Full Length Research Paper

Synthesis and characterization of reactive dye-cassava mesocarp cation exchange resins

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The synthesis of triazine based reactive dyes was carried out. The resultant dyes were characterized by thin layers chromatography, molecular weight, infrared and ultra- violet spectroscopy, and used in dyeing cassava mesocarp to produce dye modified cellulosic substrates. The dyed substrates were tested for dye fixation, fastness (acid, alkali, wash) and solvent stability. Results obtained show that the dyes have excellent dyeing properties attributable to chemical bond formation between the dye molecules and the hydroxyl groups of the substrate (cassava mesocarp). The satisfactory fastness properties and good dye fixation on the substrate are of importance in the preparation of stable and efficient dye modified cellulosic ion exchange resins.

Key words: Reactive dye, dye modified cassava mesocarp, cation exchange resins.

INTRODUCTION

Reactive dyes contain functional groups capable of forming covalent bonds with cellulosic materials (Low et al., 1992; Noah and Martins, 1995). They owe their acceptance in dyeing fibres to their ease of application and the resultant good fastness properties of the dyed substrate. In addition, they are unique being the only class of dye that actually forms covalent bond with cellulosic materials.

The dichloro triazine based dyes having chlorine atoms as their reactive group, and react with cellulosic materials by SN-type substitution reaction (Karl-Heinz, 1972). The active chlorine atoms are easily attacked by negatively charged cellulose ion (Cell-O⁻) to form ether links. Therefore if a reactive dye is brought in contact with cellulose in an aqueous alkaline medium all the hydroxyl (-OH) groups of the cellulose are available for reaction with the dye. The national initiative to use cassava for the production of biofuels increased the level of cassava cultivation in Nigeria leading to a corresponding increase in cassava residues to the point that cassava is fast becoming an agricultural produce with the highest volume of wastes in Nigeria (Akaranta, 2007). The holocellulose content of cassava mesocarp has been reported

(Akaranta and Oku, 1997) and its proximate analysis documented in open literature (Ofuya and Obilor, 1993). Cassava peels have been use to raise pigs, sheep and goats (Mantilla, 1997; Adebowale, 1985; Fetuga and Tewe, 1985; Tewe, 1982; Monitilla, 1977). The results obtained by using such an agricultural waste in feeding livestocks were not very encouraging due to its high hydrocyanic acid content (Conn, 1979). Cassava mesocarp and its chemically modified form have been use as fillers in low density polyethylene to produce plastic films that are biodegradable (Akaranta and Oku, 1997).

The aim of the present work is to synthesize triazine based dyes possessing two (2), three (3) and four (4) sulphonic acid groups that are capable of removing metal ions from aqueous solutions when anchored on cassava mesocarp, a cellulosic agricultural waste.

MATERIALS AND METHODS

Cassava

The cassava peels were obtained from a cassava processing mill at Choba, Nigeria. The epicarps of the peels were carefully removed and the mesocarp thoroughly washed with water and then reduced to chips. The chips were air dried for five days and stored in a polyethylene bag. The dried cassava mesocarp chips were reduced to powder using a manual grinding mill. The resultant product (powder) was sieved to obtain 0.40, 0.63 and 0.80 mm particle sizes.

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All the chemicals used for the study were of the analytical grade, unless otherwise specified.

## Synthesis of dichloro triazine dyes (Hildebrand, 1972).

The synthesis of dichloro triazine dyes involves the preparation of reactive intermediates, the preparation of the diazonium salts and the coupling reactions that give the reactive dyes.

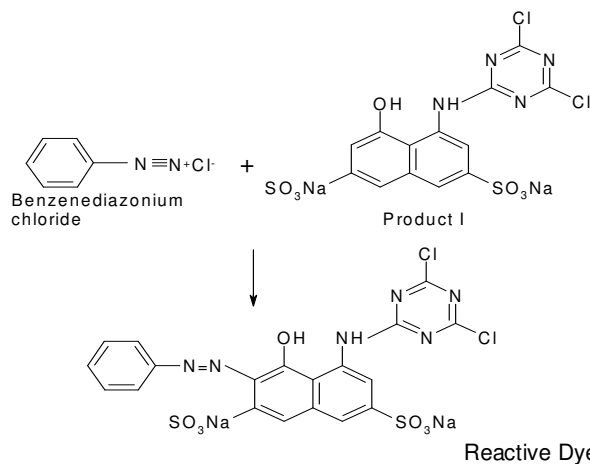## Reactive dye 1 (two sulphonic acid groups)

