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## Discharging Denim Fabrics Using Potassium Permanganate (KMnO4), As an Oxidizing Agent

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**Abstract**

This work focused on discharge printing on denim fabrics, which dyed with reactive or indigo dyestuff, using an oxidizing agent, KMnO4. Factors of printing process will be studied, different concentrations of the discharging agent and different pH values. Whiteness and color strength for all tested samples will be measured to determine the best optimum and conditions for each process. Tensile strength will also be measured to ensure suitable outcome that does not effect on the fabric's tensile strength. The processed samples will be subjected to FT-IR to clear identify any changes that may have occurred in the dye molecule

*Keywords*: Denim, Discharge printing, IC= Indigo carmine, Reactive vinyl sulphone, KMnO4= potassium permanganate

### 1. Introduction

Denim is everyone's fabric. Denim fabric is one of the most common goods in our fashion widely accepted by all classes of people. popularity of denim due to its durability, easy wearability, longer washability and a worn look for a fashionable look, is why jeans are appreciated by most of people across the world [1-5].Denim fabric is distinguished from other fabrics by its colorful warp and grey weft [6-13]. Denim has now clearly established itself as the definitive street wear fabric and has broad age and socioeconomically attractive [14-18].

Jeans (denim fabrics) are famous for their distinctive blue color due to indigo dye, Typically, twill weave, indigo-dyed warp, and white weft yarns are used to make denim fabric[19-22]. Since denim is made from 100% cotton, it can be dyed many dyes such as direct, reactive, sulfur and also pigment dyes in addition to indigo. In the past, denim has been primarily dyed with indigo (67%), sulfur black (26%) and other sulfur colors (6%). Changing fashion trends have also led to the use of vat, reactive and direct dyes and pigments to dye denim [23-27] . As the demand for denim has been increasing day by day in printing on denim should be improved. The original solid blue color is not attractive to many consumers therefore many manufacturers try to remove some of the blue color from the denim surface [17, 21, 28-32]. denim garment can be formed by locally removing the indigo dye from the fiber surface [19, 33-37]. Potassium permanganate spray is one of the most economical and traditional method which use for removing indigo from the denim surface [28, 38-40]. Now we can use

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Potassium permanganate in printing paste as oxidative Agent in discharge printing.

Discharge printing technique can be used to bleach cotton denim fabrics, in which a printed pattern, either white or colored, is obtained on a colored fabric using discharging agents which are active against indigo dyes[41, 42].

Various discharge printing methods can be used for denim including chemical, physical and biochemical with using oxidative/reduction agents, enzymes [43] and mechanical methods by using pumice stone and sandblasting, CO2 laser [19].

Potassium permanganate (KMnO4), sodium hypochlorite, hydrogen peroxide (H2O2) and sodium perborate/percarbonate are classified as oxidizing agents. Similarly, reducing agents used for this purpose such as formaldehyde sulphoxylate, thiourea dioxide, sodium dithionite and tin chloride have been abandoned due to environmental issues.[41] Enzymes have also been used in discharge printing for denim such as laccase and glucose.[44].

In this research, KMnO4 is our choice as the oxidizing agent for denim discharge printing, we have studied oxidation efficiency of discharge printing paste onto denim fabric, either dyed by reactive or indigo dyes in acidic medium and alkaline medium. In this analysis, performance characteristics were often compared with one another like tensile strength and Elongation. The whiteness, color strength and FTIR were measured for all treated samples.

## 2. Experimental

*2.1. Materials and chemicals*

*2.1.1. Fabrics: denim fabric, either dyed by reactive or indigo dyes*

Indigo warp-dyed: 3/1 twill denim fabric, 98% cotton, 2 % lycra, was purchased from (Al robaai. Co). Warp linear density 7 Ne ; weft linear density 10 Ne , ends per inch 56, picks per inch 48 , areal density 318g/m2.Indigo warp-dyed with indigo carmine ( C16H8N2Na2O8S2) as shown in Figure 1.[45]

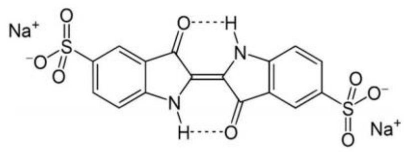

**Figure 1** Chemical structure of indigo carmine

Reactive warp-dyed: 98% cotton,2% lycra , 3/1 Twill denim fabric was purchased from (Abo-Ela .co). Warp linear density 30/2 Ne ; weft linear density 300/1 den, ends per inch 86, picks per inch 66 and areal density 258g/$m^2$.Reactive warp-dyed with Remazol vinyl sulphone group ( $C_6H_5SO_2CH{=}CH_2$) as shown in Figure 2 . [46]

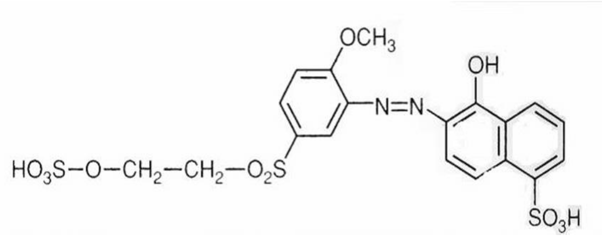

**Figure 2** Chemical structure of Remazol vinyl sulphone

### 2.1.2 Chemicals

Alco -print thickener (PTF 18) was purchased from Sharaf Chem Co , potassium permanganate ($KMnO_4$) ) was purchased from Biochem Co,Sodium carbonate $Na_2CO_3$. Sodium metabisulphite ($N_2S_2O_5$). Acetic acid glacial ($CH_3COOH$) were purchased from El-Gomhouria Co . Dispersing Agent and softener were purchased from SPI Co.

