APPLICATION OF CHITOSAN IN THE RECYCLING OF SPENT WASH-OFF LIQUOR FROM COTTON DYEING

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ABSTRACT: *Efficient use of water and wastewater treatment has become the priority in the textile industry. The present study was carried out to recycle the spent wash-off liquor from cotton dyeing by the application of chitosan used as coagulant. The objective of this experimental study was to limit water consumption by reusing the wash-off liquor after treating with chitosan. To achieve the aim of the study, cotton fabric was dyed with four different reactive dyes, the samples were then washed with the treated wash-off liquor and tested on the basis of Commission International de l'Eclairge Lab (CIE) values (ΔL^*, ΔC^* and ΔE^*). The results were organized on the basis of color removal efficiency and total color difference (ΔE^*) values. From the four dyes C.I Reactive Black 5 showed maximum results, as its total color difference ($\Delta E^*=0.04$) between standard and sample was within acceptable tolerance limit. For C.I Reactive Yellow 145 best results were produced because its color removal efficiency was 94.21 and its ΔE^* value was closer to the acceptable tolerance limit. An appropriate result for C.I Reactive Red 194 was observed as its color removal efficiency was 86.80% and its ΔE^* value (0.35) was within the acceptable tolerance limit. Color removal efficiency for the C.I Reactive Blue 221 was 48.83% so it means that chitosan (5mg/l) did not showed best results on this dye.*

KEYWORDS: Coagulation, Chitosan, Wash off treatment, Cotton dyeing, Textile wastewater

INTRODUCTION

Anthropogenic activities such as agricultural, industrial and commercial are the sources of damaging physical environment and industries produce various types of pollution, which ultimately contaminates water, land, and air [1]. Water pollution from the industrial sectors one of the major issues as high consumption of water follows large volume of wastewater generated in different processes and pretreatments [2].

Textile industry uses million gallons of water per day in different processes. It is estimated that 1 kg of textile fabric requires approximately 200 liters of water. Dying units are mainly responsible for wastewater pollution. Synthetic dyes are heavily used in the textile, cosmetics, food, paper, and leather, printing and plastic industries to offer good color varieties and fastness properties. It is estimated that about 100,000 different synthetic dyes are produced annually [3, 4& 5].

In wastewater effluent presence of even low concentration of dye is highly visible and objectionable. Dyes are mutagenic and carcinogenic and are very toxic to flora and fauna of the water bodies [6,7& 8]. Due to persistent and recalcitrant nature of dyes, textile wastewater creates environmental issues directly or indirectly, including groundwater contamination through topsoil percolation reduces dissolved oxygen of other water bodies; suppress the re-oxygenation ability of streams killing of aquatic life and eutrophication [9].

Generated wastewater contains a wide variety of chemicals such as pigments and dyes, wash-off detergent, caustic soda, starch, waxes and urea which cause the increase in BOD and COD of wastewater [4].Wastewater treatment has become a necessity for the industries before discharging into the water bodies in order to follow the environmental regulations. Treated water is less harmful when return to natural environment. Sustainable practices are also useful in the textile sector either by consuming less water which leads to obviously less wastewater generation or using recycled water after treatment. Worldwide adopted methods for de-colorization of the dyes in the textile effluents are flocculation /coagulation, adsorption and the biological treatment which are very effective in the removal of color in wastewater and economically feasible [10, 11 &12].

Currently there is a discussion to use shrimps or crabs chitin for the treatment of wastewater. These chitinous materials have many other applications including use in food processing, agriculture, medicines, cosmetics and especially in the field of biotechnology [13].Carboxyl methyl chitosan (NOCC) with a different molecular weight (Mw) and degree of the substitution (DS) have been used in removing of unfixed dyes from the reactive cotton dyeing. It has been studied that many factors involved in wash-off effectiveness of the NOCC such as an increase in pH, increases the effectiveness of NOCC. The study determines that NOCC has a potential of removing the unfixed reactive dyes from the cotton fabrics [14].

Coagulation and flocculation techniques are commonly used in textile wastewater to remove Congo Red (CR) dye by using different coagulants such as Chitosan, Maize Seed Powder (MSP) and Surjana Seed Powder (SSP). It has been studied that chitosan has the potential of maximum color removal in the wastewater [15]. Under some suitable conditions such as acidic solutions and the stoichiometric ratio between the amine groups of the biopolymer and the sulfonic groups in acid blue 92 dye, chitosan works more efficiently even in low quantity [16].

The purpose of the study is to provide an efficient and cost effective method to textile industries for treating dyes containing effluents as well as to reduce the consumption of water used in the wash-off process of dyed cotton fabric through reusing. In this regards the effectiveness of chitosan was determined and water quality parameters were tested.

