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ADSORPTION OF PLANT EXTRACTS ON CATIONIZED COTTON*

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Cotton, like most textile fibers, is negative charged in neutral and alkali aqueous solutions. Dyestuffs, optical brighteners and finishing agents in aqueous solution have the same electrical charge as cotton. Therefore, adsorption processes are difficult due to these repulsive forces. This paper studies the application of water extraction plants of St. Johns wart, marigold and hibiscus for the finishing of modified cotton – by mercerization and cationization. The mercerization is the oldest modification since 19th century, while the cationization is researched in last 10 years. In this paper cationization of cotton fabric for achieving electropositive charge and better adsorption properties was carried out with cationic compound, quaternary ammonium salt during the mercerization well as with commercial product for cationization Denimcol Fix-GF (Bezema). The cotton electrokinetic phenomena after modifications were determined by zeta potential, isoelectric point, point of zero charge and specific amount of surface charge. The adsorption ability of plant extracts with and without mordant was investigated.

Key words: cationization, electrokinetic phenomena, plant extracts.

INTRODUCTION

Cotton fibers, like most textile fibers, are negatively charged (have negative zeta potential) in neutral and alkali aqueous solutions. Dyestuffs, optical brighteners and finishing agents in aqueous solution have the same electrical charge as cotton, so adsorption processes are difficult due to repulsive forces between the particles of the same sign of electrical charge. These forces may be overcome by addition of large electrolyte amounts what is economically and ecologically unfavorable [1-3].

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Textiles are characterized by its inner and outer structure and functional groups. Specific adsorption of ions or dissociation of the surface groups in aqueous solution results with their surface charge. Fiber surface charge depends upon their chemical and physical-chemical structure, swelling capacity as well as upon ionogenity, structure and concentration of adsorbate. Different treatments, mostly alkaline modifications of fibers, change surface charge and adsorption ability. Adsorption properties of fibers are influenced by change of surface charge [1, 4, 5].

At the interface of an electrically charged textile fibers and an aqueous solution of electrolyte, surfactants or dyes set up an electric double layer. Moving one of these two charged surfaces results by electrokinetic (zeta) potential. Zeta potential is not material constant, but gives information about nature and dissociation of functional groups, hydrophilicity or hydrophobicity of fiber surface as well as ion or water sorption. This potential plays an important role in the electrical characterization of textiles in wet processing [2,4,6].

This paper studies adsorption properties of plant water extracts of St. John's wart, marigold and hibiscus for the finishing of modified cotton – by mercerization and cationization. The mercerization is the oldest modification since 19^{th} century, while the cationization is researched in last 10 years, for achieving electropositive charge [7-9].

EXPERIMENTAL PART

A chemically bleached damask fabric of 100 % cotton and mass per surface area of 180 g/m^2 was used (Sample B).

It was mercerized in a bath containing 24 % NaOH, 8 g/l anionic surfactant Subitol MLF (Bezema) in a liquor ratio 1:25, 2 min, at 18 °C, rinsed and neutralized until pH 7 (Sample BM).

It was cationized during the mercerization process (Sample BCM) using 3-chloro-2-hydroxy-propyl-trimetyl ammonium chloride (CHPTAC) (Fluka). Firstly, it was mercerized in 24 % NaOH, 8 g/l anionic surfactant Subitol MLF (Bezema) in a liquor ratio 1:25, 2 min, at 18 °C,, and before rinsing and neutralization alkali cotton fabric was cationized by impregnation with bath containing 50 g/l of CHPTAC, for 2 min, at pH 13 and 18 °C. After staying at the room temperature for 24 hours in a glass with plastic cover it was rinsed until pH 7 was reached.

Cationization with commercial product Denimcol Fix-GF (Bezema) was performed according to Bezema's procedure (Sample BG). Fabric was impregnated with bath containing 50 g/l Denimcol Fix-GF, for 2 min, at pH 10 and 18 °C, dried at 80 °C for 4 min and cured at 145°C for 2 min. Labels and pre-treatments of cotton fabrics are collected in Table 1.

