

Eco-Friendly Functional Resist Printing for Viscose Fabrics

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Abstract:

This study focused on demonstrates improving the antibacterial activity and white resist printing for viscose fabrics in one step. Chitosan is the deacetylated derivative of chitin; it is a functional biopolymer which can be safely used for textile wet process. The efficacy of resisting agent was studied in comparison with standard unprinted illuminated fabrics. Results show that an improvement in antibacterial activity and dye blocking. In all cases, the reprinted fabrics were more oversensitive towards Gram positive bacteria than Gram negative bacteria due to bacteria structure. This method can be suitable for eco-friendly resist printing on viscose fabrics.

Keywords:

Eco-Friendly, White Resists Printing, Chitosan, Viscose fabrics, Antibacterial, Reactive Dyes

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INTRODUCTION

Today, the environmental impacts are now becoming an important factor during the selection of wet process of textile industry. However, due to increased awareness of the nature of polluting textiles effluents, social pressures are increasing on textile wet processing units.

Awareness about eco-friendly and sustainability wet process of textile industry is one of the important cases since clothes used and called the second skin for human. Owing to the global consumer demand, R&D effort is being carried out in field of new technologies (Periyasamy A. P., Rwahwire S., Zhao Y. (2019) Environmental Friendly Textile Processing. In: Martínez L., Kharissova O., Kharisov B. (eds) Handbook of Ecomaterials. Springer, Cham, 1521-1558).

Viscose fibers is Regenerated fibers made from the renewable raw material "cellulose" can only be wets pun as filaments with the aid of special solvents for the base polymer. It enjoys a unique position as the most versatile of all man-made fiber in end use application. From this treatment resulted from the ability to make the fiber chemically and structurally in ways that take advantage of the properties of cellulose and advantage of synthetic fiber (Rouette H. K., (2001) Encyclopedia of Textile Finishing. 3rd Edition, Springer).

The chemical antibacterial finishes have two different aspects of antibacterial protection. The first is the protection of the textile consumer against pathogenic or odor causing microorganisms. The second is the protection of

the textile itself from damage caused by mildew producing microorganisms.

The actual mechanisms by which antibacterial finishes control bacterial growth are extremely varied, ranging from preventing cell reproduction, blocking of enzymes, and reaction with the cell membrane to the destruction of the cell walls (Schindler W., Hauser P. (2004) Chemical Finishing of Textiles. CRC Press, New York).

The antibacterial agents can be broadly classified into: organic compounds such as chitosan, triclosan, quaternary ammonium compounds, and inorganic materials like metal and metal oxides. Many of antibacterial agents and textile auxiliaries have negative impacts on the textile user as well as the environmental (Ibrahim N. A., Eid B. M., Emam E. M., El-Zairy E. R., & Barkat S. R., (2019) Environmentally Sound Approach for Imparting Antibacterial and UV-Protection Functionalities to Linen Cellulose Using Ascorbic Acid. International Journal of Biological Macromolecules, 135, 88-96).

Chitosan is the deacetylated derivative of chitin, when the degree of deacetylation reaches about 50% (depending on the origin of the polymer); it becomes soluble in aqueous acidic media and is called chitosan. It consists of copolymers of glucosamine and N-acetyl glucosamine (Pillai C., Paul W., Sharma C. P. (2009) Chitin and Chitosan Polymers: Chemistry, Solubility and Fiber Formation. Progress in Polymer Science 34 (7): 641-650.).

The chemical structure of chitosan and cellulose are nearly similar, which chitosan contains NH₂

group but cellulose contains OH group on the glucose molecule. The amino groups of chitosan are responsible for the antibacterial activity (Ul-Islam M., Shah N., Ha J.H. et al. (2011) Effect of chitosan penetration on physico-chemical and mechanical properties of bacterial cellulose. Korean Journal Chemical Engineering 28 (8), 1736-1743), (Ibrahim H. M., Emam E. M., Tawfik M. T., & El-Aref A. T., (2019) Preparation of Cotton Gauze Coated with Carboxymethyl Chitosan and its Utilization for Water Filtration. Journal of Textile and Apparel, Technology and Management 11 (5), 1-11), (Thomas, S., Abraham J., et al. (eds) (2014) Polymer Composite. Vol. 3: Wiley-VCH Verlag GmbH & Co.).

