Recovery and Reuse of Indigo Dye from Denim Wash Liquor

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Abstract

The yarn of Denim fabric is dyed with Indigo dye using slasher dyeing (sheet dyeing) or ball dyeing (rope dyeing) technique. During dyeing, preferably a ring dyeing is followed in which the dye remains mostly on the outer layer of fibre. After air oxidation, dyeings are washed through specific technique to remove the excess of color to develop unique fading property. The washed liquor is highly contaminated with indigo dye, alkali, hydrosulphite, dispersing agents and auxiliaries, which increase the pollution load eg. in X factory 200 KL/day of effluent water is generated, which is treated in ETP and discharged to drain and the sludge separated out is disposed. A study on recovery of Indigo from waste liquor has been conducted by various researchers. However the reuse of recovered Indigo dye is still on lab scale due to cost factor of recovered dye i.e. cost of chemicals, plant & manpower. evaporation and variation in pH of the wash liquor followed by filtration employing a nano filter (melt blown) and In the current study, I tried to reuse the Indigo dye after recovering by various methods namely using coagulants, suction method. Therefore in the study, no chemicals except acid or alkali are needed for Indigo separation. Method is simple, cost effective, and application seems to be possible in the industry. Concentration of indigo in the wash liquor in X factory was estimated to be 240 ppm using optical density method. 1440 Kg of Indigo/month can be recovered and reused. The maximum Indigo recovered was observed at pH 14 followed by pH- 4. Depth of dyeing with recovered dye was also more at pH 14. However better shade, nearer to standard Indigo was observed at pH- 4. Study indicates that structure of Indigo is almost intact after recovering. Light fastness properties also appear to be similar. However there is with slight deviations in shade, which is adjustable in dyeing.

1. Introduction

Indigo is one of the oldest dyes used by mankind. The current consumption of the dye is enormous due to the popularity of blue jeans, which are dyed with Indigo. The consumption of Indigo and other vat dyes reaches about 33 million kg annually [1] and the reduction of Indigo to leuco-indigo represents an important type of industrial process which is operated worldwide on a considerable scale [2]. Throughout history Indigo was derived from various plants. Dyer's Woad (Isatistinctoria L.) was cultivated in wide areas in Europe until Indigo from Indigo era species (Indigo feratinctoria) from India started to be imported in bigger scale in the 17th century [3]. In the 19th century came the synthetic dyes and now a days Indigo is mainly synthesized from by-products of fossil fuels. Recently there has been a growing interest in natural products obtained from renewable resources instead of oil supplies, which are non renewable [4]. Indigo is a so-called vat dye, which means that it needs to be reduced to its water soluble leuco-form before dyeing. The reduced form is absorbed into the fibres, and when oxidized back to its blue form it stays within the fibre [5]. Earlier the reduction and dyeing was done with fermentation [6,7]. Nowadays, the most of the reduction has been done chemically by sodium dithionite. Indigo yarn dyeing process consumes large amount of water for rinsing off unattached Indigo dye. This stream of wastewater carries high C.O.D. and valuable dye stuff. Not only water and dye are wasted, but also more chemicals are consumed. Factories with cleaner production mission are looking for ways to recover valuable resources.

2. Materials and Methods

Following materials were used in the study -

(1) Yarn -The open end (10 Ne) yarn was used and this yarn was provided free of cost from X Factory of Bhilwara (Raj.).

(2) Chemicals-Following chemicals were used in the study

- Ferric Chloride
- PolyAluminum Chloride(PAC)
- Chloroform
- Caustic Soda
- Acetic acid
- Di methyl sulphoxide (DMSO)

All chemicals used were laboratory grade reagents.