A solution of 2,4,6-trichloro-1,3,5-triazine (18.5 g) in acetone (100 ml) was stirred into a mixture of water and crushed ice (600 ml) in the presence of 2 M hydrochloric acid (2 ml) and designated solution X. An aqueous solution of 5-amino-4-hydroxyl naphthalene 2,7-disulphonic acid disodium was prepared by dissolving 34.43 g of the salt in 160 ml of water. The solution was made slightly alkaline by addition of aqueous solution of sodium carbonate and designated solution Y. Solution X was then added drop wise to solution Y over a period of 1 h. The resultant mixture was kept at $2^{O}C$ and continuously stirred to give product 1.
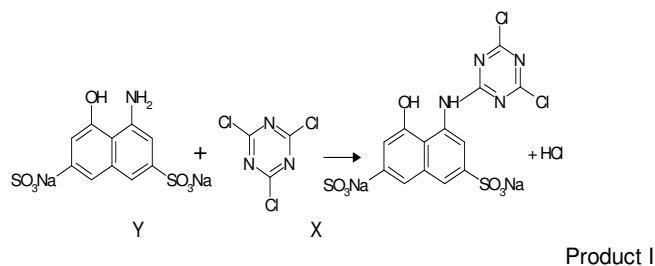
Product I

A diazonium salt of aniline was prepared at 2°C using a standard method (Vogel, 1987).
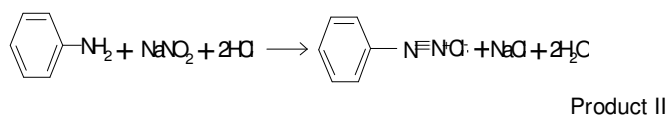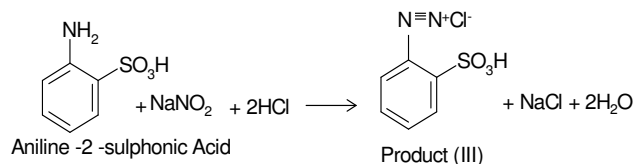

Product II

An alkaline solution of the intermediate product I was coupled with the aniline diazonium salt to produce a reactive dye having two sulphonic acid groups. The reactive dye was salted out by making the solution slightly alkaline with anhydrous sodium carbonate. The dye was filtered, thoroughly washed with water, dried and grind to fine powder.
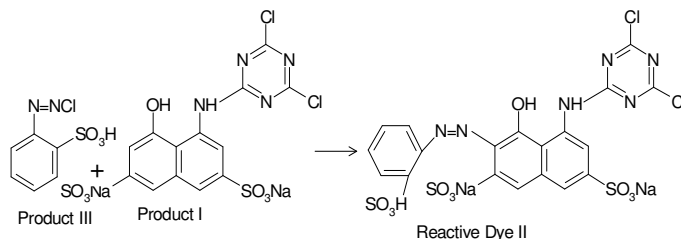

Reactive Dye I

Reactive Dye II (Three sulphonic acid groups)

Reactive dye II was synthesized using the same procedures as in reactive dye I, but replacing aniline with aniline-2-sulphonic acid.
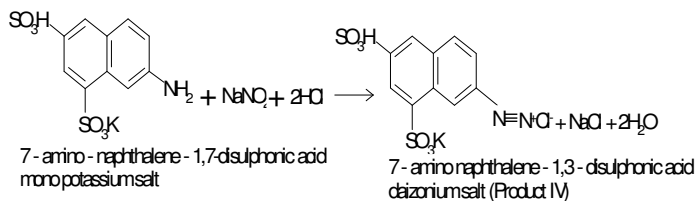

Coupling the intermediate product (1) with the aniline-2-sulphonic acid diazonium salt (product III) gave the reactive dye (II) having three (3) sulphonic acid groups.

Reactive dye III (Four sulphonic acid groups)

Reactive dye III was synthesized using the same procedures as in reactive dye I, but replacing aniline with 7-amino-naphthalene-1,3-disulphonic acid mono potassium salt.