Study Problem:

Awareness about eco-friendly and sustainability wet process of Viscose fibers for demonstrates improving the antibacterial activity and white

resist printing in one step.

Study Significance:

The present work aims to use chitosan as eco-friendly functional resisting agent for white resist printing viscose fabrics. The effects of ratio and concentration of various resist-printing agents and processing conditions are observed and discussed.

2. Experimental

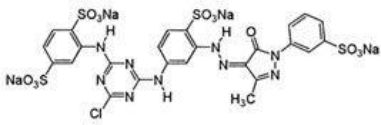
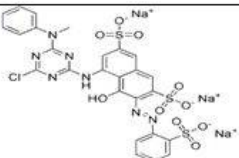
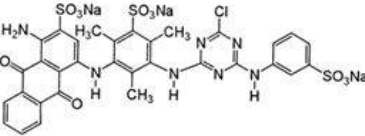
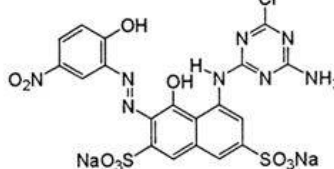
2.1. Material

The textile fabrics used in this study were commercially available scoured and bleached plain weave 100% viscose woven fabrics from Abu-Ela Co, Egypt.

2.2. Dyes

Reactive dyes were used Yellow P4G, Red P2B, Blue P3R, and Black DN reactive dyes from OHYOUNG, Korea shown in table 1.

Table 1 Chemical Structure Reactive dyes

Molecular Structure of Reactive dye	Name	C.I.
	Yellow P4G (Reactive Yellow 18) Single azo class	Yellow 18, 13245
	Red P2B (Reactive Red 24) Single azo class	
	Blue P3R (Reactive Blue 49) Anthraquinones class	Blue 49, 621526
	Black DN (Reactive Black 8) Single azo, Metal Complexes class	Black 8, 18207

2.3. Chemicals

Chitosan (degree of deacetylation of >85% Acros), Isopropyl alcohol (Acros), Citric acid, Acetic acid, Glycerin, Ammonium hydroxide (99%), Commercial sodium alginate (medium viscosity) and Commercial guar gum were used in this study.

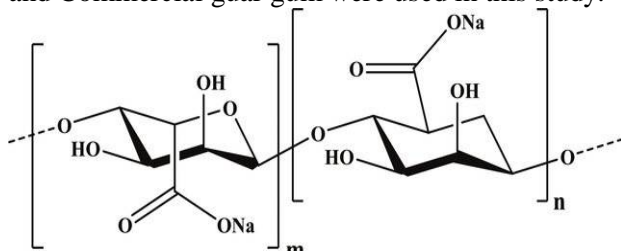


Figure 1 Chemical Structure of Sodium Alginate

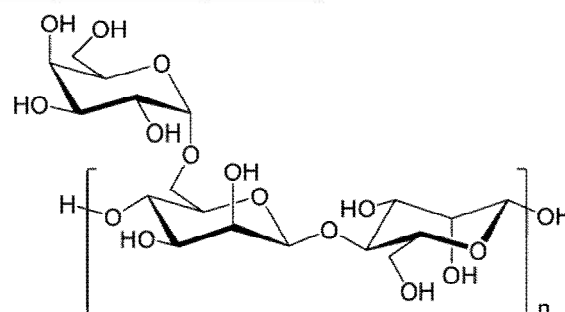


Figure 2 Chemical Structure of Guar Gum

2.4. Methods

2.4.1. Preparation of Resist Agent for Printing Paste

The stock solution of resist agent preparation

following blew:

1. Fill flask with 98ml of purified water.
2. Complete to 100 ml with pure Glacial acetic acid.
3. Put the beaker on a hot plate magnetic stirrer for 5 minutes.
4. Rise the temperature to 30 °c.
5. Put the chitosan gradually (from 0.4%-2%) otherwise it may cause a rapid rise in viscosity which may cause the stirrer to halt down.
6. Keep stirring for 6 hours (overnight) and every hour put a portion of the chitosan to avoid rapid rise in viscosity.
7. After that put 10 grams of citric acid and stir for 15 minutes.