2.1 Methods of application-

Diagram of filtration system

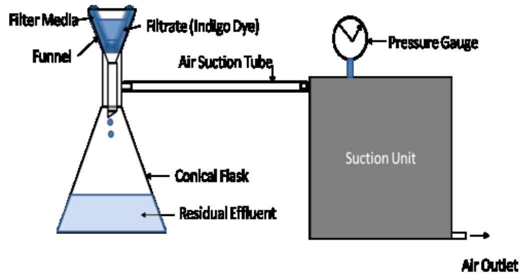


FIG. 2.1 SCHEMATIC DIAGRAM OF SUCTION UNIT AND FILTRATION SYSTEM

FIG. 2.2 - ASSEMBLY WITH SUCTION PUMP AND VACUUM FLASK EMPLOYED FOR FILTRATION AND RECOVERY OF INDIGO

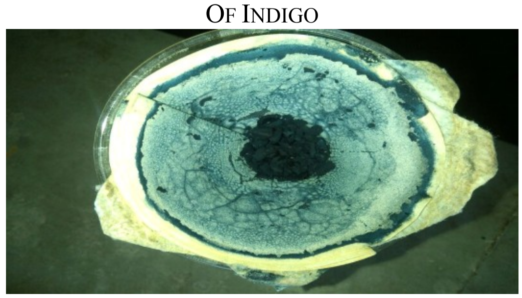


FIG. 2.3 - INDIGO RECOVERED FROM DENIM WASTE

2.2 Process of Recovery

The scheme given below describes this procedure.

Indigo wash liquor taken from X Factory

↓

Precipitation (With the help of different methods mentioned above)

↓

Filtration (With the help of Whatman & Melt blown nano filter By suction)

↓

Purification (With help of light organic solvent petroleum spirit to remove impurities such as wax and gum Arabic)

↓

Reuse

3. Results and Discussions

The results of various tests conducted are as follows –

TABLE 3.1

FILTRATION TIME, QUANTITY AND COLOUR OF FILTRATE OF INDIGO RECOVERED BY VARIOUS METHODS

By using special filter (Whatman + Melt blown) papers

S/N	Sample	Volume of sample	Filtered indigo(gms)	Filtration Time (mins.)	After filter color
1.	Indigo waste liquor (direct filter)	500 ml	0.05	60	Light blue
2.	Indigo waste liquor with $FeCl_3$	500 ml	0.1	35	Light yellow
3.	Indigo waste liquor with PAC	500 ml	0.11	32	Light blue
4.	Indigo waste liquor at pH-4	500 ml	0.2	20	Light blue
5.	Indigo waste liquor at pH-5	500 ml	0.15	24	Light blue
6.	Indigo waste liquor at pH-8	500 ml	0.1	32	Light blue
7.	Indigo waste liquor at pH-11	500 ml	0.11	25	Light blue
8.	Indigo waste liquor at pH-12	500 ml	0.14	20	Light blue
9.	Indigo waste liquor at pH-14	500 ml	0.23	15	Clear
10.	Indigo waste liquor microwave drying process	500 ml	0.10	-	-
11.	Boiling & evaporation	500 ml	0.1	-	-
12.	Indigo waste liquor with chloroform separation	500 ml	0.12	-	-

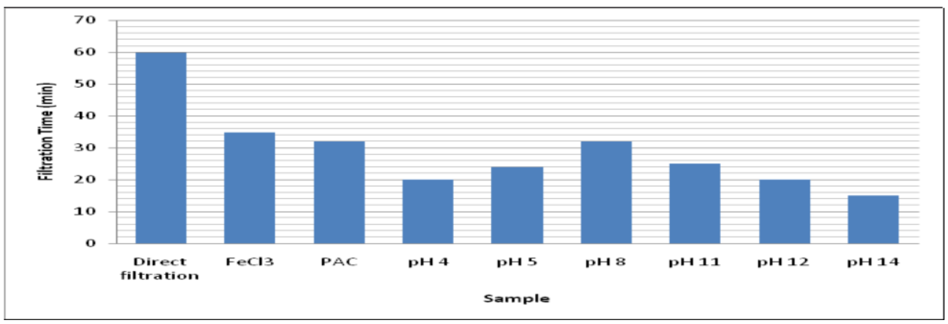


FIG. 3.1 – AMOUNT OF INDIGO RECOVERED BY VARIOUS EXPERIMENTS

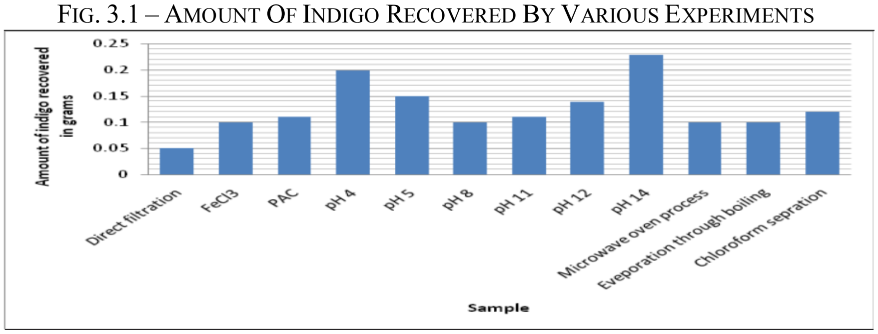


FIG. 3.2 – TIME REQUIRED IN FILTRATION OF INDIGO BY VARIOUS METHODS

The maximum amount of dye (0.23gm) is recovered at pH – 14. The state of indigo in washed liquor is suspended particle. The high amount of precipitation may be attributed due to neutralization of the charged particle by OH^- ions, which are then encouraged to collide with each other to form large particle and settle [9].