Coupling the intermediate product (1) with the 7-amino naphthalene-1,3-disulponc acid diazonium salt (product IV) gave the reactive dye III having four (4) sulphonic acid groups.
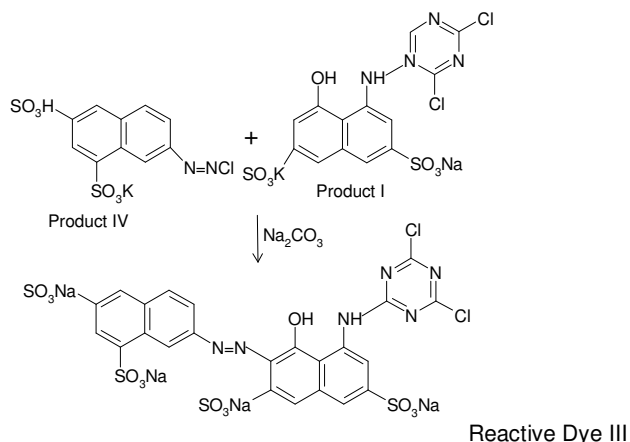
Reactive Dye III

Characterization of the reactive dyes

The three reactive dyes synthesized were characterized by

Table 1. Physical characteristics of the reactive dyes.

Dye	Colour	Yield (%)	Melting point (^{o}C)	Mol. mass	R_f value	UV (Max.)
I	Reddish-Brown	54.02	>550	622.60	0.88	205
II	Bluish-red	63.52	>550	781.08	0.87	205
III	Dark-orange	64.02	>550	870.50	0.91	280

Table 2. Percent dye fixation on cassava mesocarp of various particle sizes.

Dye	Particle size (mm)		
	0.40	**0.63**	**0.80**
I	71.21	76.85	72.04
II	61.33	66.62	64.69
III	68.38	77.82	73.96

Liquor ratio 5:1, Temperature 32°C, $NaCO_3$ (10 g/l), NaCl (40 g/l).

chromatographic separation (TLC), spectroscopic analysis (IR, UV), molecular mass determination, and melting point.

Dyeing of cassava mesocarp

A 2% of the dye solution in water was used in dyeing the cassava mesocarp powder in a liquor ratio of 5:1. 2 g of the reactive dye were dissolved in water (100 ml) to give the 2% dye solution. 20 g of the cassava mesocarp of each particle size were in turn dyed with the reactive dye using sodium carbonate to make the dye liquor alkaline. The dyeing process was by exhaustion technique. The exhaustion of the dyes on the various particles sizes of the cassava mesocarp was assessed by percent uptake. A schematic representation of the reaction between the dye molecule and the cassava mesocarp particles can be illustrated as shown below:

HO—
|
|—OH + Cl
| Dye-SO$_3$Na $\longrightarrow$ O—
HO— |—O - Dye - SO$_3$Na + HCl
                                          |
                                          O—

Cassava Mesocarp   Dye Molecule   Dyed Cassava Mesocarp
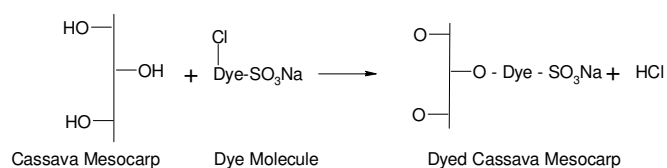
Characterization of dyed cassava mesocarp

The dyed cassava mesocarp substrates were characterized by wash, alkali and acid fastness tests. The solvent stability of the dyed substrates was also assessed.

RESULTS AND DISCUSSION

The colour, yield, melting point, molecular mass, R_f valves and UV_{max} of the dyes are shown in Table 1. Dye I has a reddish-brown colour while Dye II has a bluish-red colour. The additional sulphonic acid group (-SO_3H) in Dye II may be responsible for the change in colour from reddish brown to bluish-red. Dye III has four sulphonic acid groups (-SO_3H) and two fused rings (naphthalene)

when compared with dye I which has one benzene ring carrying one sulphonic acid group and a fused ring (naphthalene). These groups were responsible for the colour of dye III. The triazine ring is common to the three dyes. The long conjugate bonds in dye III is a strong auxochrome/chromophore for colour enhancement in a dye molecule. The yield of the dyes increased as the molecular mass increased. The reason for this trend is not clear.

