Development of Halochromic Sensor Material using Textile Substrate

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Abstract
The major focus of this work is to study the effect of cationization on the exhaustion of pH indicator dyes on the textile substrate. As pH paper is of cellulose content with dyes incorporated into it, the idea behind the work is to dye wood pulp cellulose after the process of cationization with pH sensitive halochromic dyes. To enhance the adsorption property of the cellulose substrate, the source is pretreated with a cationic agent 3-chloro-2 hydroxy Propyl trimethyl ammonium chloride (CHPTAC). The treated cellulose substrate is dyed with different pH sensitive dyes which are sensitive to each pH range. The dyed sample is tested with each pH indicating solution selected within that pH range. The dyed sample efficiency is analyzed for each control and cationized sample before and after testing the sample with the help of a UV-VIS spectrophotometer. Better results were achieved with the cationized substrate when compared to the control.
Keywords: *Wood Pulp, Cationization, pH sensitive dyes, Halochromic, Spectrophotometry*

I. Introduction

pH measurement is usually done by pH indicator paper which is dyed with pH sensitive dyes [1-3]. pH sensitive dyes such as Indigo carmine, Methyl orange, Methyl red, Phenol red, Phenolphthalein and Thymol blue are used for the preparation of strips [4]. It is well known that the cotton fibre on immersion in water acquires a negative charge and requires additional auxiliaries such as salt and alkali for exhaustion and fixation [5]. In order to improve the better binding of the dye to the cotton substrate, cationization is one of the effective routes. 3-chloro-2-hydroxytrimethyl ammonium chloride is one of the effective cationizing agent [6] which can be applied by exhaust process and can increase dye yield on the substrate. In the case of pH sensitive dyes, applied on cellulose substrate, similar challenges exist and it was proposed to study the effect of cationization on cellulose substrate with these dyes. Cotton fibres laid by wet laying technique [7] were used as a substrate for the study. The effect of cationization on the performance of the developed substrates was studied in detail.

II. Materials And Methodology

2.1 Materials

Wood Pulp was Purchased from South Indian Textile Research Association (SITRA), Coimbatore, India. 3-Chloro 2 hydroxy Propyl trimethyl ammonium chloride (CHPTAC) was Purchased from Sigma Aldrich, India. pH indicator dyes of Indigo carmine, Methyl orange, Methyl red, Phenol red, Phenolphthalein, Thymol blue and other auxiliary chemicals such as sodium hydroxide and acetic acid were purchased from SRL Chemicals Pvt. Limited, Mumbai, India.

2.2 Pretreatment and cationization of wood pulp fibres

Wood pulp fibres from the web sheet were soaked overnight in water and the fibres were pretreated with 18% sodium hydroxide with an MLR ratio of 1:30 for about 15 minutes [8]. The treated wood pulp was further washed multiple times and neutralized with 1% acetic acid.

To carry out the cationization process, the fibres were treated with sodium hydroxide (10% w/v) followed by treatment with cationizing agent CHPTAC which is of 65% concentration at an M:L ratio of 1:60 and temperature of 80°C for 30 minutes [9]. The unfixed compounds were removed by cold and hot wash. The fabrics were neutralized with acetic acid before proceeding to dyeing.

2.3 Combined dyeing and wet laying of nonwoven

One pot dyeing and wet laying process were adopted to prepare the web. 1.5 gms of fibres were well dispersed in 500ml of water along with 1% of dye [10]. Dyeing was carried out using pH indicator dyes of Thymol Blue (1.2-2.8), Methyl orange (3.2-4.4), Methyl red (4.4-6.2), Phenol red (6.4-8.0), Phenolphthalein (8.3-10), Indigo carmine (11.5-14).