The amount of indigo recovery in alkaline pH is in order pH 14 > 12 > 11 > 8

Similarly high amount of indigo recovery in acidic pH may be due to neutralization of the charge by H^+ ions. The amount recovered is maximum at pH 4 than 5. At pH < 4, amount recovery reduces (not documented). The optimum acidic pH is 4.

$FeCl_3$ and PAC are also effective coagulants for indigo from the waste wash liquor because they have ability to form multi charged polynuclear complexes with enhanced adsorption characteristic. Metal ions Al and Fe hydrolyse rapidly forming metal hydroxide species [8].

Amount of recovered indigo is minimum 0.05 gm in native sample, due to lack of coagulation (no chemical & coagulants).

Minimum of filtration time was in order pH 14 < pH 4 < pH 12 < pH 5 < pH 11 < pH 8

In PAC & $FeCl_3$ filtration time was 32 & 35 mins. respectively.

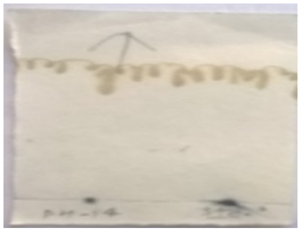
Indigo recovery has also been expressed in the bar diagram. (fig.3.1& 3.2)

(1) Thin layer chromotography -

Solvent separation method

Chromotography trials were taken by dissolving indigo in acetone, diethyl ether & chloroform . However, the dye solubility was not perfect in acetone & diethylether. Therefore only chloroform was used.
R_f = Distance covered by component/Distance covered by solvent
Distance covered by solvent – 5 cm
Distance covered by standard indigo – 1.7 cm
Distance covered by recovered indigo (pH –4) –1.7 cm
Distance covered by recovered indigo (pH –14) – 1.7 cm

STD. WITH INDIGO RECOVERED AT PH – 14



STD. WITH INDIGO RECOVERED AT PH - 4

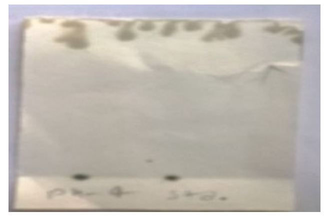


FIG.3.3 - COMPARISON BETWEEN INDIGO STANDARD AND PH – 14 & PH – 4 ON T L C PAPER

R_f value of both indigo standard & recovered at pH – 14 & pH – 4 is same. Which indicate identical properties of std. indigo and recovered indigo at pH – 4 & 14.

(2) Effluent quality tests -

TDS of all filtrate samples was determined by evaporation method. It is shown in table 3.2

TABLE 3.2

TOTAL DISSOLVED SOLID CONTENTS OF FILTRATE SOLUTION

S/N	Sample	Total dissolved solid in PPM
1.	Indigo wash liquor (control)	1800
2.	Filterate indigo wash liquor with $FeCl_3$ 1%	1850
3.	Filterate indigo liquor with PAC * 1%	2550
4.	Filterate indigo liquor at pH-4	1540
5.	Filterate indigo liqour at pH-5	1600
6.	Filterate indigo liqour at pH-8	1650
7.	Filterate indigo liqour at pH-11	1700
8.	Filterate indigo liqour at pH-12	1550
9.	Filterate indigo liqour at pH-14	1500

* PAC – Poly Aluminum Chloride

The native indigo wash liquor has TDS value of 1800 PPM .The TDS value increases to 1850 in sample number 2, in which $FeCl_3$ has been used as coagulant for precipitation. TDS is maximum 2550 PPM in sample number 3, where PAC has been used. TDS value of solution filtered at pH 8 ,11,12 is more due to incomplete filteration & precipitation. However at pH 4 & 14, the TDS value of effluent filtrate is minimum due to comparatively more precipitation of indigo.