The melting points of the dyes were greater than 550°C. This means that the dyes can be used in high temperature applications. The three dyes are significantly ionic which explains the high melting points of the molecules. Dyes I and II have very close R_f values. This may be due to the similarities in the structures of the two molecules. Dye III with a distinctive molecular structure has a higher R_f value. R_f values have been used to confirm the purity of unknown compounds. The UV values are similar to the R_f value. This is as expected since UV absorption spectra are molecular structure induced characteristic of compounds. The fixations of the three dyes on cassava mesocarp are shown in Table 2. The percent fixation increased from 71 to 76% for particle sizes 0.40 and 0.63 mm, respectively and decreased to 72% for particle size 0.80 mm. The fixation trend appears to confirm that the dye-cassava mesocarp reaction is a surface phenomenon. The 0.40 mm particle size ordinarily should have the highest surface area and in turn the highest dye fixation. It could be concluded that the low dye fixation obtained for this particle size (0.40 mm) may be due to clustering/aggregation of the particles thereby reducing the surface area available for the dye-mesocarp reaction. At higher particle size (0.80 mm) it is expected that the surface area will decrease leading to a decrease in dye fixation. For the substrate (cassava mesocarp), the particle size (0.63 mm) is the optimum for good dye fixation for the dyes used in this work.

Figures 1, 2, and 3 are the infra red spectra of the synthesized dyes I, II and III and Figures 4, 5, 6, are the infra spectra of the dyed cassava mesocarp dyed with Dye I, II and III, respectively. The spectra of the reactive dyes and those of dyed cassava mesocarp are the same except for the appearance of a few new peaks. Tables 3 and 4 represent bonds causing absorption in dyes and dyed cassava mesocarp samples, respectively. The absorption peak on the mesocarp in the region 1472-1435 cm^{-1} indicates the presence of -CH_2-O (acyclic CH_2 scissoring).   Also the absorption peaks in the region 1022-1020 cm^{-1} indicate the presence of = C-O-C
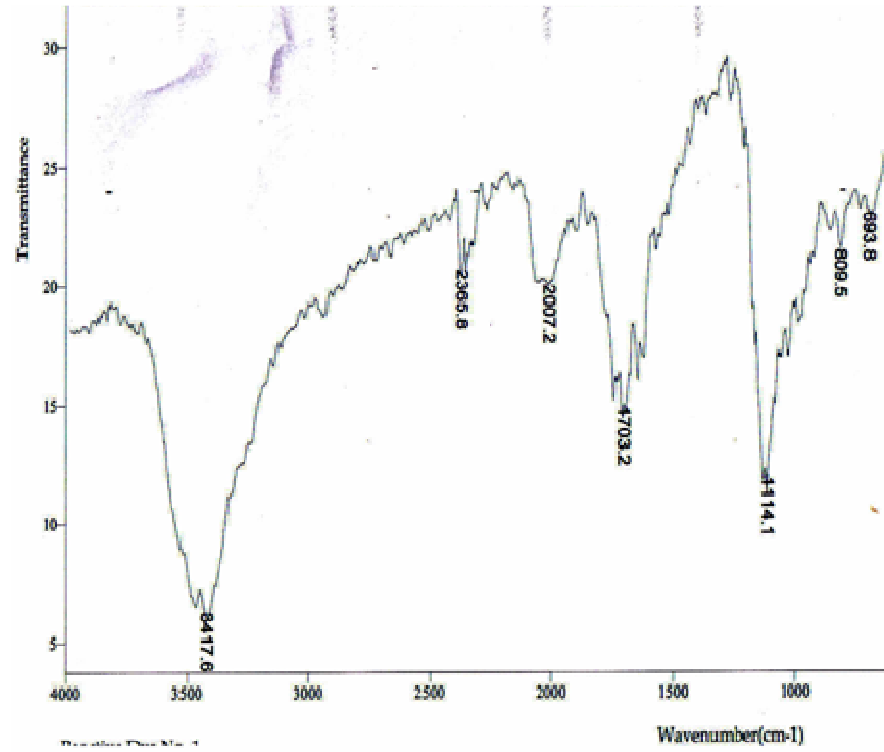
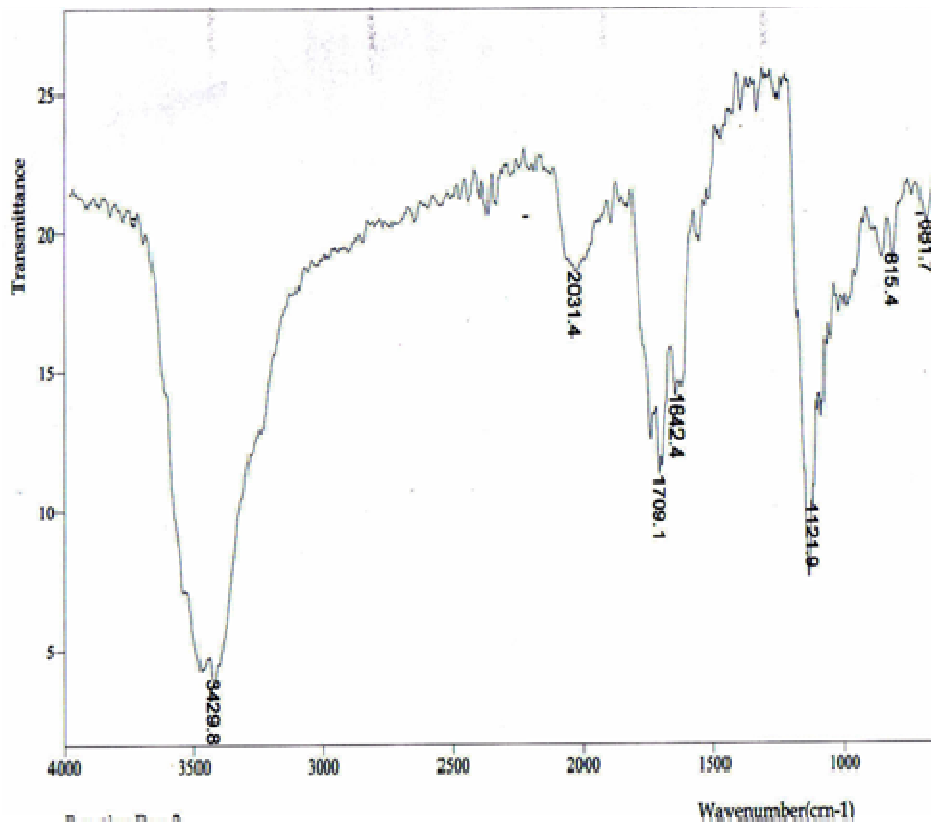**Figure 1**. Infra-red spectrum of Reactive Dye I.