*2.2. Methods*

*2.2.1. Desizing*

denim fabric dyed with indigo dyes was desized at pH 5.5 using 2.0 g/l of amylase and 1.0 g/l of antipilling agent on a laboratory scale jigger machine (EL-Sham Co. El- Obor city, Egypt) at 50$^{\circ C}$ for 20 min, followed by hot washing at 60$^{\circ C}$ for 3 min and rinsing with cold water.

*2.2.2. Printing paste preparation*

Denim fabric samples were printed using pastes containing different concentration of $KMnO_4$ (20-40-60-80-100 g\kg ) and (30-35 g/kg) of a synthetic thickener (Alco-print PTF18), it was prepared with good stirring to ensure homogeneity and suitable viscosity in pH (5-8), using silk-screen technique with mesh-count 43/inch and medium squeegee 65/D. The pH was adjusted in two medium using acetic acid to get pH 5 and sodium carbonate to get pH 8. Printing pastes were prepared according to suggested recipe. all the printed samples were kept to dry at room temperature, for 30 min. samples were subjected to air for oxidation the color of potassium permanganate turned from dark purple to brown. then samples treated with a Sodium metabisulphite solution (1 g/l) at 70° for 10 min followed by rinse the samples gently using cold water, rinse samples using hot water, rinse the samples using non-ionic soap 2 g /l at 45°C for 20 minutes. Finally, the samples are rinsed with cold water. The washed samples are left to dry at room temperature.

*2.2.3. Recipe of printing paste:*

Stock thickening paste was prepared using the following recipe:

| | |
|---|---|
| Thickener alco print (PTF 18) | 30-35 g\kg |
| KMnO4 | (x) [20 – 40 - 60 -80-100 g\kg] |
| water | (Y) |
| Total | 1000 g |

*2.3. Analysis and Measurements*

*2.3.1. Whiteness:*

The whiteness of the fabric samples from the discharged areas was measured by (Digital Whiteness Meter) consists of light filter, sample clamp and photo-detector. The total whiteness is the whiteness of blue light R457. The instrument is strictly designed according to standard light source A and the condition of illumination test 45/0 stipulated by CLE. It has been tested and trial run seriously and conforms to JJG512-87 national measurement testing regulations and is designed according to many national standards.

*2.3.2. Color strength(K\S):*

The printed samples were tested according to AATCC and ISO standards. The color strength values (K/S) were determined using CIE Lab: D-65 10 standard.

*2.3.3. Fourier transform Infrared (FT-IR) spectroscopy:*

FT-IR is a technique based on the unique vibrational frequencies and vibrational modes of covalent bonds in a molecule. It is obtained by passing infrared radiation through a sample of fabric and determining what fraction of the incident radiation is absorbed at a given energy.[47]FT-IR spectrophotometer (JASCO FT-IR-6100) using the KBr pellet disk method for transmittance measurements, in the region of 4000 - 400 $cm^{-1}$with spectra resolution of $4cm^{-1}$.

*2.3.4. Mechanical properties of the Printed denim fabrics*

Tensile strength (TS) and Elongation must be measured at a temperature of 25°C and relative humidity of 65 % using the tensile strength apparatus FMCW 500 (Veb Thuringer Industrie Werk Rauenstein 11/2612 Germany) following ASTM test method D5035, Three specimens for each treated fabric were tested in the warp direction and the average value was recorded to represent the fabric-breaking load (Lb).[48]

## 3. Results and Discussion

*3.1. Effect of $KMnO_4$ Concentration onto Whiteness of Denim Fabrics:*

The printing pastes were prepared as mentioned in methods with the fixed recipes with different concentrations of $KMnO_4$, [20 - 40 - 60 -80-100 g\kg], each recipe was applied onto the fabric and fixed in aqueous medium [5&8]at certain conditions as mentioned, the whiteness and color strength(K\S) were measured the results were shown in Figures 3 and 4.

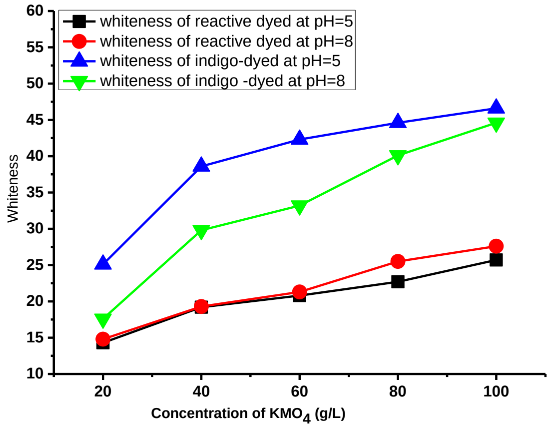


**Figure 3** Effect of $KMnO_4$ concentration onto whiteness of denim fabrics

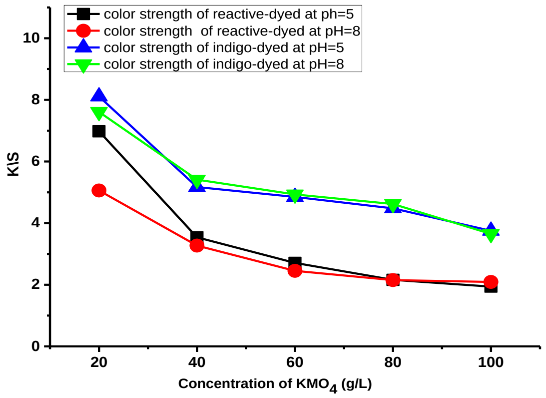


**Figure 4** Color strength of denim Fabrics in pH=8 and pH=5

The illustrated figures showing that: the whiteness was increased with the increase of the $KMnO_4$ concentration. While the color strength K\S was decreased with the increase of $kmno_4$ concentration.

onto indigo-wrap dyed the values of maximum whiteness achieved at pH 8 are 44.1 and 44.6 while at pH 5, the maximum whiteness achieved are 44.6 and 46.6 at concentration of $KMnO_4$ is 80gm/kg and 100gm/kg respectively.