(3) O.D. measurement of std. Indigo & Indigo wash liquor using U.V. visible Spectrophotometer

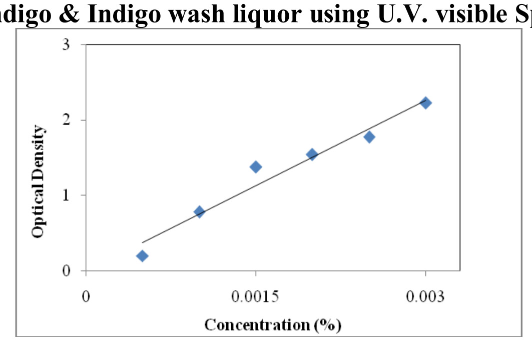


FIG.3.4 – PLOT OF O.D V/S CONCENTRATION IN DMSO OF STANDARD INDIGO POWDER AT λ MAX 619 NM

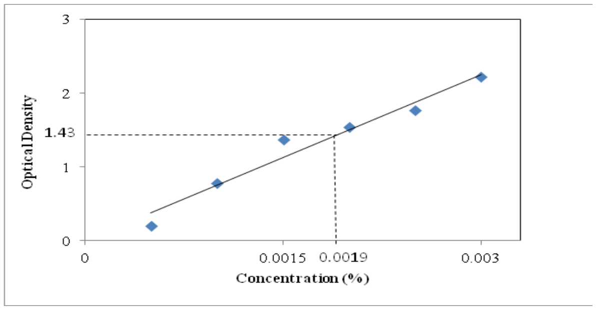


FIG.3.5 – CALCULATION OF CONCENTRATION OF RECOVERED INDIGO FROM FIG. 4.4

Determination of indigo concentration in indigo waste water-

(1) O.D of std. indigo powder was measured by dissolving in DMSO at 0.0005, 0.001, 0.0015, 0.002, 0.0025, 0.003 concentration (Table 3.3)

(2) Graph between O.D & Concentration plotted. (fig.3.4)

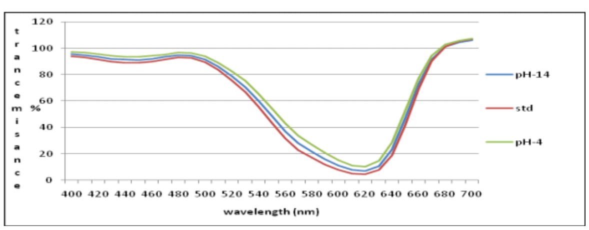
(3) Concentration of indigo in waste water was measured by filtering 25ml of waste water at pH 4 and digesting the residue in 50 ml of DMSO. O.D was measured by diluting it 13.33 times.

Filtration → Digest in DMSO → O.D measurement

TABLE 3.3 OPTICAL DENSITY OF STANDARD INDIGO POWDER IN DMSO

Conc.%	λ max	O.D
0.0005	618	0.200
0.0010	619	0.779
0.0015	619	1.374
0.0020	619	1.538
0.0025	619	1.770
0.0030	617	2.222

Concentration of indigo in waste water (13.33 times dilution) by dilute DMSO solution from graph was 0.0019%. Therefore the indigo concentration in waste water was calculated to be 0.240 gm/l or 240 PPM.
In the dyeing,dyeing assistants facilitates dyeing by neutralizing charge of fibre or dye or by reverse of it.At high concentration of assistants which change the charge of fibre or dye,association of dye molecules started and macro molecules formulation.



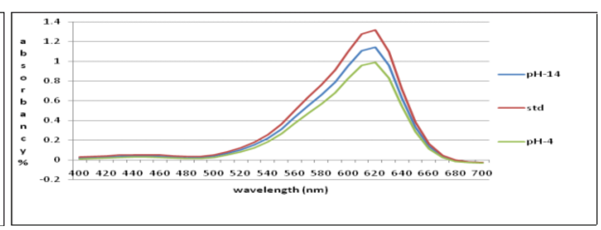


FIG.3.6 - TRANSMISSION V/S WAVELENGTH CURVE

FIG.3.7 – ABSORBANCE V/S WAVE LENGTH CURVE

Transmittance curve and absorbance curve of recovered Indigo at pH – 4, pH – 14 & std. Indigo are presented in the fig. no. 3.6, 3.7 respectively. The maximum absorbence peak of all sample lye at 620 nm. The absorbance curves are according to the strength of the dye. Curve of std. Indigo at top, pH 14 at middle & pH 4 at bottom.
In simple dye solution if no association of dye molecules take place then we have following equation