2.4 Characterization

The surface morphology of the control and cationized samples were studied using Scanning Electron

Microscope (S-3400 SEM, HITACHI, Japan). The colour of the fabric was characterized using a UV-Visible spectrophotometer (HITACHI U-3210, Japan). The color strength of the fabric was calculated using Kubelka - Munk equation as shown in equation (1).

$$\text{Colour strength } (K/S) = \frac{(1-R^2)}{2R} \text{ ------ (1)}$$

Where, K = Absorption coefficient; S= Scattering coefficient; R= Reflectance Value.
The relative colour strength of fabrics was calculated using equation (2)

$$RCS\,(\%) = \frac{K/S \text{ of cationized fabric}}{K/S \text{ of control fabric}} \times 100 \text{ -----(2)}$$

The CIE color parameters such as L^*, a^*, b^* were calculated using the following Equations (3-5)

$$L^* = 116^* (Y/Y_0)^{(1/3)} - 16 \qquad \text{--------(3)}$$
$$a^* = 500^*[(X/X_0)^{(1/3)} - (Y/Y_0)^{(1/3)}] \qquad \text{---------(4)}$$
$$b^* = 200^*[(Y/Y_0)^{(1/3)} - (Z/Z_0)^{(1/3)}] \qquad \text{---------(5)}$$

Where, L^*- lighter/darker; a^*- redder/greener; and b^*- yellower/bluer tone of the fabric.

III. Results And Discussion

The surface morphology of the web prepared with and without cationization is given in Fig. 1. From the figure, it can be seen that the convoluted morphology is less in the case of the cationized sample due to the usage of alkali[9]. Cationization process leads to positive charge on the backbone of polymer and it also aids in better dispersion of fibres.
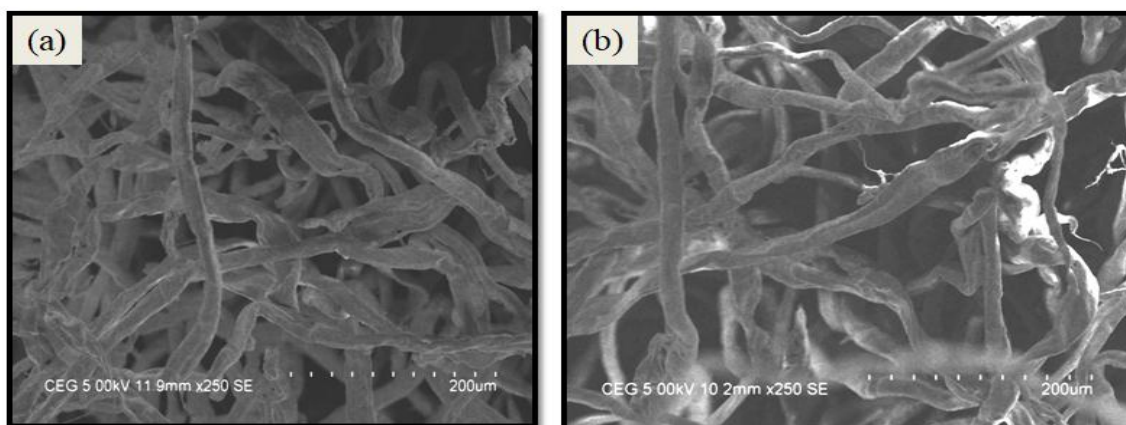

Fig. 1. SEM Image a) Control web b) Cationized web

The one pot dyeing and preparation of the web were dyed in this work using 1% shade. The colour strength and colour parameters are given in Table 1.

Table 1. CIE $L^*a^*b^*$ values of control and cationized web before testing.

Dye	Before pH exposure								
	Control Web				Cationized Web				
	L^*	a^*	b^*	K/S	L^*	a^*	b^*	K/S	RCS %
Thymol Blue	35.69	7.28	0.74	5.59	26.73	12.87	-20.43	14.78	262
Methyl Orange	74.45	30.95	73.46	6.57	60.75	50.60	75.94	24.13	367
Methyl Red	78.12	23.00	87.24	10.46	78.83	28.00	97.44	22.37	213
Phenol Red	48.61	49.62	24.62	5.45	28.14	59.39	7.61	36.34	666
Phenolphthalein	93.82	7.52	8.87	0.03	94.29	7.88	7.67	0.04	133
Indigo Carmine	55.70	-25.86	-9.34	0.52	32.47	2.17	-28.84	1.09	321