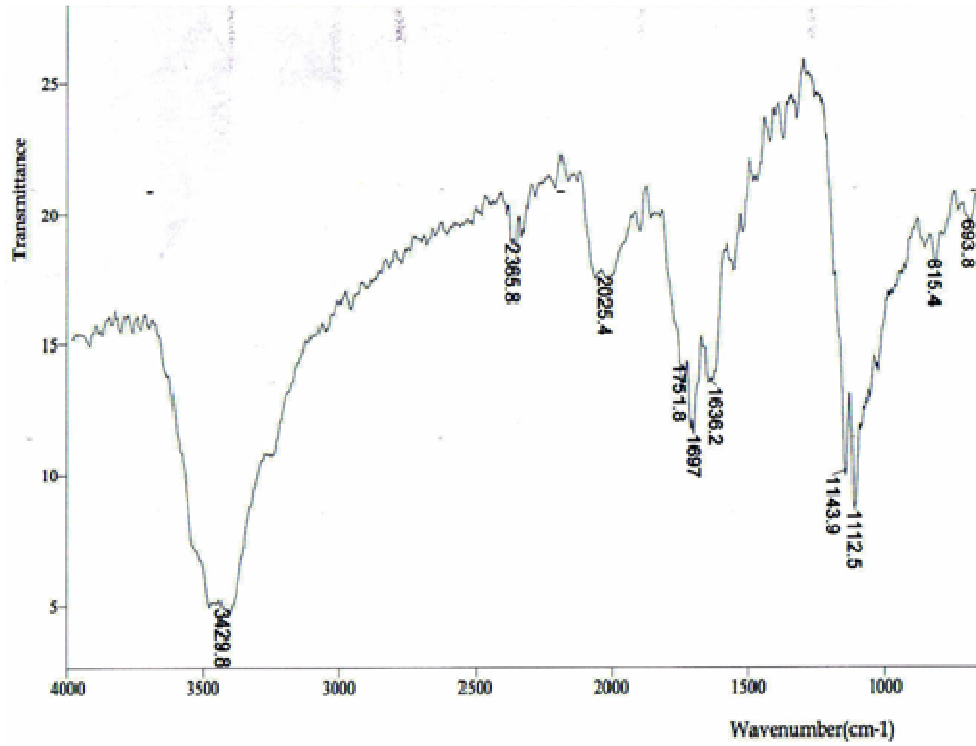**Figure 2**. Infra-red spectrum of Reactive Dye II.