$$\log (I_0 /I_T) = € b c \quad (1)$$

Where I_0 and I_T are intensities of light entering and leaving the medium respectively. However in dye associated condition the equation become as follows -

$$\log (I_0 /I_T)= € b c/ 1+gc^x \quad (2)$$

where g and x are empirical constants related to a progressive change in the distribution of size of molecular aggregates, towards a greater average size with rise in concentrations. Since the larger the particle, the lower its € value. So if light is direct and monochromatic a curvilinear Beer's law plot for dye indicates progressive aggregation with rise in concentration, and all such deviations from linearity are evidence of dye association[10]. In the current study equation no. 1 is valid since indigo was dissolved in DMSO. Various types of experiments show that probably all dyes associate in aqueous solution, to varying extents, according to particular features in their molecular structure, the intermolecular attraction, apparently, is mainly due to van der walls forces. Dimmers are probably formed first and these grow by addition of further molecules (or dye ions) to give lameller micelles in which the dye molecules are stacked up like cards in a pack [11,12] .The general structure of Indigoid class of vat dyes are given below

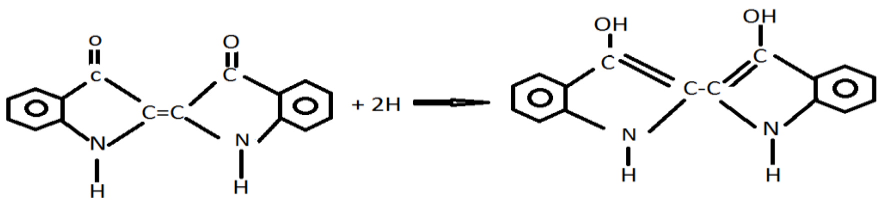


FIG. 3.8 INDIGO DYE STRUCTURE

In the dyeing, dyeing assistants facilitates dyeing by neutralizing the charge of fibre or dye or by reverse of it. At high concentration of assistants which change the charge of fibre or dye, association of dye molecules started and macro molecules formalation takes place

In acidic pH solution -

In presence of acetic acid H^+ formation takes place. The released H^+ combined with –NH group [13] of the dye and form $–NH_2^+$ and dye molecule become positively charged.

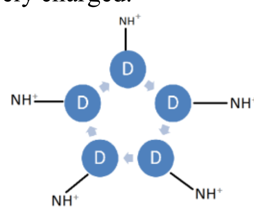


FIG. 3.9 MICELLER FORMATION [13]

$$D – NH + H^+ \longrightarrow D - NH_2^+ \quad \text{---------------- (3)}$$

As per equation no. (3), in highly acidic pH (In presence of acid), the released H^+ react with nitrogen of dye molecules which contain lone pair of electron and dye molecules acquire positive charge. The other dye molecule in water has negative charge, combined with positively charged molecules and in this way size of molecules start to increase. Since Indigo dye molecule contain benzene structure so it also possesses vander walls force of attraction and large molecular association takes place and thus micelle formations. Which facilitate dye molecules separation in filtration.

In basic pH solution –

$$D – R\,NH + H_2O \rightarrow D - R\,NH^+OH^- + D - R\,NH^+OH^- + \quad \text{---- -----(4)}$$

Here, D – Stands for dye

In basic solution the amino group combines with water molecules and reaction [13] takes place as per equation no.(4). The combined entity further react with another molecule and in this way molecular aggregation takes place and large size molecules easily filtrate in high alkaline pH solution. Again wander walls force of attraction play its role in big molecule formation and thus micelle formation.

(4) Functional group study by I R Spectophotometer

IR studies on standard indigo dye was done on FTIR, Make - Perkin Elmer, Model – Spectrum – 2 (Double beam spectrophotometer).

[redacted]

FIG.3.10 – IR GRAPH FOR INDIGO STANDARD

Figure shows the following functional group of standard Indigo pure dye in the IR graph.

N-H 3271.4 CM^{-1},
C=O 1628.3 CM^{-1} ,
C=C 1490.4 CM^{-1}

Standard values of functional groups reported in literature are

C=O (ketone group) range cm^{-1} 1610 – 1690
N- H (Amine group) range cm^{-1} 3200 – 3400
C=C (Alkine group) range cm^{-1} 1300 – 1500

Therefore the functional groups in native Indigo are in accordance with the standard value in literature.