Constituent	Parts
Resist agent paste	X = (0.4%, 0.8%, 1.2%, 1.6%, 2%)
Citric acid	Y = (5%, 10%, 20%, 30%, 40%)
Acetic acid	2
Glycerin	5
Isopropyl alcohol	5
water	Z
Total	100

2.4.2. Preparation of Reactive Printing Paste

Reactive Dye Printing Recipe following blew:

Constituent	g/Kg
Reactive dye	25
Thickener	350
Urea	250
Sodium carbonates	15
water	410
Total	1000

2.4.3. Printing procedure

All printing recipes (resist or reactive) were applied to fabric via flat screen printing technique to determine the optimum recipe for white resist printing. The resist printing recipe were applied first then dried at 100 °c for 4 minutes, then printed by reactive dye using manual flat screen printing method. The printed fabric is then fixed by steaming at 102 °c for 10 minutes. An additional resist-printing paste, with a constant resist agent concentration of (from 0.4%-2%) and individually mixed with citric acid (from 5%-40%) was prepared for comparison. The printed fabrics then washed by using a hot water with non-ionic detergent, then cold water then dried.

2.5. Measurements

Nitrogen content was determined using micro-Kehjeldal Procedure (Vogel, A.I., (1962) Practical organic chemistry. Longmans, Green, London. 627), color strength of the prints (k/s) was

measured at the wave length of the maximum absorbance using a spectrophotometer model (CM-3700A), and calculated by the Kubelka Munk equation (Ibrahim H., El-Zairy E., Emam E. M., & Saad E. A., (2019) Combined antimicrobial finishing & dyeing properties of cotton, polyester fabrics and their blends with acid and disperse dyes. Egyptian Journal of Chemistry 62 (5), 965-976.)

$$K/S = (1-R) / 2R$$

Where K and S are the absorption and scattering coefficient respectively, and R and 2R are the decimal fractions of the reflectance of the printed and unprinted fabrics, respectively. A smaller (k/S) value represent of a higher resist-printing effect.

Dye resist effectiveness (RE) of each studded factors was quantified by calculating the difference between values from the reflectance values (K/S) of the areas printed with resisting pasts and unprinted ground (Haarer J., & Hocker H., (1994) New Reactive Auxiliaries for the Dye-Resist Treatment of Wool: Part II. textile Res. J. 64(10), 578-583).

The antibacterial activity against Gram positive (G+ve, S.aureus) and Gram negative (G-ve, E. coli) pathogenic bacteria was qualitatively determined according to AATCC test method (147-1988) expressed as zone of growth inhibition (ZI, mm).

$$[(K/S \text{ unprinted background}) - (K/S \text{ resist-printed area})]$$

$$RE = \frac{[(K/S \text{ unprinted background}) - (K/S \text{ resist-printed area})]}{(K/S \text{ unprinted background})} \times 100$$

3. Results and Discussion

This study focused on demonstrates upgrading the antibacterial activity and white resist printing for viscose fabrics in one step. Chitosan was used as the eco-friendly physical by its shelf and chemical resist-printing agent in acidic medium.

Physical resist printing agents is used firstly to prevent permeation of dyes (to make them water-repellant), whereas chemical resist printing agents is conducive for: (1) dye dissolution (oxidative or reductive), (2) dye insolubility (by adding anti-solution agent), and (3) the blocking of dye sites on fibers (Yen M. S., Chen C. W., (2011) Effect of chitosan on resist printing of cotton fabrics with reactive dyes. African Journal of Biotechnology, 10 (8), 1421-1427).