Also the values of color strength k\s at pH 5 are 4.48 and 3.75 while the achieved results at pH = 8 are 4.3 and 3.6 at concentration of $KMnO_4$ 80gm/kg and 100gm/kg respectively.

onto reactive- dyed denim the values of maximum whiteness achieved at pH 8 are 25.5 and 27.6 while at pH 5, the maximum whiteness achieved are 22.7 and 25.7 at concentration of $KMnO_4$ is 80gm/kg and 100gm/kg respectively. Also the values of color strength k\s at pH 5 are 2.16 and 2.09 while the achieved results at pH = 8 are 4.48 and 3.75 at concentration of $KMnO_4$ 80gm/kg and 100gm/kg respectively .

Meaning that, both concentrations giving acceptable results on denim fabrics , while the tensile strength of each sample will insure which is the perfect recipe.

The whiteness increased when pH O of printing paste decreased toward the acidic direction. The pH impacts the rate of reaction and whether oxidation occurs by a one, three, or five electron exchange. Eq. (1) is used to neutral and alkaline settings, whereas Eq. (2) is applied to acidic ones, depending on the pH. As the pH decreases, the oxidation potential (Eo) rises, and the Eo in acidic solution is significantly higher than in alkaline solution.[49].

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^- + 0.59V\,(E^0) \quad (1)$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O + 1.51V\,(Eo) \quad (2)$$

**Scheme 1.** The oxidation potential (E°) of potassium permanganate (KMO₄)

The $KMnO_4$ oxidizes the dye chromophore to make it colorless and converts itself to $MnO_2$.So the more acidic in printing paste, the more powerful the oxidation of potassium permanganate. Meaning that the best whiteness can be obtained in the strong acidic medium[50] .

In the indigo-wrap dyed ,indigo dye converts to isatin and to anthranilic acid by oxidation using $KMnO_4$[51]. In the case of $MnO_2$ which is a good adsorber/absorber and reservoir for $O_2$, higher dosage provides more photogenerated reactive oxygen species such as OH radicals. The formation of .OH radicals in indigo carmine (IC).[52, 53]

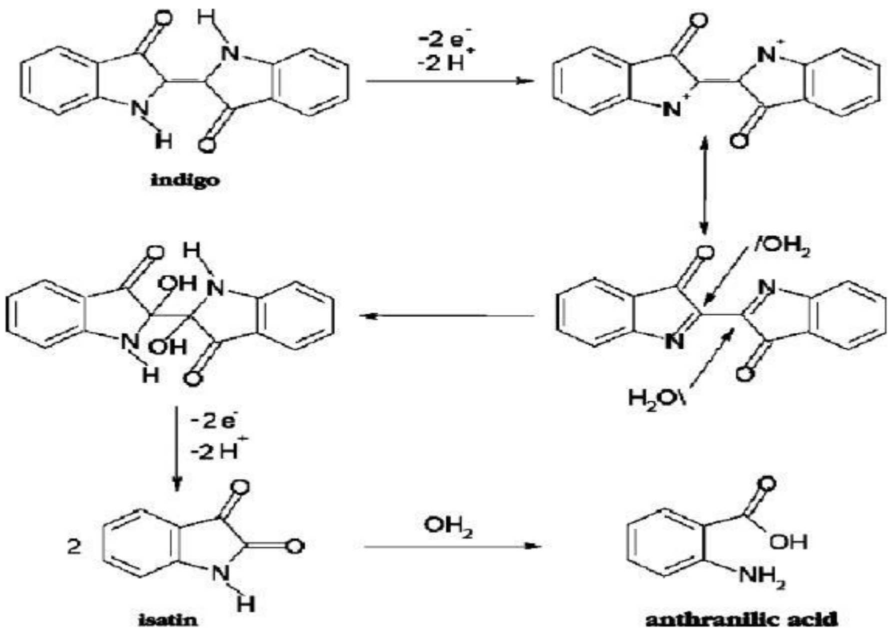


**Figure 5** The oxidation reaction for indigo dye

The whiteness of reactive dye assumed by the breaking of the C–N bond as a result of the formation of $N^+$ or an oxonium ion in the presence of acid. In Remazol, the positive charge is shuffled to the nitrogen of vinyl sulphone aniline and, ultimately, the C–N bond may break between anthraquinone and aniline, while vinyl sulphone may be mineralized and aniline produced, which on further oxidation converts into nitrobenzene. During discharging, potassium permanganate was consumed and Manganese Sulphate ($MnSO_4$) was formed. [46].

The whiteness of textile fabrics including denim is achieved through bleaching (oxidation reaction), and while $MnO_2$ does not truly impart any sort of whiteness, it might stain bleached fabric, resulting in lower whiteness, if not properly removed. $MnO_2$ impedes the access of active oxygen to the indigo dye present on the fabric resulting in a diminished bleaching effect. Hence, the removal of $MnO_2$ by changing it to a solubilized form ($Mn^{2+}$) can be done with the help of sodium bisulfite, which is known for its ability to remove stains of $MnO_2$ by converting the $MnO_2$ into $Mn^{2+}$. Sodium bisulfite was used to reduce $MnO_2$ in water-soluble form of $Mn^{2+}$, in order to get the effect of white discharge. [52, 53]