It can be seen from the table that the relative colour strength of the samples was found to be higher for cationized samples compared to that of control samples. The increased colour value can be attributed to the

attraction of anionic dye towards the cationic backbone of cellulose. The decrease in $L*$ value which indicates lightness and darkness suggest that the sample moves to the darker side due to the majority of dye uptake in cationized. The lower $b*$ values in the case of Indigo Carmine and Thymol Blue suggests that the sample moved strongly to the bluer side. The increased $a*$ values for Methyl red, Methyl orange and Phenol red suggests that the sample moves to the redder side. However, for Phenolphthalein dye, no significant changes were noted in terms of colour parameters for control and cationized fabrics. The images of the residual drain of all dyed samples are shown in Fig. 2. From the figure, it can be seen that the cationized samples exhibited better exhaustion.
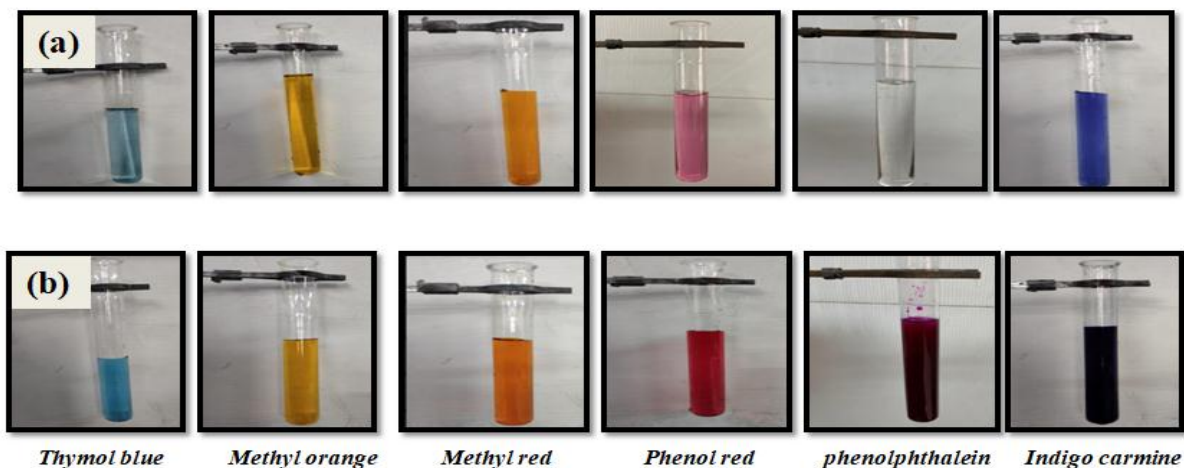

Fig. 2. Residual Dye collected from the drain a) Indigo carmine b) Methyl Orange c) Methyl red d) phenol red e) Phenolphthalein f) Thymol blue.

The pH sensitivity studies were carried out in pH sensitive dyes of respective dyes. The RCS after exposure to different indicators was calculated and given in Table 2. The indicating solution of Thymol blue, Methyl orange, Methyl red, Phenol red, Phenolphthalein and Indigo carmine are Citric acid, Hydrochloric acid, Coffee, Pure water, Sodium Carbonate and Sodium hydroxide. From Table 2 it can be seen that cationized samples had the highest color strength compared to control samples after pH exposure. The drastic change in colour parameters in terms of $L*$, $a*$ and $b*$ for cationized samples suggests that they are more sensitive to pH compared to that control samples.

Table 2. CIE $L*a*b*$ values of control and cationized web exposed to pH

Dye	Exposed to pH								
	Control Web				Cationized Web				
	$L*$	$a*$	$b*$	K/S	$L*$	$a*$	$b*$	K/S	RCS %
Thymol Blue	76.67	17.79	17.13	0.52	67.07	31.89	12.50	0.96	184.6
Methyl Orange	56.62	40.11	2.29	0.74	64.93	36.69	12.56	1.24	166
Methyl Red	29.70	56.45	10.56	1.35	58.03	48.65	9.72	2.38	176
Phenol Red	69.54	25.39	48.46	3.54	32.33	62.92	-1.01	29.87	841
Phenolphthalein	68.65	38.28	51.94	5.28	75.67	22.88	7.46	0.44	120
Indigo Carmine	76.67	17.79	17.13	5.32	65.95	30.30	10.22	17.19	209

IV.   Conclusion

Cellulosic substrate cationized with CHPTAC in fibrous form was used to develop halochromic substrates. The cationization of fibrous led to excellent exhaustion and the developed substrates were highly sensitive to the pH range of the study. The study shows that cationization of fibres can increase the sensitivity of detection of pH by visual colour change.

DECLARATION
There is no conflict of interest.

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