[redacted]

FIG.3.11– IR GRAPH FOR INDIGO RECOVERED AT PH –4

N- H 3271.4 CM^{-1},
C=O 1634.3 CM^{-1} ,
C=C 1484.4 CM^{-1}
are observed in the standard IR graph.

[redacted]

FIG. 3.12– IR GRAPH FOR INDIGO RECOVERED AT PH - 14

Figure 3.12 shows the functional group of recovered Indigo at pH - 14

N- H 3265.4 CM^{-1},
C=O 1628.3 CM^{-1} ,
C=C 1484.4 CM^{-1}

Study indicates all the functional groups are present in recovered Indigo at pH 4 & pH 14, with slight deviation from standard indigo graph but within the tolerance range.

(5) Light fastness testing

Light fastness of fabric dyed by Indigo recovered at pH-4 and pH-14 was determined using MBTF light fastness tester, by simultaneously exposing the recovered dye sample, standard Indigo dyed sample and standard blue wool under following condition.

Temperature - $51^{0}C$
Time – 40 Hrs

Light fastness of recovered indigo and standard Indigo was found to be same as no fading occurred even after 40 Hrs of exposure to MBTF light. Light fastness is > 4.

(6) Study the various color parameters by Computer Color Matching system

In CCM system, the following color parameters were studied in standard Indigo and recovered Indigo after dyeing on cotton yarn.
(1) - L a b values
(2) - K/S value and strength at ƛ max.
(3) - Reflectance curves and their comparison.

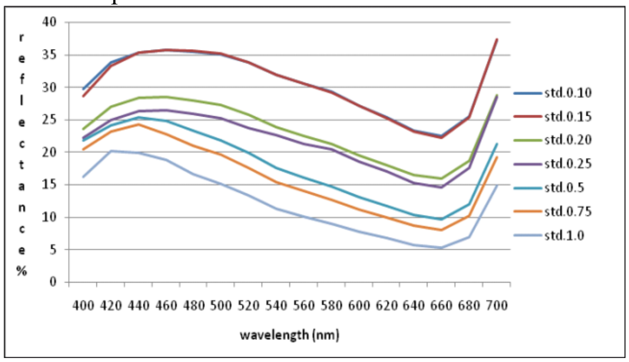


FIG.3.13 - REFLECTANCE OF STANDARD INDIGO DYED AT VARIOUS CONCENTRATION LEVEL

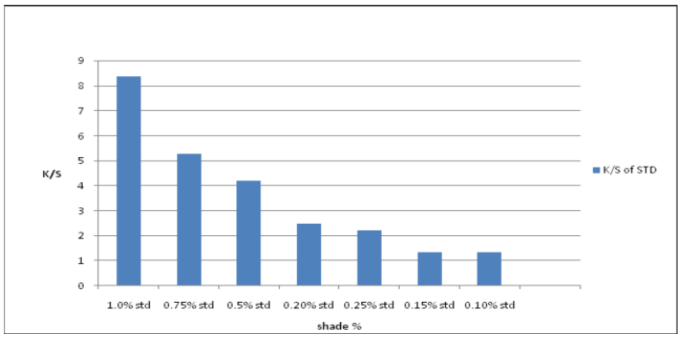
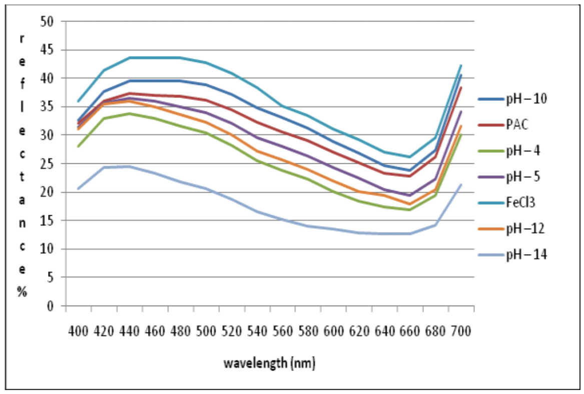


FIG.3.14 - K/S OF DIFFERENT SHADE % OF INDIGO STANDARD (BAR DIAGRAM)

Reflectance value of Indigo dye dyed at various concentration level i.e. 0.1, 0.15, 0.20, 0.25, 0.50, 0.75, 1.00 are shown in table 3.4. Wavelength of maximum absorption (ƛ max.) in all samples lye at 660 nm (Red region) and minimum absorption at 460 nm (Blue region).
In table 3.4 the corresponding L a b value and calculated K/S at ƛ max. has also been shown.
Reflectance curves of all standard Indigo dye samples are shown in fig. 3.13. K/S values have also been depicted in the bar diagram (fig. 3.14).