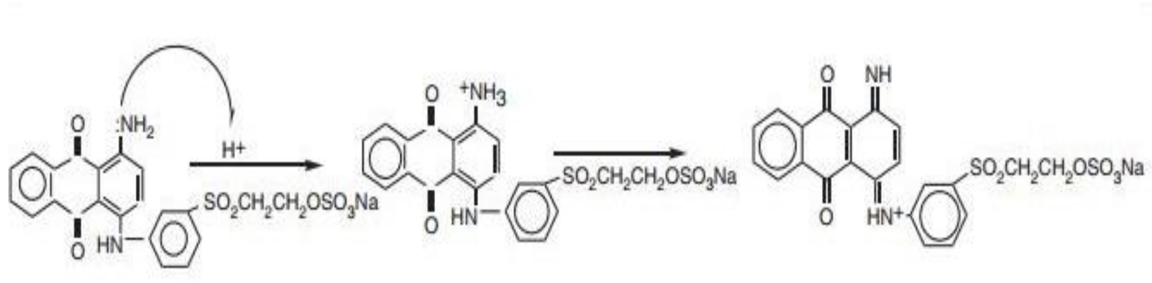


**Figure 6:** The oxidation reaction for of reactive dye

*3.2. Effect of PH values onto denim fabrics whiteness*

The printing paste was prepared as usual with the best concentration of $KMnO_4$ (60 g\l), effect of different pH values [5,6,7,8,9, and 10], were applied, each recipe was applied onto the fabric and fixed in aqueous medium at certain conditions as mentioned. The discharging results of such value was shown in Figure 7

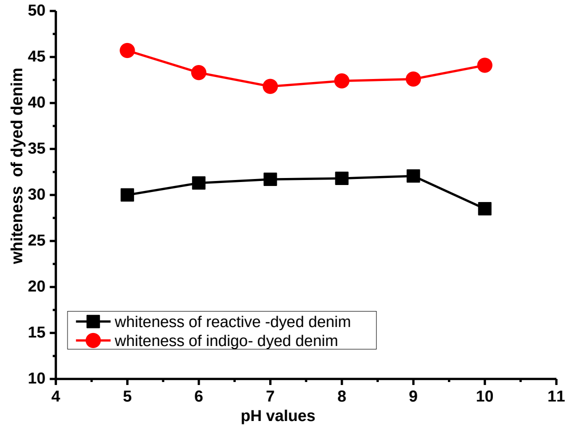


**Figure 7** Effect PH values onto denim fabric whiteness

The whiteness of the indigo-dyed fabric was decreased with the increase of the pH value; the maximum whiteness result was achieved at pH 5 that is why, will study the effect of $KMnO_4$ concentrations at this successful pH value. The whiteness of discharged reactive-dyed denim fabric was increased with the increase of pH value until reach pH 8, then decreased with the increase of pH value.

### *3.3. Mechanical properties.*

The mechanical properties such as tensile strength, elongation in warp direction will ensure which is the pH [5&8] were measured and recorded in Table 1

**Table 1** Tensile Strength and elongation in warp direction at different concentrations of $KMnO_4$ at pH values (5&8) for Denim Fabrics**.**

| CONC OF $KMnO_4$ g/Kg | Loss in Tensile strength in warp direction (KgF) | | | | Elongation at break in warp direction (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | Indigo –dyed denim | | Reactive-dyed-denim | | Indigo –dyed denim | | Reactive-dyed-denim | |
| | Blank fabric 127 | | Blank fabric 100 | | Blank fabric 20 | | Blank fabric 30 | |
| | pH 8 | pH 5 | pH 8 | pH 5 | pH 8 | pH 5 | pH 8 | pH 5 |
| 40 | 121.05 | 117.03 | 74.88 | 52.33 | 21.4 | 21.12 | 20.3 | 19.1 |
| 60 | 102.72 | 99.16 | 65.28 | 49.92 | 20.3 | 19.5 | 19.7 | 17.8 |
| 80 | 95.11 | 83.01 | 60.13 | 44.23 | 19.2 | 17.3 | 18.6 | 15.4 |
| 100 | 66.8 | 48.4 | 39.36 | 24.96 | 15.1 | 12.2 | 14.1 | 12.2 |

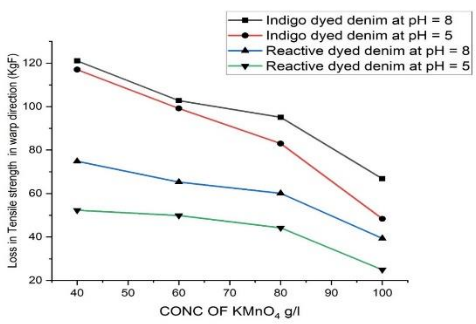


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**Figure 8** Tensile Strength in warp direction for Denim Fabrics

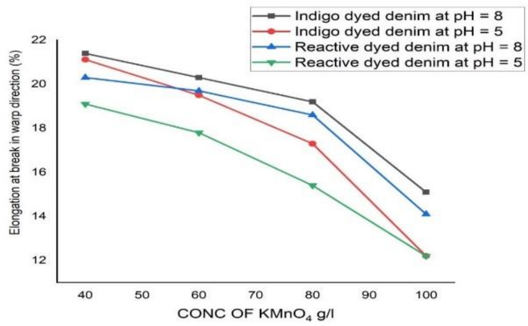


**Figure 9** Elongation in warp direction at pH values (5&8) for Denim Fabrics

From the illustrated Table 1and Figure 8 and Figure 9, we found that: the Tensile strength in warp direction of all tested samples were decreased with the increase of $KMnO_4$ concentrations compared with the blank sample.

The TS in warp direction decreased to the minimum value at conc. of 100gm/l even at pH 5 or pH 8, sever loss in tensile strength was noticed.