3.1. Effect of Chitosan Concentration on the Resist-Printing Effectiveness and Antibacterial Activity

Resist- printing pastes containing different concentrations of chitosan were prepared to

observe the effect of chitosan on processed viscose fabrics. Four different reactive dyes were evaluated.

From Table 2 and Figure 3 are shows that the resist-printing effect increases with increasing

chitosan concentration up to 1.6% for C.I. Reactive yellow 18, C.I. Reactive Red 24 and C.I. Reactive Blue 49 and up to 0.8% for C.I. Reactive Black 8.

Table 2 Effect of Chitosan Concentration on the Resist-Printing Effectiveness (RE)

Background K/S	C.I. Reactive Yellow 18		C.I. Reactive Red 24		C.I. Reactive Blue 49		C.I. Reactive Black 8	
	15.13		30.41		12.44		22.47	
	K/S	RE%	K/S	RE%	K/S	RE%	K/S	RE%
0	0.48	96.82	0.65	97.86	0.37	97.01	0.61	97.28
0.40	0.45	97.02	0.48	98.42	0.26	97.90	0.46	97.95
0.80	0.30	98.01	0.41	98.65	0.24	98.07	0.44	98.04
1.20	0.22	98.23	0.34	98.88	0.22	98.23	0.94	95.81
1.60	0.20	98.67	0.28	99.07	0.21	98.61	1.21	94.61
2.0	0.39	97.42	0.50	98.35	0.28	97.74	0.89	96.03

-Printing paste: see experimental part, citric acid 10% the samples were fixed with saturated steam at 102°C for 10 minutes.

These results indicate that the molecular structure of chitosan plays an important role in this treatment which is same as viscose fabrics except for hydroxyl group which is substituted with amino group in case of chitosan may distinguish a chemical resist-printing effect by blocking of dye sites on fibers as a negatively charged polymer.

Furthermore, chitosan induces a physical resist-printing effect by prevent penetration of dyes (Yen M. S., Chen C. W., (2011) Effect of chitosan on resist printing of cotton fabrics with reactive dyes. African Journal of Biotechnology, 10 (8), 1421-1427).

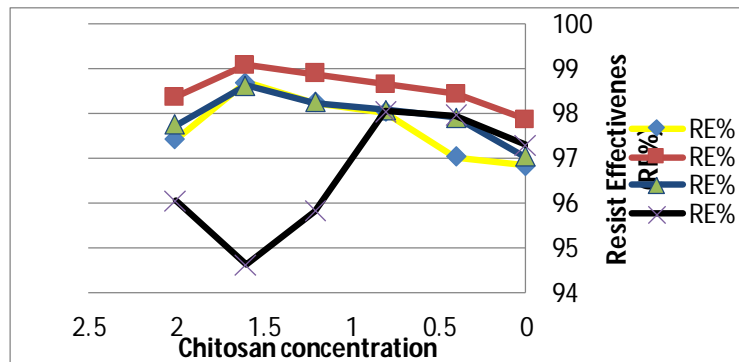


Figure 3 Variations of RE% for Printed Samples by Different Chitosan Concentration

Table 3 Effect of Chitosan Concentration on Antibacterial Activity

Dyes	Chitosan Conc. %	Blank			0.4%			1.6%		
		^a ZI (mm)		^b N (%)	^a ZI (mm)		^b N (%)	^a ZI (mm)		^b N (%)
		G+ve	G-ve		G+ve	G-ve		G+ve	G-ve	
C.I. Reactive Yellow 18		0	0	0.310	8.5	6	0.391	10.5	8	0.480
C.I. Reactive Red 24		0	0	0.311	8	6	0.385	9	6	0.488
C.I. Reactive Blue 49		0	0	0.245	7	5	0.350	8	6	0.444
C.I. Reactive Black 8		1.5	0	0.321	9	7	0.401	12	8.5	0.497

-Printing paste: see experimental part, citric acid 10% the samples were fixed with saturated steam at 102°C for 10 minutes, ^aZI (mm); zone of growth inhibition; G+ve: *S. aureus*; G-ve: *E. coli*; ^bN (%): nitrogen content.