Quality of dyeing (according to color difference, total color difference and color fastness) of coagulant treated fabrics is compared with regard to the conventionally washed fabric.

MATERIALS AND METHODS

Materials used in the study were fabrics auxiliary, chemicals, dyes, glass wares (Pyrex, IWAKI) and lab equipment. A 100% pure knitted fabric (cotton) having 200GSM bleached (grams per square meter) was used in the present research work. For exhaustion and fixation sodium carbonate (Na2CO3) and sodium chloride (NaCl) were used respectively as well as acetic acid was used for neutralization in wash-off process. Soaping agent Dekol SN 1g/l was used in the soaping step. Chitosan was used as a coagulant. Reactive dyes were selected in this study because of their usage in textile (cotton) dyeing. The dyes used in this study were reactive Red194, Yellow145, Blue221 and Black5 provided by KISCO. The wastewater collected from the wash-off step was analyzed for general parameters like COD, pH, TDS, color, turbidity and conductivity.

The dyeing was completed using an isothermal process. 1:15 liquor ratios were retained to dye cotton fabric. Standard dyeing was done by taking the 5% depth shade of dye at 60°C. For the standard dyeing 80g/l salt was well mixed in the dye solution. 5g of cotton sample was put in the solution and then left that sample in water bath for heating purpose which will be upto60°C. When the temperature reached 60°C, 20g/l of sodium carbonate (soda) was added and mixed well. Kept the sample in water bath for 45 minutes at 60°C and the temperature should be maintained. To reduce the unevenness dyeing on the fabric, constant mixing should be done in the whole process.

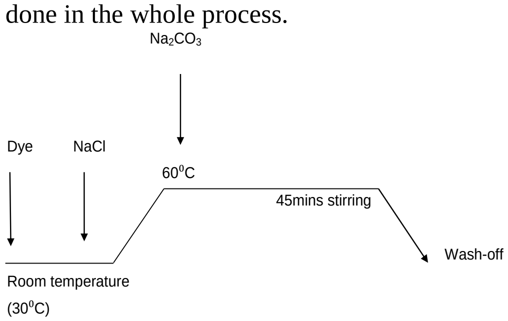


Fig-1.1 Standard Isothermal for Dyeing

Wash-off Process

After the dyeing process, fabric was pressed to remove extra dye liquor and further subjected to the wash-off processes. Wash-off process was performed with 1:10 liquor ratio. The dyed fabric (cotton sample) was then rinsed with water, squeezed and dried in the open air.

Wash-off Process (standard): the dyed fabric was rinsed to remove unfixed dyes which deposited on the surface of the cotton fabric. Wash-off operation steps are given in table 1.

Sample Wash-off Process

Coagulant (Chitosan) was then added in the spent standard wash-off liquor and its pH was maintained at 6. After 2hrs the mixture was filtered by using filtration assembly and was used in the sample wash-off process.

Table 1: Standard Wash off cycle

Step	Operation	Temperature
1	Cold Rinse	30^0C
2	Neutralization with Acetic Acid	30^0C
3	Warm Wash	50^0C
4	Hot Wash	80^0C
5	Warm Wash	50^0C
6	Cold Rinse	30^0C

Measurement and Analysis

Analytical measurement include the determination of fastness properties, color removal (%) and color differences (ΔL*, Δa*, Δb*, ΔC*, ΔH* and ΔE*) between coagulant washed fabric and reference [17].

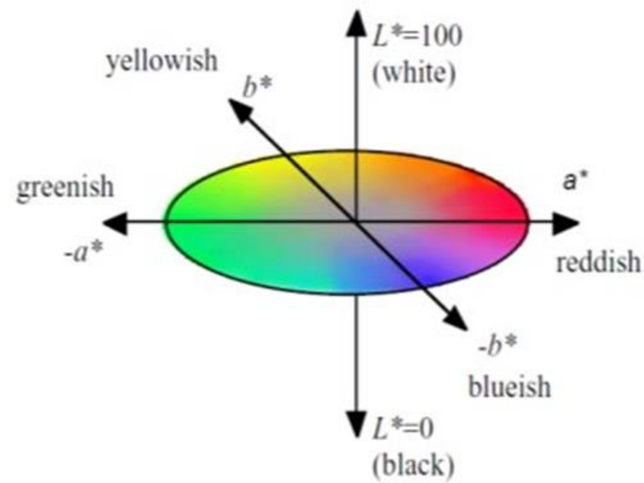


Fig-1.2 Color Coordinates

RESULTS AND DISCUSSION

The results of this study were revealed according to color removal efficiency and CIE lab values (ΔL*, ΔC* and ΔE*), which show the total color difference and depth of shade between standards along with sample respectively. K/S value, dry and wet rubbing fastness was also studied. All the values (ΔL*, Δa*, Δb*, ΔC*, ΔH*, ΔE*) were taken by D65, 10 degree illuminating source and spectrophotometer was used to study K/S values, dry and wet fastness. The color removal efficiency was measured by the following formula:

$$Color\ removal\ (\%) = Ao - \frac{A}{Ao} X\ 100$$

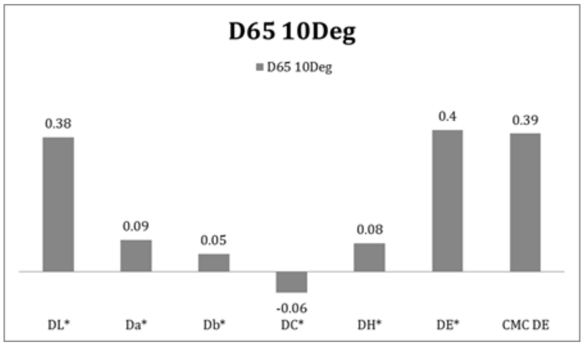
Where,

A_o = Absorbance of the liquor from conventional wash-off

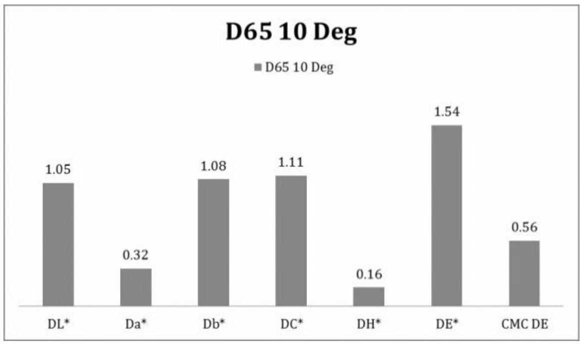
A = Absorbance of the liquor from coagulant wash-off

Color Measurement

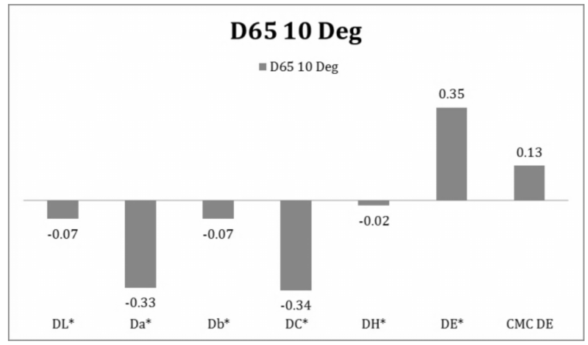
Chitosan wash-off fabric after the wash-off is subjected to CIE lab test. The color difference values measured in terms of ΔL*, Δa*, Δb*, ΔC*, ΔH*, ΔE*.



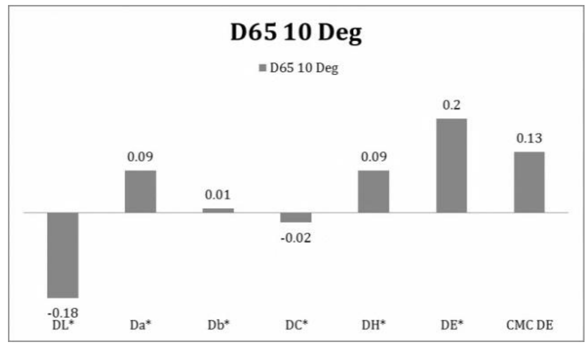
Graph 1.1-Values of CIE lab of Sample dyed with C.I Reactive Black 5



Graph 1.2- Values of CIE lab of Sample dyed with C.I Reactive Yellow 145



Graph 1.3- Values of CIE lab of Sample dyed with C.I Reactive Red 194



Graph 1.4- Values of CIE lab (Sample dyed with C.I Reactive Blue 221

Graph 1.1 shows the color difference values of sample with respect to standard fabric, both dyed with the C.I Reactive Black 5. As ΔL* value is 0.38 which means that the sample is lighter in color than the standard and ΔC* reading is -0.06 which means sample is duller than standard. Graph 1.2 shows that ΔL* for C.I Reactive Yellow 145 is 1.05 which means sample is lighter than the standard. In graph1.3ΔL* value for C.I Reactive Red 194 is -0.07 which shows the sample is darker than standard and ΔC* reading is -0.03 that means the cotton sample is duller than the standard. Graph 1.4 shows that ΔL* for C.I Reactive Blue 221 is -0.18 that means the cotton sample is darker than the standard while ΔC* reading -0.02 indicates sample is duller than standard.