The decrease in tensile strength by increase in duration of reaction indicates the progressive degradation of cellulose molecules.[22, 31, 54, 55] Actually, the loss of tensile strength at pH 5 is not acceptable at all $KMnO_4$ concentrations due to the acidic medium, which has a negative effect onto the cotton fiber. pH 8 achieved good results than pH 5 for all tested samples this is due to the acidic medium.

From TS study we can come to the conclusion that: the best $KMnO_4$ concentration is 80gm/l at pH 8, the loss in tensile strength still in an acceptable limit. Also, the concentration of 60gm/l showing very good TS results even at pH 5 or pH 8, while the discharging efficiency at this point is not satisfied as the whiteness record a value of 33.2 and 42.3 at pH 8 and pH 5 respectively for indigo –wrap dyed and record 19.3and 20.8 at pH 8 and pH 5 respectively for reactive-wrap dyed.

Generally, the discharging of indigo-dyed denim fabric with oxidizing agent achieved good result than that achieved on discharging reactive-dyed denim fabric it may be due to the structure of the dyestuff itself.

The achieved discharging results onto denim fabrics was due to the strong efficiency of oxidizing agent which may destroy the skeleton of dye molecule or illuminate some chromophoric groups, the FT-IR study will clarify, what is the actual efficiency of the oxidation process

### *3.4. FT-IR study of Denim fabrics.*

This study led to know what is the differences between blank sample and the discharged samples at some $KMnO_4$ concentrations and different pH values, to insure about the changes that occurred in dye molecule even in skeleton or chromophoric groups.

#### *3.4.1. FT-IR spectra of indigo-wrap dyed:*

*Figure 10 and Figure 11* showing the FT-IR spectra of indigo-wrap dyed corresponding to -OH and – NH stretching, peaks at 2900 $cm^{-1}$ for CH stretching, peaks at 1630 $cm^{-1}$ -C=O vibration for COOH group, peaks at 1459 $cm^{-1}$ for $SO_3$ functional group of Indigo dye, peaks at 1279 – 1199 $cm^{-1}$ for Anti-symmetric stretching of C-O-C bridge, band peak at 1051 $cm^{-1}$ for Skeletal vibrations involving the C=O stretching and the group band peaks at 745-697-664 $cm^{-1}$ corresponding for C=C aromatic group binding for dye[56] .Samples from 10g-100g shows these band peaks with different peaks absorption and places due to the effect of potassium permanganate on the denim fabrics at pH 8 shown in Figure 10. Where in sample treated with 10gm $KMnO_4$ shows corresponding of both denim fabrics and indigo dye peaks at 3329, 2915, 1630, 1456, 1157,1105 and 1051 $cm^{-1}$; for sample treated with 20 gm KMnO4 shows corresponding band peaks at 3330, 3280, 2915, 1630, 1612, 1459, 1200, 1159, 1051, 697 and 664 $cm^{-1}$ and so on for the rest of treatments.

FT-IR study for the blank sample and the discharged indigo-dyed fabric with the concentration of 10,10,30,40,60,80and 100gm/l $KMnO_4$ at pH values 5 and 8 shown in Figure 10 and Figure 11 meaning that lower intensity absorption with the increase of oxidizing agent, the changes of band peaks meaning that the chromophoric groups which enhance the color of the dye molecule were oxidized or completely eliminated by sever effect of the oxidation process.

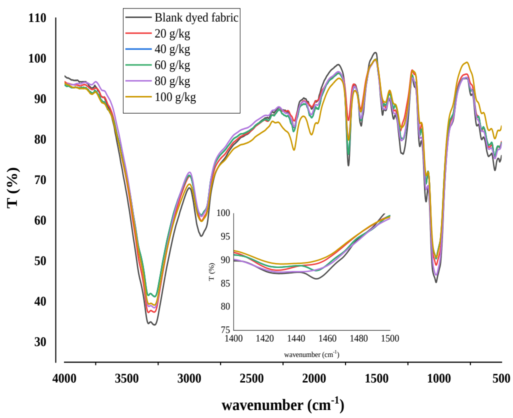


**Figure 10 :**FT-IR for indigo-dyed denim fabric with different concentration of $KMnO_4$ at pH 8

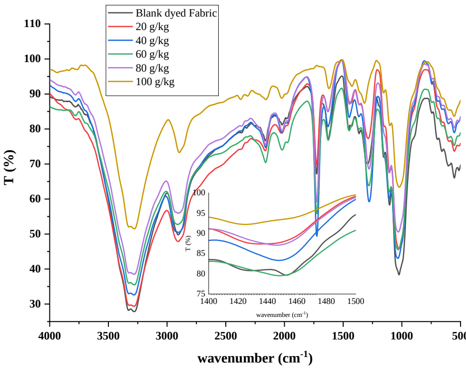


**Figure 11:** FTIR for (indigo-dyed denim) fabric in different concentration of $KMnO_4$ at PH 5

*3.4.2. FTIR study of discharged reactive-dyed denim fabric*

Figure 12 and figure 13 showing the FT-IR of reactive-warp dyed. The stretching frequency fits to an alcohol (–OH group), – NH stretching, peaks at 2900 $cm^{-1}$ for CH stretching, peaks at 1630 $cm^{-1}$ -C=O vibration for -COOH group, two peaks at 1600$cm^{-1}$ and 1500$cm^{-1}$ fits to benzene ring, peaks at 1459 $cm^{-1}$ for $SO_2$ functional group of reactive dye(vinyl sulphone group), peaks at 1279 – 1199 $cm^{-1}$ for Anti-symmetric stretching of C-O-C bridge, band peak at 1051 $cm^{-1}$ for Skeletal vibrations involving the -C=O stretching and the group band peaks at 745-697-664$cm^{-1}$ corresponding for -C=C aromatic group .The intensity of such chromophoric groups was decreased after processing compared with blank sample, the intensity decreased with the increase of the oxidizing agent concentration until reach the maximum changes at 100gm/l $KMnO_4$.