Figure 3. Infra-red spectrum of Reactive Dye III.
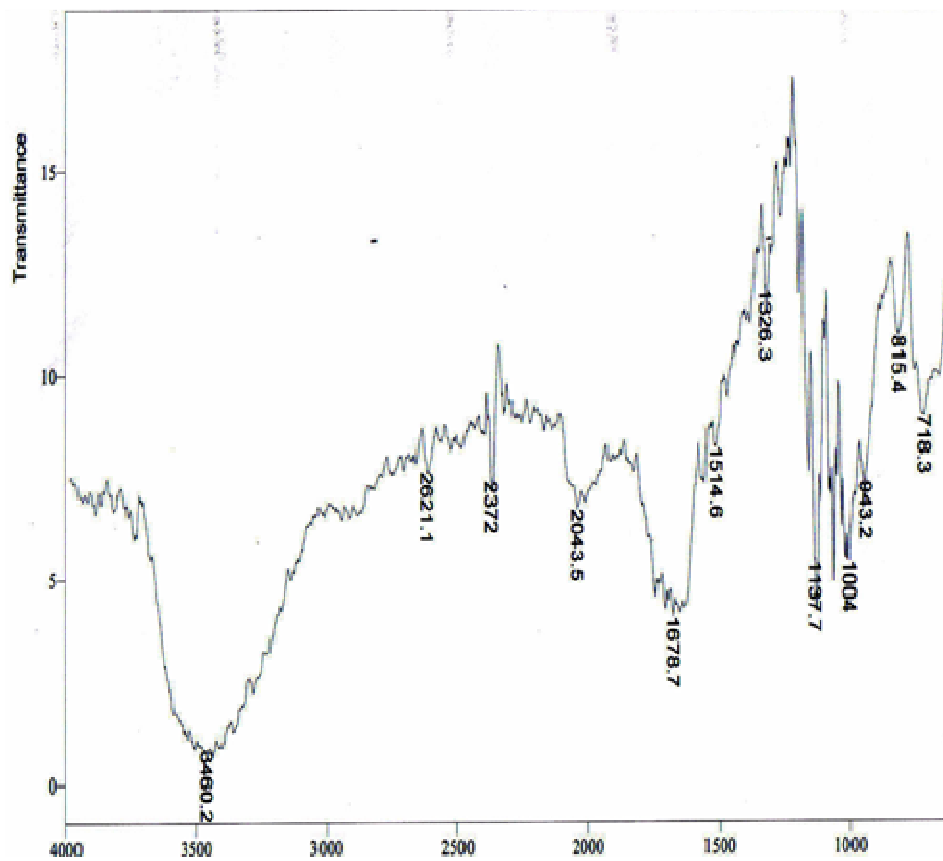
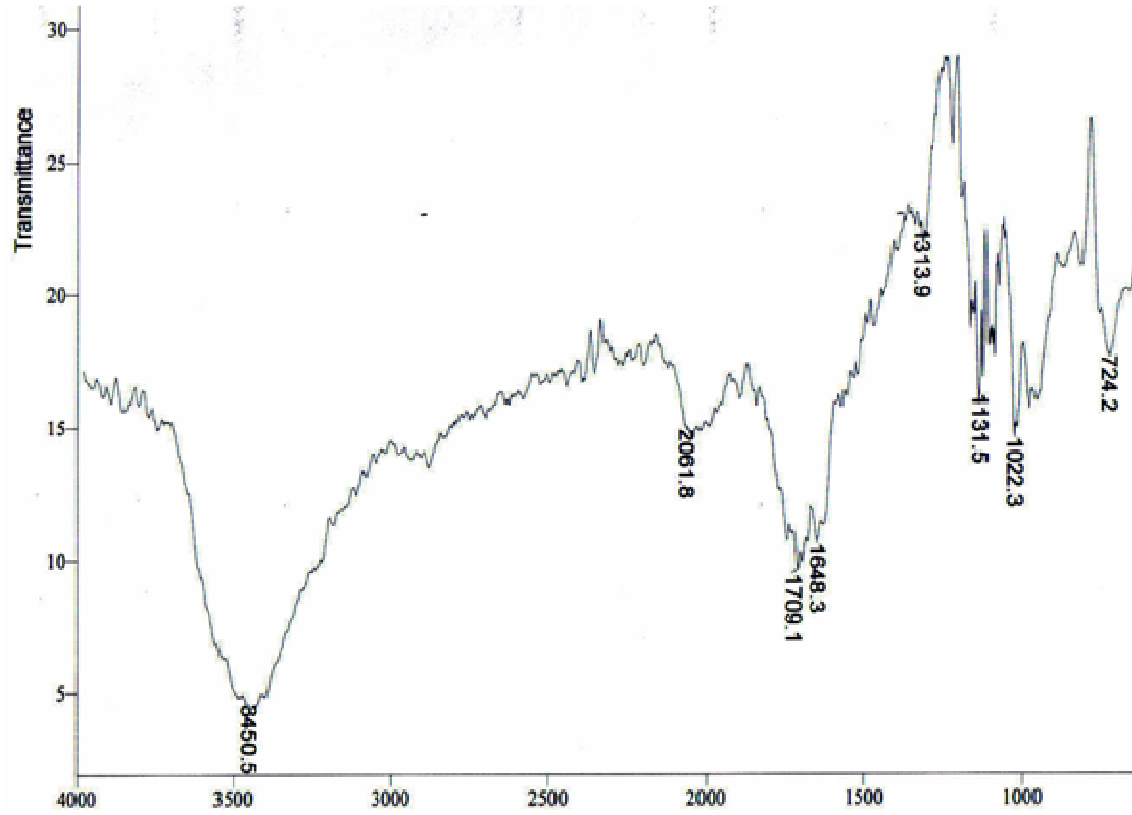**Figure 4**. Infra-red spectrum of dyed cassava mesocarp I.