Table 1. Labels and pre-treatments of cotton fabrics

Fabric	Treatment of cotton fabric
B	Bleached
BM	Bleached, mercerized
BCM	Bleached, cationized during the mercerization with CHPTAC
BG	Bleached, cationized with Denimcol Fix-GF

The water extracts of St-John's-wart, marigold and hibiscus flowers were used for adsorption on cationized cotton fabric. The flowers were collected in the wide region of Leskovac, Serbia. The extraction was performed in water at boiling temperature at bath ratio (BR) 1:22 for 60 min. After staying at room temperature for 12 h it was filtered and applied to cotton fabrics. Treatment with water extracts of St-John's-wart, marigold and hibiscus was performed in Linitest, Ahiba laboratory dyeing apparatus at 50 °C, for 60 min at BR 1:60. The samples were than rinsed with hot and cold water, washed with the addition of 1 g/l non-ionic detergent (Hostapal CV, Clariant) at 60 °C for 30 min, rinsed again and dried at room temperature. The treatment was repeated with addition of mordant (3 % $SnCl_2$ and 3 % $KAlSO_4$).

The zeta potential of cotton fabrics was measured by streaming current method on Brookhaven-Paar Electrokinetic Analyzer (EKA) using stamp cell depending on pH and surfactant addition for determination of IEP and point of zero charge, PZC [8].

Specific quantity of surface charge was calculated after back-titration method applying Mütek's Partical Charge Detector. As standard solution 100 % p.a. surfactant solution was used for dwelling and as titrant in back titration method. Surfactant solutions used were Hyamine 1622 (benzetonium chloride) as cationic, and SDS (sodium dodecyl sulphate) as anionic one [8].

Spectral parameters according to CIE were measured using remission spectrophotometer Spectraflash SF 600-PLUS CT (Datacolor) after treatment with plant water extracts. Obtained values are used to characterize differences between the modified cotton fabrics.

RESULTS AND DISCUSSION

The electrokinetic phenomena - zeta potential and specific surface charge of modified cotton fabrics by mercerization and cationization was determined.

The results of zeta potential measured by streaming current method depending on pH and surfactant addition for determination of IEP and point of zero charge, PZC are shown in Fig. 1 and 2, and Tab. 2.

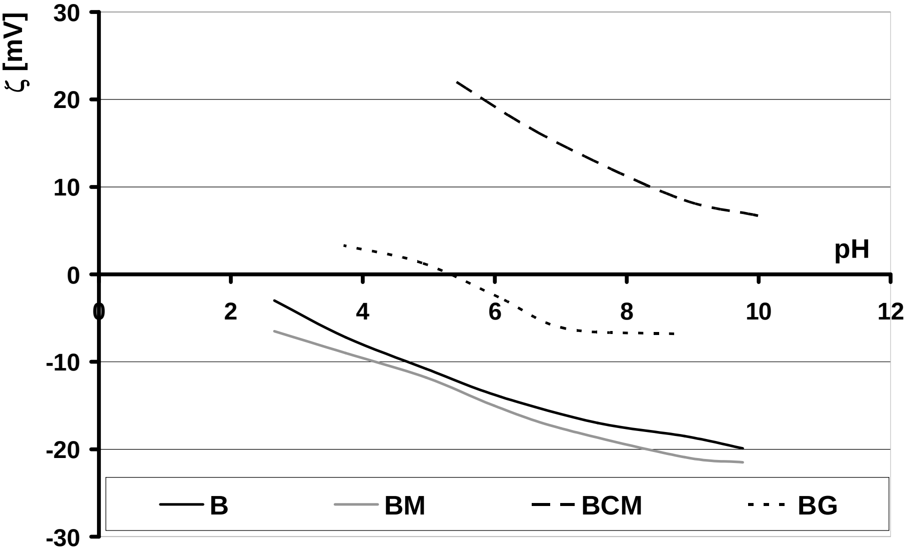

Figure 1 - Zeta potential of bleached and modified cotton fabrics upon pH of 1 mmole/l KCl

The results of specific surface charge determined by back titration method are presented in Tab. 2.