The peak intensity of $SO_3$ was decreased as the concentration of $KMnO_4$ increased, that indicated the effect of $KMnO_4$ on the discharging performance of the indigo dye in alkaline medium. In addition, as the concentration of $KMnO_4$ increased up to 80 g/kg the decreasing of the peak intensity was decreased and any further increasing in the $KMnO_4$ concentration didn't provide any further enhancement.

Oxygen plays an important role in photocatalytic degradation reactions in aqueous solutions by scavenging the electrons generated on the photocatalyst thereby inhibiting the recombination of electrons and holes. The formation of highly reactive superoxide radical anion which is responsible for the photocatalytic degradation is the outcome of this reaction.

By scavenging the electrons produced on the photocatalyst and preventing the recombination of electrons and holes, oxygen plays a significant role in photocatalytic degradation events in aqueous solutions. The result of this reaction is the creation of the extremely reactive superoxide radical anion, which is in charge of the photocatalytic destruction.

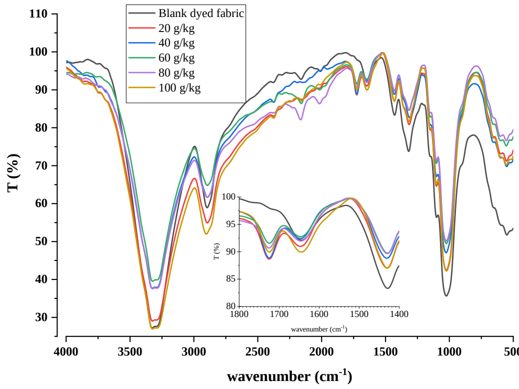


**Figure 12**. FTIR for reactive-dyed denim fabric in different concentration of $KMnO_4$ at pH 8

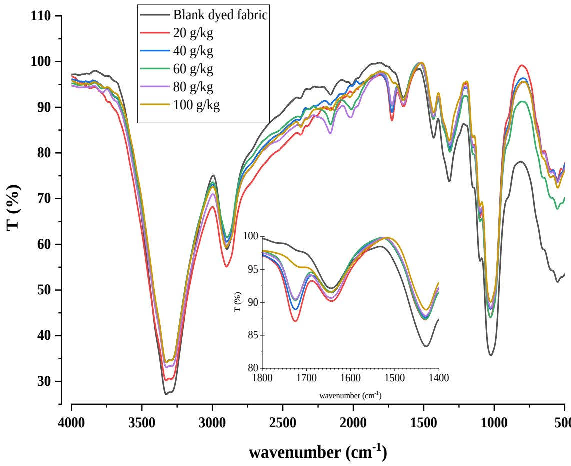


**Figure 13**: FTIR for reactive-dyed denim fabric in different concentration of $KMnO_4$ at PH 5 .

## 4. Conclusion

In this research, we studied discharge of denim fabric either dyed by reactive or indigo dyestuff, using the oxidizing agent $KMnO_4$ to release IC and reactive dye from denim at pH [5&8] in 30 minutes of reaction time. the best results for discharging indigo-dyed denim fabric were 80 g/Kg of $KMnO_4$ at a pH value 8, as the loss in tensile strength was still within an acceptable limit. While discharging reactive-dyed denim fabric, the best results were 80 g/kg $KMnO_4$ at pH 8, and 60 g/kg achieved a good result at pH 8. FTIR spectra showing the changes that actually occurred to the dye molecule**.**

## 5. References

[1] M. Ghoranneviss, S. Shahidi, B. Moazzenchi, A. Anvari, A. Rashidi, H. Hosseini, Comparison between decolorization of denim fabrics with oxygen and argon glow discharge, Surface and Coatings Technology 201(9-11) (2007) 4926-4930.

[2] N. Akter, M.R. Repon, D. Mikučionienė, M.A. Jalil, T. Islam, M.R. Karim, Fabrication and characterization of stretchable denim fabric using core spun yarn, Heliyon 7(12) (2021) e08532.

[3] C.-w. Kan, W.-y. Wong, Color properties of cellulase-treated cotton denim fabric manufactured by torque-free ring spun yarn, Textile Research Journal 81(9) (2011) 875-882.

[4] S.S. Muthu, Sustainability in denim, Woodhead Publishing2017.

[5] S. Farag, H.M. Ibrahim, A. Amr, M.S. Asker, A. El-Shafai, Preparation and characterization of ion exchanger based on bacterial cellulose for heavy metal cation removal, Egyptian Journal of Chemistry 62 (2019) 457-466.

[6] D. Arjun, J. Hiranmayee, M.N. Farheen, Technology of industrial denim washing, International Journal of Industrial Engineering & Technology 3(4) (2013) 25-34.

[7] S.A. Didar, S.U. Patwary, S. Kader, M.M.K. Akter, T. Ahmed, Development of different denim effect on knitted fabric and comparative analysis with conventional woven denim on the basis of physical and dimensional properties, Research Journal of Engineering Sciences ISSN 2278 (2015) 9472.

[8] O. Babaarslan, E. Sarioğlu, H.İ. Çelik, M.A. Avci, Denim fabrics woven with dual core-spun yarns, Engineered fabrics (2018) 19-39.

[9] H.M. Ibrahim, A.A. Aly, G.M. Taha, E.A. El-Alfy, Production of antibacterial cotton fabrics via green treatment with nontoxic natural biopolymer gelatin, Egyptian Journal of Chemistry 63 (2020) 655-696.