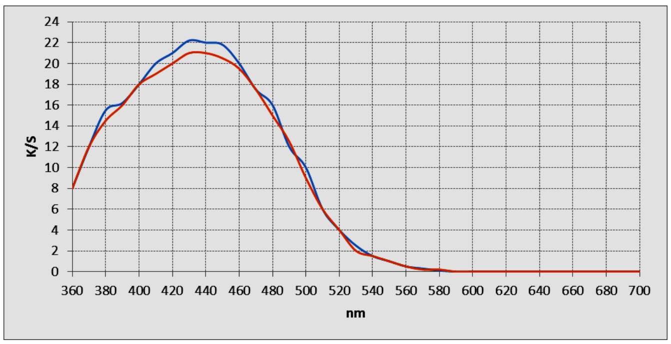
Table 2: Wash fastness test of all dyed and coagulant treated samples

Sr.#	Fabric	Cellulose Acetate	Un-Mercerized Cotton	Nylon 6.6	Polyester Terylene	Acrylic (Courtelle)	Wool Worsted	Crocking
1	Standard Black	5	4.5	5	5	5	4.5	Dry 4.5 Wet 2
2	Trial Black	5	5	5	5	5	4.5	Dry 4.5 Wet 2
3	Standard Yellow	5	4.5	5	5	5	4.5	Dry 4.5 Wet 2.3
4	Trial Yellow	5	4.5	5	5	5	4.5	Dry 4.5 Wet 2.3
5	Standard Red	5	4.5	4.5	4.5	4.5	4.5	Dry 4.5 Wet 2
6	Trial Red	5	4.5	4.5	4.5	4.4	4.5	Dry 4.5 Wet 2
7	Standard Blue	5	4.5	4.5	5	5	4.5	Dry 4.5 Wet 2.3
8	Trial Blue	5	4.5	5	5	5	4.5	Dry 4.5 Wet 2.3

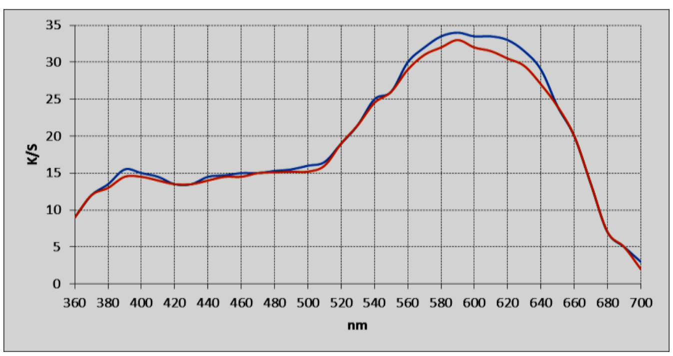
Measurement of Wash Fastness

Wash fastness test of all the dyed and coagulant treated samples was carried out by ISO 105:C06/C2S wash test (50^{0}C) using SDC multi-fiber as adjacent fabric.

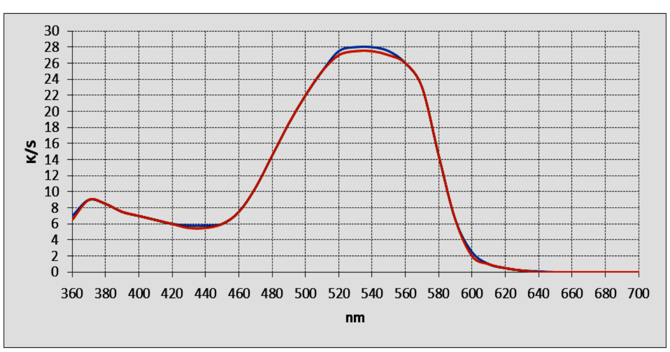
For the C.I Reactive Black 5 un-mercerized cotton fabric standard value is 4.5 while for sample it is 5 which show little shade change. For C.I Reactive Yellow 145 un-mercerized cotton fabric standard and sample value is same (5) which indicates no shade change. For C.I Reactive Red 194 and C.I Reactive Blue 221 un-mercerized cotton fabric values for standard and sample (4.5) are same wh ich indicates that there is no change in shade. Cellulose acetate value of sample and standard for all the dyes is same which also indicate that the results were excellent. standar d and sample (4.5) are same which indicates that there is no change in shade. Cellulose acetate value of sample and standard for all the dyes is same which also indicate that the results were excellent.