From table 3 these results indicate that the increasing in chitosan concentration antibacterial activity increased of reprinted fabrics and increasing in nitrogen content.

Increasing of antibacterial activity towards gram-positive higher than gram-negative in reprinted fabrics.

The zone of inhibition (diameter) was recorded in each case. The results of untreated samples show clear growth of bacteria under them with no zone of inhibition, indicating that the unprinted fabric by itself does not inhibit bacterial activity. The investigated treated samples inhibit bacterial growth as is evident from the absence of growth under all samples. In all cases, the treated fabrics were more susceptible towards Gram positive bacteria (*S. aureus*) than Gram negative bacteria (*E. coli*) due to bacteria structure.

3.2. Effect of Citric Acid Concentration on the

Resist-Printing Effectiveness

In an alkali medium, Most of reactive dyes chemical reaction of cellulose fabrics. So for this reason organic acids and acid salts may be used as chemical blocking agents for preprint resists under reactive dyes especially vinyl sulphone class (Miles L. W. C., (2003) Textile Printing, Revised Second Edition, Society of Dyers and Colourists, 217-225).

Citric acid is nonvolatile organic acid; it has a tri carboxylic acid that is only active in alkali solution.

From Table 4 and Figure 4 can be investigate the effect of using citric acid in the resist printing paste in different ratios to chitosan for show the effect of combination of chemical and physical resist printing effect, different printing pastes were prepared using various concentrations of citric acid ranging from 0 to50 %

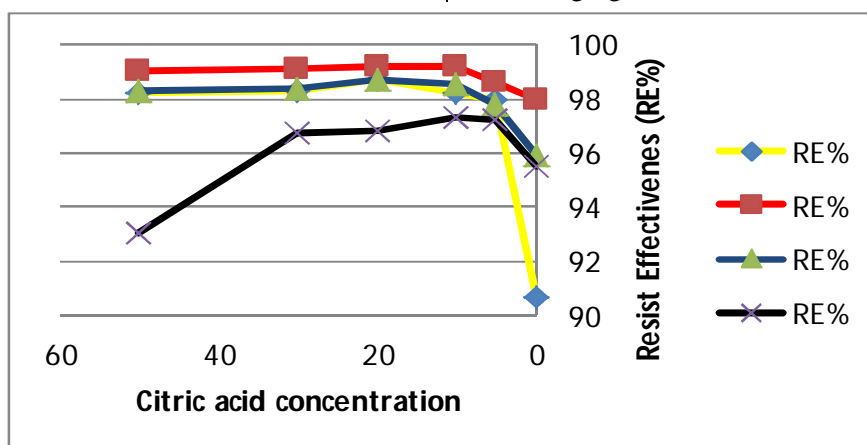


Figure 4 Variations of RE% for Printed Samples by Different Citric Acid Concentration

It is obvious that increasing the citric acid concentration decreases the color strength until it reaches to 20% for C.I. Reactive yellow 18 and to 10% for C.I. Reactive Blue 49, C.I. Reactive Red

24 and C.I. Reactive Black 8. The reaction between reactive dyes used and citric acid shown in Figure 5:

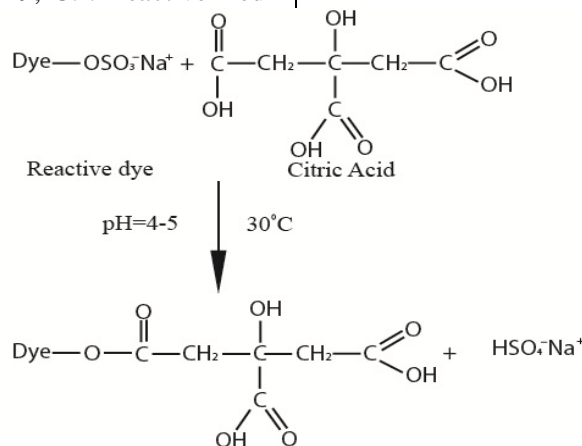


Figure 5 the Reaction between Reactive Dyes Used and Citric Acid

At low pH, chitosan is present as a cationic polymer, with a high charge density, and therefore may function as a good flocculent for negatively charged polymers (Rekaby M., El-Hennawi H. M.,