[10] M.F. Mahmud, A.M. Rahman, A.A.H. Sarker, S. Akter, M.R. Islam, Evaluation of the impact of cotton sheath linear density of core spun yarn on the performance of denim fabrics, Heliyon 8(8) (2022) e09998.

[11] N. Uren, A. Okur, Analysis and improvement of tactile comfort and low-stress mechanical properties of denim fabrics, Textile Research Journal 89(23-24) (2019) 4842-4857.

[12] M.F. Mahmud, A.N.M.M. Rahman, A.A.H. Sarker, S. Akter, M.R. Islam, Evaluation of the impact of cotton sheath linear density of core spun yarn on the performance of denim fabrics, Heliyon 8(8) (2022) e09998.

[13] M.M. Bakr, M.A. Taha, H. Osman, H.M. Ibrahim, Novel green printing of cotton, wool and polyester fabrics with natural safflower dye nanoparticles, Egyptian Journal of Chemistry 64(11) (2021) 6221-6230.

[14] A. Kumari, K. Khurana, Regenerated cellulose-based denim fabric for tropical regions: an analytical study on making denim comfortable, Journal of Textiles 2016 (2016).

[15] M. Easey, Fashion marketing, John Wiley & Sons2009.

[16] A. Brooks, Clothing poverty: The hidden world of fast fashion and second-hand clothes, Bloomsbury Publishing2019.

[17] F.A. Mohamed, E. Shaban, H.M. Ibrahim, Synthesis and antibacterial activity of some novel nucleus N-aminorhodanine based bis monofunctional and bifunctional reactive dyes and their application on wool and cotton fabrics, Egyptian Journal of Chemistry 65(2) (2022) 597-608.

[18] N.I. Abdel Sayed, K. El Badry, H.M. Abdel Mohsen, Conductimetric studies of charge transfer complexes of p-Chloranil with some alicyclic amines in polar media, Journal of the Chinese Chemical Society 50(2) (2003) 193-199.

[19] A.S. Maryan, M. Montazer, R. Damerchely, Discoloration of denim garment with color free effluent using montmorillonite based nano clay and enzymes: nano bio-treatment on denim garment, Journal of Cleaner Production 91 (2015) 208-215.

[20] R. Salama, H. Osman, H.M. Ibrahim, Preparation of biocompatible chitosan nanoparticles loaded with Aloe vera extract for use as a novel drug delivery mechanism to improve the antibacterial characteristics of cellulose-based fabrics, Egyptian Journal of Chemistry 65(3) (2022) 581-595.

[21] M.A. Ali, E.A. Bydoon, H.M. Ibrahim, Bioactive Composite Nonwoven Surgical Dressing based on Cellulose Coated with Nanofiber Membrane using the

layer-by-layer technique, Egyptian Journal of Chemistry 65(4) (2022) 525-542.
[22] R.M. Mosaad, M.H. Alhalafi, E.A.M. Emam, M.A. Ibrahim, H. Ibrahim, Enhancement of Antimicrobial and Dyeing Properties of Cellulosic Fabrics via Chitosan Nanoparticles, Polymers 14(19) (2022).
[23] R. Chavan, Indigo dye and reduction techniques, Denim, Elsevier2015, pp. 37-67.
[24] A.K. Sarkar, Dyeing technologies for denim garments, Denim, Elsevier2015, pp. 271-285.
[25] W. Schrott, R. Paul, Environmental impacts of denim manufacture, Denim, Elsevier2015, pp. 563-580.
[26] T.A. Khattab, M.S. Abdelrahman, M. Rehan, Textile dyeing industry: environmental impacts and remediation, Environmental Science and Pollution Research 27(4) (2020) 3803-3818.
[27] A. Abou-Okeil, R. Refaei, E.M. Khalil, S.E. Moustafa, H.M. Ibrahim, Fabrication of novel green magnetic electrospun nanofibers based on Fe3O4 nanoparticles/PVA/chitosan/collagen, Egyptian Journal of Chemistry 65(8) (2022) 283-299.
[28] R.V. Adivarekar, Study of Decolouration Effect on Denim by Ceric Sulphate Treatment using Statistical Modeling, Trends in Textile Engineering & Fashion Technology 4(1) (2018).
[29] F. Ahmed, A.N.M.M. Rahman, M.R. Islam, M.A. Hossain, I. Aabrar, Influence of Laser Treatment and Chemical Washing on the Performance Attributes of Cotton Woven Denim Fabrics, Journal of Natural Fibers (2022) 1-14.
[30] M.A.B. Siddiquee, A.T.M.G. Moula, J.K. Saha, M.H.K. Khan, Z. Kaisar, A. Roy, Sustainable Denim Washing by Process Optimization, Journal of Textile Science and Technology 8(4) (2022) 149-162.
[31] F.A. Mohamed, M.B. Sheier, M.M. Reda, H.M. Ibrahim, Synthesis, Application, and Antibacterial Activity of New Direct Dyes based on Chromene Derivatives, Current Organic Synthesis 19(6) (2022) 757-766.
[32] F.A. Mohamed, M.M. Reda, H. Ibrahim, Enhancement of Dyeing and Antimicrobial Properties of Chitosan and Chitosan Nanoparticles-Treated Cotton and Viscose Fabrics with Acid Dyes, Egyptian Journal of Chemistry 65(13) (2022) 339-344.
[33] C. Bağıran, A. Körlü, S. Yapar, Wastewater treatment of a denim washing plant by using waste pumice stones to recycle wastewater and reuse, Sustainable Textile and fashion value chains, Springer2021, pp. 151-168.
[34] H. Ibrahim, E.M.R. El- Zairy, E.A.M. Emam, E. Adel, Combined antimicrobial finishing dyeing properties of cotton, polyester fabrics and their blends with acid and disperse dyes, Egyptian Journal of Chemistry 62(5) (2019) 965-976.
[35] H.M. Ibrahim, S. Zaghloul, M. Hashem, A. El-Shafei, A green approach to improve the antibacterial properties of cellulose based fabrics using Moringa oleifera extract in presence of silver nanoparticles, Cellulose 28(1) (2021) 549-564.
[36] S. Farag, A. Amr, A. El-Shafei, M.S. Asker, H.M. Ibrahim, Green synthesis of titanium dioxide nanoparticles via bacterial cellulose (BC) produced from agricultural wastes, Cellulose 28(12) (2021) 7619-7632.
[37] A. Abou-Okeil, H.M. Fahmy, M.M.G. Fouda, A.A. Aly, H.M. Ibrahim, Hyaluronic Acid/Oxidized K-Carrageenan Electrospun Nanofibers Synthesis and Antibacterial Properties, BioNanoScience 11(3) (2021) 687-695.
[38] R. Nayak, M. George, L. Jajpura, A. Khandual, T. Panwar, Laser and ozone applications for circularity journey in denim manufacturing-A developing country perspective, Current Opinion in Green and Sustainable Chemistry (2022) 100680.
[39] S. Katode, S. Maiti, S. Biranje, R.V. Adivarekar, Study of decolouration effect on denim by ceric sulphate treatment using statistical modeling, Trends in Textile Engineering and Fashion Technology 4(1) (2018) 1-6.
[40] N.A. Ibrahim, G.A. Kadry, B.M. Eid, H.M. Ibrahim, Enhanced antibacterial properties of polyester and polyacrylonitrile fabrics using Ag-Np dispersion/microwave treatment, AATCC Journal of Research 1(2) (2014) 13-19.
[41] A. Siddique, T. Hussain, W. Ibrahim, Z.A. Raza, S. Abid, Optimization of discharge printing of indigo denim using potassium permanganate via response surface regression, Pigment & Resin Technology (2018).
[42] S. Moawaed, A. Hashad, M. Mohamed, A. El-Aaty, A.G. Hassabo, E. Abdel-Aziz, H. Othman, Overview of Discharge Printing Techniques on Denim Fabric, Journal of Textiles, Coloration and Polymer Science 19(2) (2022) 211-221.
[43] M. Montazer, A. Sadeghian Maryan, Influences of different enzymatic treatment on denim garment,