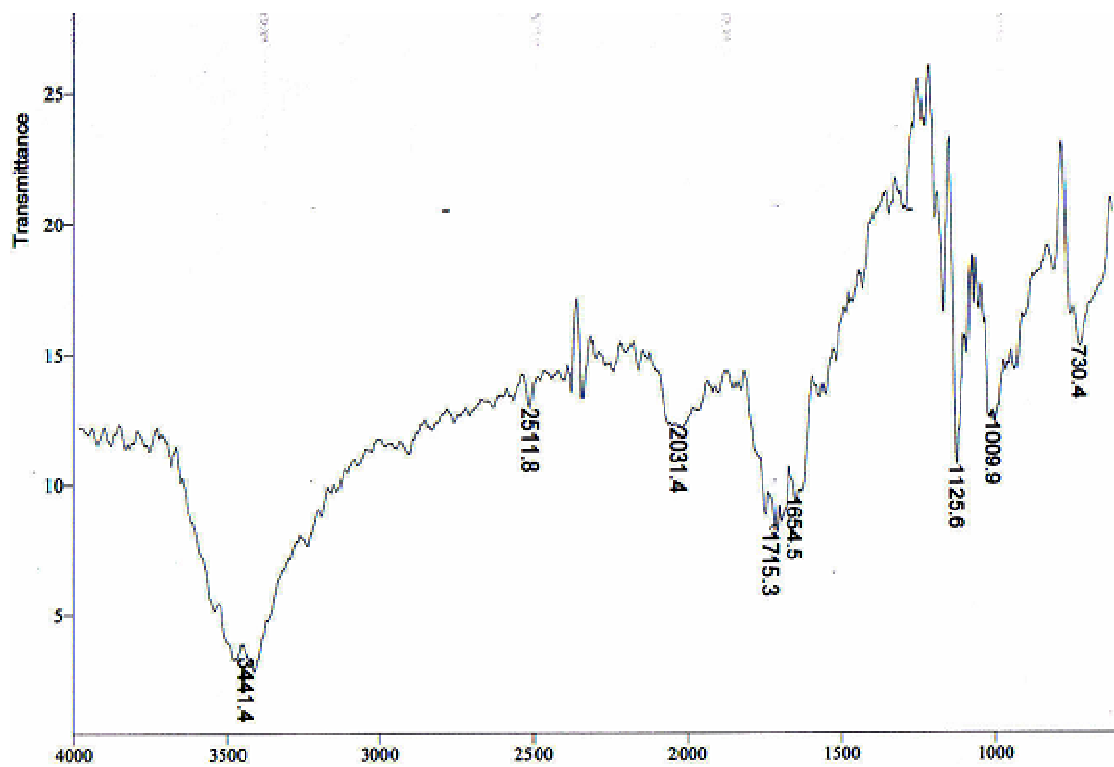**Figure 5.** Infra-red spectrum of dyed cassava mesocarp II.

Figure 6. Infra-red spectrum of dyed cassava mesocarp III.