Shahin A. A., Ragheb A. A., (2013) Utilization of biopolymer in resist printing of linen fabrics using reactive dyes. Carbohydrate Polymers, 98, 1540-1546).

The results indicate that using the citric acid in resist printing paste, the bond strength between the dyes and the processed viscose fabrics is decreased, resulting in a chemical resist-printing effect. The mechanism of acidic medium from acids addition show in equation:

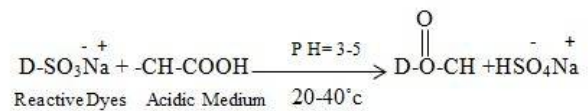


Table 4 Effect of Citric Acid Concentration on the Resist-Printing Effectiveness (RE)

Background K/S	C.I. Reactive Yellow 18		C.I. Reactive Red 24		C.I. Reactive Blue 49		C.I. Reactive Black 8	
	15.13		30.41		12.44		22.47	
	K/S	RE%	K/S	RE%	K/S	RE%	K/S	RE%
Citric acid Conc. %								
0	1.41	90.68	0.63	97.93	0.51	95.90	1.02	95.46
5	0.31	97.95	0.41	98.65	0.27	97.83	0.62	97.24
10	0.27	98.21	0.24	99.21	0.18	98.55	0.61	97.29
20	0.20	98.67	0.25	99.18	0.16	98.71	0.71	96.84
30	0.26	98.28	0.26	99.15	0.20	98.39	0.74	96.70
50	0.27	98.21	0.30	99.01	0.21	98.31	1.56	93.06

-Printing paste: see experimental part, chitosan con.1.6%, the samples were fixed with saturated steam at 102°C for 10 minutes.

3.3. Effect of Steaming Temperature on the Resist-Printing Effectiveness

Steaming operation of the printed samples is the most important technological step. It is necessary to swell the thickener film, swell the viscose fibers to allow penetration of the used chemicals. In this step the chemical reaction between resist agent and reactive dyes will be done depend on the

effect of saturated steam temperature on the resist-printing effectiveness. For a given resist-printing conditions, it appears that steaming at 102°C for 10min. would be the proper conditions for attuning higher RE values. Further rising in using temperature, i.e. beyond 130°C for 10min., has practically no effect.

Table 5 Effect of Steaming Temperature on the Resist-Printing Effectiveness (RE)

Background K/S	C.I. Reactive Yellow 18		C.I. Reactive Red 24		C.I. Reactive Blue 49		C.I. Reactive Black 8	
	15.13		30.41		12.44		22.47	
	K/S	RE%	K/S	RE%	K/S	RE%	K/S	RE%
Steaming temperature								
102°C	0.17	98.88	0.22	99.28	0.14	98.87	0.33	98.53
110°C	0.23	98.48	0.25	99.18	0.17	98.63	0.27	98.80
120°C	0.26	98.28	0.32	98.95	0.21	98.31	0.29	98.71
130°C	0.25	98.35	0.26	99.15	0.19	98.47	0.37	98.35

-Printing paste: see experimental part, chitosan con.1.6%, citric acid 10%, the samples were fixed with saturated steam for 10 minutes.

From Table 5 and Figure 6 show that The best result for steaming temperature was 102°C for reactive dyes (yellow 18, red 24 and blue 49) but

the best steaming temperature was 110°C for reactive black 8, at temperatures above 120°C, the resist-printing effect subsided.