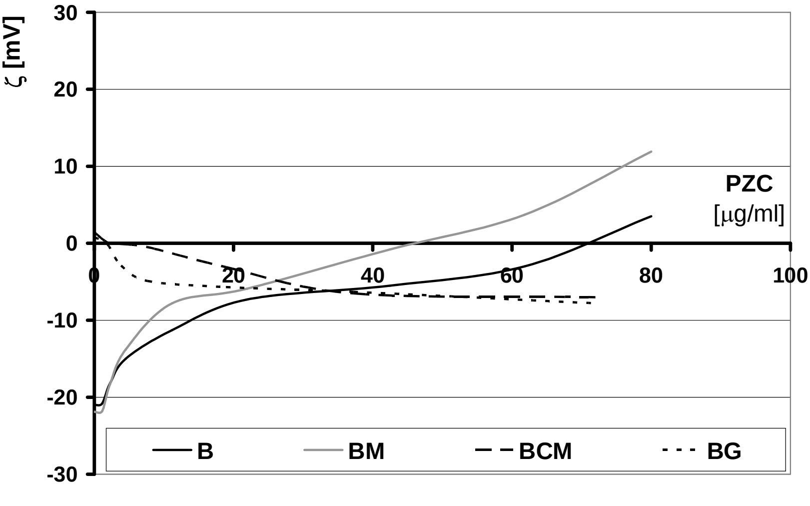

Figure 2 - Zeta potential of bleached and modified cotton fabrics upon surfactant addition to 1 mmole/l KCl

Bleached and mercerized cotton fabrics are electronegative according to the zeta potential and specific surface charge. Zeta potential of bleached fabric is -19.9 mV at pH 10 due to the presence of carboxyl and hydroxyl groups. Mercerization increase number of accessible surface groups lowering zeta potential. Zeta potential and the specific surface charge results imply that cotton electric charge was noticeable changed by cationization. Cationized fabric during mercerization with CHPTAC is electropositive in whole pH range (pH 10 to pH 2) while cotton fabric treated with commercial product Denimcol Fix-GF is slightly electronegative (-5 mV).

Table 2 – Zeta potential at pH 10 (ζ), Isoelectric point (IEP), Point of zero charge (PZC) and Specific surface charge (q) cotton fabrics

Fabric	$\zeta_{\text{pH 10}}$ [mV]	*IEP* [pH]	*PZC* [μg/cm^3]	*q* [C/g]
B	-19.9	< 2.5	70.21	-2.13
BM	-21.5	< 2.5	61.82	-2.01
BCM	6.7	-	3.54	1.50
BG	-5.8	5,72	0.87	0.38

For bleached and mercerized cottons IEP has been not determined, because zeta potential is lower than pH 2.5. On the other hand, fabric treated with commercial product Denimcol Fix-GF have IEP at 5.7, while fabric cationized during mercerization have no IEP. Different modification of cotton fabrics results in different accessibility of its carboxyl and hydroxyl groups, and different surface charge, therefore cotton fabrics have different surfactant adsorption what results in different PZC. Never the less, PZC is in correlation to specific surface charge.
The adsorption ability of plant extracts - St. Johns wart, marigold and hibiscus with and without mordant were investigated. The spectral characteristics are collected in Tables 3-5.

Table 3 – The spectral characteristics of cotton fabrics treated with St. Johns wart plant extract with and without mordant

Fabric		L*	a*	b*	C*	h*
without mordant	B	77.11	2.50	14.79	15.03	80.39
	BM	94.21	-0.33	1.82	1.82	100.00
	BCM	91.84	0.21	2.34	1.90	99.97
	BG	92.64	-0.08	2.44	2.02	99.78
mordant 3 % $SnCl_2$	B	73.62	3.75	14.84	15.31	75.83
	BM	73.89	3.6	14.48	14.92	76.02
	BCM	71.44	4.17	15.66	16.22	75.08
	BG	66.57	4.86	22.17	22.74	77.64

From the Table 3 it is evident that water extract of St-John's-wart shows cationic character. Therefore, only bleached cotton absorbs it (Sample B), and gives of the highest K/S value. On the other hand, when using mordant – 3 % $SnCl_2$, highest absorption of St-John's-wart water extract have cationized cotton.