Table 3. Infra red absorption bands of reactive dyes.

Band causing absorption	Reactive dye I (cm^{-1})	Reactive dye II (cm^{-1})	Reactive dye III (cm^{-1})
O–H stretching	3475	3475	3472
N–H stretching (secondary amide)	3417	3429	3429
-C = NH conjugated cyclic system	2365, 2350, and 2007	2031	2365, 2025
C- H out of plane bend (polynuclear aromatic)	1726 and 1703	1750, 1709	1751
-C = N – stretching	1625	1642	1697
C – C, C-N ring stretching (skeletal bands)	1236	1321	1320
S0$_2$O$^-$, S(=O)$_2$ stretching	1135	1162	1112
-SO$_2$O$^-$,S(=O)$_2$ stretching	1146	1121	1103
-S0$_2$ O-, S(=O)$_2$ stretching	1114		1143
C – OH, stretching	1037	1020	1021
- CH = CH – aromatic	992.5	996	997
2 adjacent hydrogen C-H out of plane bending	809	805	815
Cl vibration	730	730	729
C – C bend out of plane ring	693	681	693

Table 4. Infra-red absorption bands of undyed cassava mesocarp (UDCM) and dyed cassava mesocarp (DCM).

Band causing absorption	UDCM (cm^{-1})	DCMI (cm^{-1})	DCMII (cm^{-1})	DCMIII (cm^{-1})
N – H and O – H stretch	3428	3590 and 3460	3450	3476, 344
C – H stretch (aromatic)		2985	250	2943
- C = NH stretch		2621	2061	2031
- C= N stretch		1690 and 1640	1648	1654
- N – H stretch		1570 and 1514	1510	1521
- C = C – ring stretch		1621,1610,1447	1623	1621
- CH$_2$–O–(acyclic CH$_2$ scissoring	1472	1421	1470, 1435	1472
Asymmetric C – O – C		1326	1326	1303
Asymmetric C–O–C stretch		1245		1125
S(= 0)$_2$ stretch		1176	1135	1135
- C – O stretch	1132	1137,1070, 1004	1130, 1110	1125
Symmetrical = C- O –C stretch		1022	1022	1020
Aromatic in plane C–H band		1038	1095, 1016	1016
S – O – C stretch		1008	1048	1009
Substituted aromatic ring, Naphthalene 3 adjacent hydrogen CH = CH – stretch		943	944	940
Out of plane C – H Band	815	815		
Out of plane ring C – C Band		718	795	730

symmetrical stretch. These are caused by formation of ether bonds as a result of the reaction between the chlorine atoms of the reactive groups of the dye and the OH$^-$ groups of the cellulose. There is absence of the absorptions band at 730 cm^{-1}, (that is, Cl vibration) in the dyed cassava mesocarp when compared with the structure of the reactive dye.

The colour of dyed cassava mesocarp and the colour fastness tests are shown in Table 5. The colour fastness tests results show that the fastness properties of the dyes on cassava mesocarp were excellent. This means that the colours of the dyed cassava mesocarp will not be affected by changes in pH. The solvent stability test shows that pyridine, as a solvent, could not extract the dyes from the substrate (cassava mesocarp). This may be as a result of the covalent bonds formed between the dye molecules and the hydroxyl (-OH) groups of the cassava mesocarp.

Table 5. Colour of dyes cassava mesocarp and colour fastness tests.

Dye	Cassava Mesocarp (off white colour)	Colour on dyeing	Alkaline Fastness 5% NaOH	Acid Fastness 5% HCl	Wash Fastness	Solvent Stability (Pyridine)
I	0.40 mm	Reddish brown	++	++	++	++
	0.63 mm	Brown	++	++	++	++
II	0.40 mm	Dark- brown	++	++	++	++
	0.63 mm	Dark-brown	++	++	++	++
III	0.40 mm	Brown	++	++	++	++
	0.63 mm	Brown	++	++	++	++

++: Original colour of dyed cassava mesocarp retained.

Conclusion

The triazine dyes showed excellent dyeing properties on the substrate (cassava mesocarp). This is attributable to chemical bond formation between the dye molecules and the hydroxyl 1 groups of the substrate. The fastness test results showed that the dyed substrate were stable in both acid and alkaline media, therefore can be used for the removal of metal ions in solution for a wide range of pH values. The efficiency of the dyed substrate in removing metal ions from aqueous solution will be the subject of future articles.

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