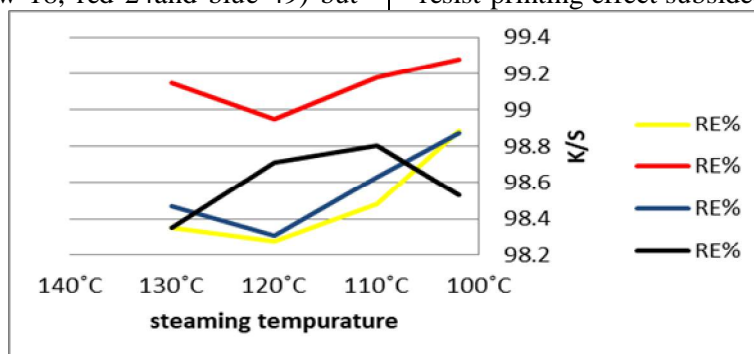


Figure 6 Variations of RE% for Printed Samples by Different Steaming Temperature

3.4. Effect of Steaming Time on the Resist-Printing Effectiveness

Table 6 and Figure 7 show the effect of steaming time on the resist-printing effectiveness. It's clear that prolonging the steam fixation time up to 10min. at 102°C is accompanied by an improvement in RE values of obtained resist-

prints, most probably due to the enhancement in the adsorption and diffusion. Further increase in fixation time, i.e. up to 30min. at 102°C has practically a slight negative impact on the resist-printing effectiveness that because of adversely affecting the thickener film properties.

Table 6 Effect of Steaming Time on the Resist-Printing Effectiveness (RE)

Background K/S	C.I. Reactive		C.I. Reactive		C.I. Reactive		C.I. Reactive	
	Yellow 18		Red 24		Blue 49		Black 8	
	15.13		30.41		12.44		22.47	
Steaming time	K/S	RE%	K/S	RE%	K/S	RE%	K/S	RE%
5 min	0.19	98.74	0.17	99.44	0.14	98.87	0.21	99.06
10 min	0.18	98.81	0.16	99.47	0.12	99.04	0.20	99.11
15 min	0.20	98.68	0.19	99.37	0.15	98.79	0.23	98.98
20 min	0.22	98.55	0.20	99.38	0.13	98.95	0.24	98.93
30 min	0.25	98.35	0.22	99.28	0.13	98.95	0.40	98.22

-Printing paste: see experimental part, chitosan con. 1.6%, citric acid 10%, the samples were fixed with saturated steaming at 102°C.

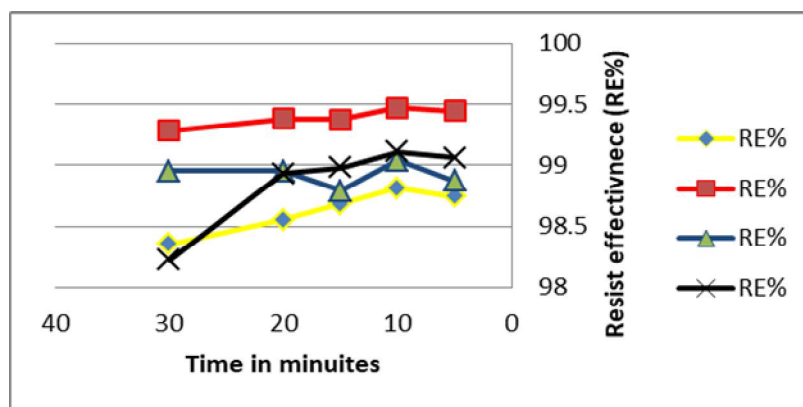


Figure 7 Variations of RE% for Printed Samples by Different Steaming Time

The data in Figure 7 show an increasing resist-printing effect with steaming time. However, steaming times greater than 10 minutes were unnecessarily long and would not be cost-effective.

The last duration considered more suitable steaming time to permit the sufficient supply steam especially at elevated temperatures to swell the substrate and diffuse the chemicals as well as resisting agent.