Table 4 – The spectral characteristics of cotton fabrics treated with marigold plant extract with and without mordant

Fabric		L*	a*	b*	C*	h*
without mordant	B	84.63	-0.11	15.48	15.48	90.39
	BM	84.65	0.19	14.63	14.63	89.26
	BCM	69.46	2.31	16.81	16.96	82.21
	BG	72.83	2.03	18.23	18.34	83.65
mordant 3 % $SnCl_2$	B	78.51	1.54	15.64	15.71	84.36
	BM	77.60	1.79	16.67	16.77	83.88
	BCM	76.67	2.08	22.01	22.11	84.61
	BG	78.00	1.76	20.11	20.18	85.01

In the case of marigold, the situation is opposite. It is evident from Table 4 that marigold water extract shows anionic character. Therefore, mercerized and cationized cotton show higher dye uptake than bleached one. Cationized cottons are darker, having the lowest lightness (L*), because of the higher marigold water extract adsorption. When using mordant - 3 % $SnCl_2$, there are no significant difference between cotton fabrics. Therefore, it is to point out that mordant addition is no necessary if the fabric was cationized.

Table 5 – The spectral characteristics of cotton fabrics treated with hibiscus plant extract with and without mordant

Fabric		L*	a*	b*	C*	h*
without mordant	B	73.12	2.49	9.78	10.09	75.70
	BM	72.22	2.51	9.87	10.86	76.32
	BCM	70.04	2.58	11.35	11.64	77.19
	BG	68.65	2.47	11.62	11.89	77.99
mordant 3 % $KAlSO_4$	B	69.03	3.45	10.76	11.31	72.25
	BM	69.47	3.25	10.67	11.16	73.05
	BCM	66.78	3.12	11.80	12.20	75.19
	BG	68.32	3.39	10.43	10.96	72.01

In the case of hibiscus it is to point out that this water extract is obviously non-ionic. Therefore, it gives of almost the same adsorption on anionic and cationic cotton fabrics. It is to notice that anionic cottons – bleached and mercerized have a little bit

better adsorption which leads to lower lightness (L*). Addition of mordant 3 % $KAlSO_4$ leads to slightly better water extract adsorption.
Results presented in Tables 3-5 confirm that cationized surface have high adsorption of anionic substances. Mercerized and cationized cotton fabrics show higher water extract uptake than untreated one. Cationized cottons are darker, having the lowest lightness (L*) and higher chromacity (C*) because of the higher adsorption.

CONCLUSION

Mercerization and cationization, as modification processes of cotton fabrics, cause the change of its ionic character resulting in different zeta potential, surface charge and plant water extract adsorption.
By cationaization, an electrical charge of cotton fabrics was noticeable changed, from negative to positive values.
Electropositive cotton shows better adsorption of anionic substances because the adsorption occurs mainly by electrostatic interactions between charged particles and specific accessible cotton fiber groups.
Based on all achieved results, it is evident that St-John's-wart water extract shows cationic, marigold anionic and hibiscus non-ionic character.
Therefore, from the environmental point of view it is a good substitution of chemical dyestuffs with plant extracts, considering the ionic character of both, fabric and plant extract solution.
That is providing not only a strategy for reducing risks and pollutants, but also an opportunity for new markets and new businesses that could be developed implementing environment to market policy.

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IZVOD

ADSORPCIJA EKSTRAKTA BILJAKA NA KATIONIZIRAN PAMUK

(Scientific paper)

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Pamuk, kao i većina tekstilnih vlakana je negativno nabijen u neutralnim i alkalnim vodenim otopinama. Bojila, optička bjelila i sredstva za oplemenjivanje također su negativno nabijena u vodenim otopinama. Adsorpcija tih sredstava je otežana radi postojanja navedenih odbojnih sila. Rad istražuje adsorpciju ekstrakata bilja na modificiran pamuk mercerizacijom i kationizacijom. Mercerizacija je najstariji postupak modifikacije pamuka još iz 19. stoljeća, dok je kationiziranje prisutno posljednjih desetak godina. U ovom radu kationiziranje pamuka provedeno je sa kationskim sredstvom tijekom mercerizacije i trgovačkim produktom Denimcol Fix-GF (Bezema). Elektrokinetička svojstva modificirane pamučne tkanine istražena su preko zeta potencijala, izoelektrične točke, točke nul-naboja i specifične količine površinskog naboja. Istražena je adsorpcija ekstrakta bilja sa i bez močila, te biomočila.

Ključne reči: katjonizacija, elektrokinetička svojstva, biljni ekstrakti.

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