Applied biochemistry and biotechnology 160(7) (2010) 2114-2128.
[44] H.S. Sharma, textile biotechnology in Europe-microbiological degradation of wastewater dyes, AATCC review 5(11) (2005) 45.
[45] D. Donneys-Victoria, D. Bermúdez-Rubio, B. Torralba-Ramírez, N. Marriaga-Cabrales, F. Machuca-Martínez, Removal of indigo carmine dye by electrocoagulation using magnesium anodes with polarity change, Environmental Science and Pollution Research 26(7) (2019) 7164-7176.
[46] R. Saeed, M.J. Mughal, M. Naeem, S. Nizami, T.H. Usmani, Decolorisation of Remazol vinyl sulphone reactive dyes by potassium permanganate, Coloration Technology 125(5) (2009) 277-283.
[47] Y. Ner, J.A. Stuart, G. Whited, G.A. Sotzing, Electrospinning nanoribbons of a bioengineered silk-elastin-like protein (SELP) from water, Polymer 50(24) (2009) 5828-5836.
[48] A. Sedik, M.M. Mosaad, H. Othman, A. Mohamed, Incorporation of Alginate/Chitosan Nano capsules Loaded with Sesame Oil or Omega-3 Oil in Cellulose Fabrics for Wound Healing Bandage, Egyptian Journal of Chemistry 65(5) (2022) 1-2.
[49] J. Walton, P. Labine, A. Reidies, The chemistry of permanganate in degradative oxidations, Chemical oxidation, CRC Press2021, pp. 205-221.
[50] X.-R. Xu, H.-B. Li, W.-H. Wang, J.-D. Gu, Decolorization of dyes and textile wastewater by potassium permanganate, Chemosphere 59(6) (2005) 893-898.
[51] J. Poulin, Identification of indigo and its degradation products on a silk textile fragment using gas chromatography-mass spectrometry, Journal of the Canadian Association for Conservation 32 (2007) 48-56.
[52] K.V. Lekshmi, S. Yesodharan, E. Yesodharan, MnO2 and MnO2/TiO2 mediated, persulphate enhanced photocatalysis for the removal of indigo carmine from water, European Chemical Bulletin 6(5) (2017) 177-191.
[53] R.-a. Chi, G.-c. Zhu, S.-m. Xu, J. Tian, J. Liu, Z.-h. Xu, Kinetics of manganese reduction leaching from weathered rare-earth mud with sodium sulfite, Metallurgical and Materials Transactions B 33(1) (2002) 41-46.
[54] A. Siddique, T. Hussain, W. Ibrahim, Z.A. Raza, S. Abid, A. Nazir, Response Surface Optimization in Discharge Printing of Denim Using Potassium Permanganate as Oxidative Agent, Clothing and Textiles Research Journal 35(3) (2017) 204-214.
[55] H.M. Ibrahim, G.M. Taha, E.A. El-Alfy, M.K. El-Bisi, Enhancing antibacterial action of gauze by adding gelatin nanoparticles loaded with spectinomycin and chloramphenicol, Cellulose 29(10) (2022) 5677-5688.
[56] C. Chung, M. Lee, E.K. Choe, Characterization of cotton fabric scouring by FT-IR ATR spectroscopy, Carbohydrate Polymers 58(4) (2004) 417-420.