4. Conclusion

Chitosan was used as eco-friendly physical and chemical resist-printing agent with a good antibacterial activity. The resist-printing effectiveness increases with increasing chitosan concentration up to 1.6% for C.I. Reactive yellow 18, C.I. Reactive Red 24, C.I. Reactive Blue 49 and up to 0.8% for C.I. Reactive Black 8. These results indicate that chitosan may distinguish a chemical resist-printing effect by blocking of dye

sites on fibers as a negatively charged polymer. Furthermore, chitosan induces a physical resist-printing effect by prevent penetration of dyes. The increasing of citric acid concentration decreases the color strength until it reaches to 20% for C.I. Reactive yellow 18 and to 10% for C.I. Reactive Blue 49, C.I. Reactive Red 24 and C.I. Reactive Black 8. The results indicate that using citric acid in resist printing paste; the bond strength between the dyes and the processed viscose fabrics is decreased, resulting in a chemical resist-printing effect. For a given resist-printing conditions, it appears that steaming at 102°C for 10min. would be the proper conditions for attuning higher RE values. Further rising in using temperature, i.e. beyond 130°C for 10min., has practically no effect.

References:-

1. AATCC test method (147-1988) expressed as zone of growth inhibition (ZI, mm).

2. Haarer J. & Hocker H., (1994) New Reactive Auxiliaries for the Dye-Resist Treatment of Wool: Part II. *textile Res.* 64 (10), 578-583.
3. Ibrahim H., El-Zairy E., Emam E. M., & Saad E. A., (2019) Combined antimicrobial finishing & dyeing properties of cotton, polyester fabrics and their blends with acid and disperse dyes. *Egyptian Journal of Chemistry* 62 (5), 965-976).
4. Ibrahim H. M., Emam E. M., Tawfik M. T., & El-Aref A. T., (2019) Preparation of Cotton Gauze Coated with Carboxy methyl Chitosan and its Utilization for Water Filtration. *Journal of Textile and Apparel, Technology and Management* 11 (5), 1-11.
5. Ibrahim N. A., Eid B. M., Emam E. M., El-Zairy E. R., & Barkat S. R., (2019) Environmentally Sound Approach for Imparting Antibacterial and UV-Protection Functionalities to Linen Cellulose Using Ascorbic Acid. *International Journal of Biological Macromolecules*, 135, 88-96.
6. Martínez L., Kharissova O., Kharisov B. (eds) *Handbook of Eco-materials*. Springer, Cham, 1521-1558.
7. Miles L. W. C., (2003) *Textile Printing. Revised Second Edition*, Society of Dyers and Colourists, 217-225.
8. Periyasamy A. P., Rwahwire S., Zhao Y. (2019) Environmental Friendly Textile Processing.
9. Pillai C., Paul W., Sharma C. P. (2009) Chitin and Chitosan Polymers: Chemistry, Solubility and Fiber Formation. *Progress in Polymer Science* 34 (7): 641-650.
10. Rekaby M., El-Hennawi H. M., Shahin A. A., Ragheb A. A., (2013) Utilization of biopolymer in resist printing of linen fabrics using reactive dyes. *Carbohydrate Polymers*, 98, 1540-1546.
11. Rouette H. K., (2001) *Encyclopedia of Textile Finishing*. 3rd Edition, Springer.
12. Schindler W., Hauser P. (2004) *Chemical Finishing of Textiles*. CRC Press, New York.
13. Thomas, S., Abraham J., et al. (eds) (2014) *Polymer Composite. Vol. 3: Wiley-VCH Verlag GmbH & Co.*
14. Ul-Islam M., Shah N., Ha J.H. et al. (2011) Effect of chitosan penetration on physico-chemical and mechanical properties of bacterial cellulose. *Korean Journal Chemical Engineering* 28 (8), 1736-1743.
15. Vogel, A.I., (1962) *Practical organic chemistry*. Longmans, Green, London. 627.
16. Yen M. S., Chen C. W., (2011) Effect of chitosan on resist printing of cotton fabrics with reactive dyes. *African Journal of Biotechnology*, 10 (8), 1421-1427.