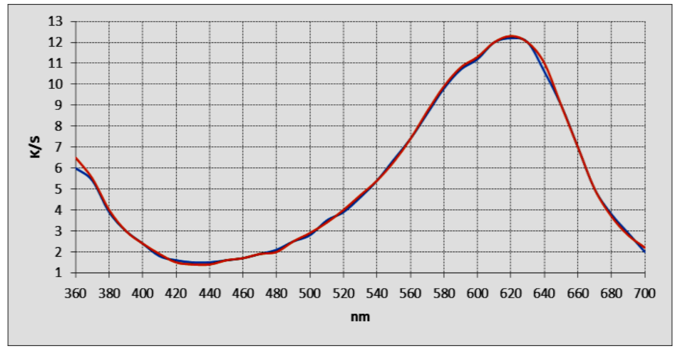
Graph 1.5- Values of K/S (Sample dyed with C.I Reactive Black 5)



Graph 1.6- Values of K/S (Sample dyed with C.I Reactive Yellow 145)



Graph 1.7 Values of K/S (Sample dyed with C.I Reactive Red 194)



Graph 1.8- Values of K/S (Sample dyed with C.I Reactive Blue 221)

Color Strength (K/S Value)

Strength indices describe how weak or strong a sample is in comparison to the reference standard used. Blue line indicates the standard while red line indicates the sample.

Graph 1.5 shows that K/S value of sample is less than standard which is 34 and its approximate % age color strength is 91.4 which mean sample is weaker in color than standard. Graph 1.6 shows K/S value for sample is less as compare to standard which is 22 and its approximate % age color strength is 97.72. Graph 1.7 shows that K/S value for sample is less than standard which is 28 and its approximate % age color strength is 99.28. For graph 1.8 K/S value for sample is also less than standard which is 12.3 its approximate % age color strength is 99.18 all these values shows that sample is weaker than standard in color.

Quality of Water Parameters

To check the quality of water used in dying and wash-off process, different water quality parameters were observed such as pH, conductivity, chemical oxygen demand (COD), temperature, and total dissolved solids (TDS). TDS values for sample were more than that of standard at all wash-off stages. Apparently total dissolved solids for sample increased but they were reduced because for sample wash-off we used the recycled standard wash-off liquor. The value of conductivity also increased for sample as compare to standard at each wash-off stage which means that the water became more polluted. Chitosan was observed as an effective coagulant in reducing COD level (72.5%) and turbidity (94.9%) in the treatment of textile waste water [18].

Color Removal Efficiency

The color removal efficiency of chitosan was 94.2% for C.I Reactive Yellow 145, 86.80% for C.I Reactive Red 194 and for C.I Reactive Blue 221 it was 48.83%.In the similar study conducted by Zoonozi et al, 90% color removal was detected in the Acid blue 292 and Acid red 398 by using chitosan [19]. In a research conducted in India, Maize Seed Powder (MSP), Surjana Seed Powder (SSP) and Chitosan as coagulants were used for the removal of dyes in which 62.8%, 47.0% and 42.8% were observed respectively [15].

CONCLUSIONS

Coagulation treatment is an important treatment in the field of water and waste water treatment. For C.I Reactive Yellow 145 and C.I Reactive black 5 ΔL* values 1.05 and 0.38 respectively show the samples are slightly lighter than the standard. The values of ΔE* (1.54 and 0.04), respectively, for the C.I Reactive Yellow 145 and C.I Reactive black 5,reveal the total color difference between the sample and standard which are closer to the acceptable tolerance limit i.e. ΔE*≤1.00. For C.I Reactive Yellow 145 and C.I Reactive black 5 K/S values are 21.5 and 32 which are below the standard, color strengths are 97.72% and 91.42% whereas the wet fastness is 2.3 and 2 subsequently The color removal efficiency of the former is 94.21%. The value of dry fastness for both is 4.5.For C.I Reactive Red 194 and C.I Reactive Blue 221 ΔL* values -0.07 and -0.18 respectively, show that the samples are darker and duller in color than the standard. ΔC* value (-0.34 and -0.02) and ΔE* value (0.35 and 0.20) shows that the samples are duller than the standard and within the acceptable tolerance limit. K/S values, respectively, for C.I Reactive Red 194 and C.I Reactive Blue 221 are 27.8 and 12.2 which are less than the standard, their color strengths are 99.28% and 91.8% whereas the wet fastness is 2 and 2.3, color removal efficiencies are 86.80% and 48.83%. Dry fastness is 4.5 for both.

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