Scale for assessing change in colour and eight blue wool standards, respectively for the wash and light fastness as reported in Table 3.

Table 3: Fastness Properties to Wash, Light and Chlorinated Water

Dye Used	**MCC Powder**			**Cellulose fabric**		
	Wash	Light	Chlorinated water	Wash	Light	Chlorinated water
Procion Violet H-3R	3-4	5	2	3	6	2
Solophenyl Yellow PFL	3	4	4	2	4	4
Foron Yellow S.E-2GL	4	4	3	4	4	2

As shown in Table 3, the rating obtained for disperse dyed microcrystalline cellulose was higher for wash fastness than the reactive and direct dyed counterparts. This may be attributed to sparingly solubility nature of the disperse dye in an aqueous medium and its smaller molecular size that has made it to firmly held within the microscopic pores of MCC. The wash fastness of the disperse dye on cellulose fabric was poor. Both reactive dyed samples fastness to light rated higher than thedisperse and direct dyed counterparts. This outcome could probably be due to the role of covalent bonding in the reactive-cellulose system thus, making the system less susceptible to ultraviolet attack from the light. Procion Violet H-3R (reactive dye) exhibited poor fastness to chlorinated wateron both samples as shown in the Table 3. It can be attributed to the oxidative action of chlorine molecule in the bleaching liquor probably occurring at the point of chemical bonding between the cellulose and the dye. Therefore,this affirmed that reactive dyes are more susceptible to damage from chlorine (Dianne *et al.*, 2003).

Solophenyl Yellow PFL displayed a very good fastness to chlorinated water than the Foron Yellow S.E-2GL which shows a fair rating. This may be attributed to the fact that no real chemical bonding occurred in the direct dye-cellulose attraction other than Van-der-Waals and hydrogen bonding forces of attraction, thus, making them less prone to the oxidation effect of chlorine in the test medium, likewise in the case of disperse dye-cellulose attraction.

IV. Conclusion

Microcrystalline cellulose was successfully extracted from cornstalks by acid hydrolysis method.The colouration of microcrystalline cellulose was successfully carried out with the selected commercial dyes. And based on percentage exhaustion, disperse dye (Foron Yellow S.E- 2GL) found to have better substantivity for microcrystalline cellulose than their direct (Solophenyl Yellow PFL), and reactive (Procion Violet H-3R) dyes counterpart. The colour fastness result of the dyed microcrystalline cellulose to chlorinated water was very good for Solophenyl Yellow PFL but fair to wash and light fastness. Procion Violet H-3R displayed good fastness to light than others. Foron Yellow S.E- 2GL exhibited very good fastness to wash test than Procion violet H-3R and Solophenyl Yellow PFL which have good and fair fastness respectively. And based on these findings, the colour fastness tests that were conducted have revealed that any of the three dyes could be used for MCC coloration depending on the area of use. Hence, this work has shown a way of effectively turning agricultural wastes (cornstalks) to produce microcrystalline cellulose at a low production cost.

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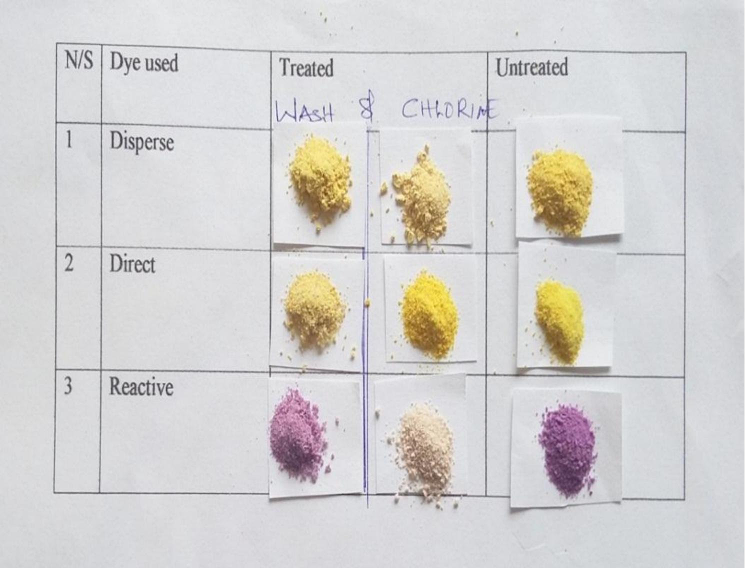
Appendix

Plate 1: Cornstalks Cellulose

Plate 2: Extracted Microcrystalline Cellulose



N/S	Dye used	Treated	Untreated
		WASH & CHLORINE	
1	Disperse		
2	Direct		
3	Reactive		

Plate 3: Dyed Microcrystalline Cellulose