TABLE 3.4
VARIOUS COLOUR PARAMETERS OF RECOVERED INDIGO (ƛ MAX. = 660 NM)
FIG. 3.15 – REFLECTANCE CURVES OF RECOVERED INDIGO DYED AT 1% CONCENTRATION LEVEL

Sample	%of shade	L*	a*	b*	%R (at ƛ max.)	K/S
$FeCl_3$	1%	64.742	-6.68	-7.324	23.85	1.21
PAC	1%	62.792	-5.689	-7.763	22.78	1.31
pH-14	1%	47.356	-5.209	-14.114	12.76	2.98
pH-12	1%	57.047	-6.251	-12.157	17.90	1.88
pH-10	1%	66.109	-6.393	-4.295	26.16	1.04
pH-5	1%	60.673	-6.023	-9.894	19.4	1.67
pH-4	1%	58.704	-5.782	-12.105	16.96	2.03



Reflectance values of all recovered Indigo samples i.e. cotton yarn dyed by Indigo recovered by $FeCl_3$, PAC without coagulant at pH 4, pH 5, pH 10, pH 12, pH 14 at 1% concentration have been presented in fig.3.15. Interestingly, the absorption maximum of all the samples lye at 660 nm indicating blue tone, similar to standard Indigo dyed samples. However, the absorption minima fluctuate with change of pH. At pH 4, it lye at 460 nm (similar to std. indigo) at pH 10 & 14 it falls at 440 nm, indicating slight tonal deviation at alkaline pH, may be due to auxochromic difference and reason assigned earlier, indicated slightly shift in IR NH band (fig.3.12). In standard Indigo and pH – 4, NH band lyes at 3271.4 cm^{-1}, whereas in Indigo recovered at pH – 14, it lyes at 3265.4 cm^{-1}. L a b values and K/S values calculated at (660 nm for 1% shade of all Indigo recovered samples are shown in table 4.8. The K/S value is maximum for indigo recovered at pH 14 (K/S = 2.98) followed by pH 4 (K/S = 2.03) due to effect of OH^- and H^+ ions on dye aggregation. K/S value at other pH are less than these two values, indicating less strength of recovered dye then pH 4 & pH 14. The K/S value of Indigo recovered by $FeCl_3$ & PAC are 1.21 and 1.31 respectively. Along with less K/S values, the shade of recovered Indigo is also dull which is indicated by plateau of reflectance curve in the region 460 – 520 nm. Therefore $FeCl_3$ & PAC increases the coagulation rate of indigo, however the recovered dye may not be suitable for reuse due to dullness in tone. K/S values are also represented in the bar chart fig. 3.16.

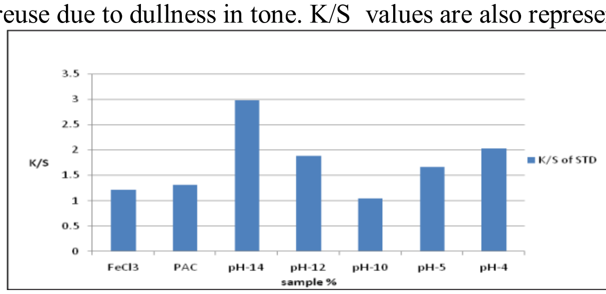


FIG. 3.16– K/S VALUE OF SAMPLES DYED AT 1% SHADE BY INDIGO RECOVERED BY VARIOUS METHODS

Sample	% Shade	K/S	Strength (K/S of sample / K/S of standard)
Control	0.5	4.21	1.00
$FeCl_3$	1.0	1.21	0.287
PAC	1.0	1.31	0.311
pH-14	1.0	2.98	0.708
pH-12	1.0	1.88	0.446
pH-10	1.0	1.04	0.247
pH-5	1.0	1.67	0.397
pH-4	1.0	2.03	0.482

TABLE 3.5 STRENGTH COMPARISON OF VARIOUS RECOVERED INDIGO AFTER DYEING WITH STD. INDIGO 0.5% SHADE AS CONTROL SAMPLE

λ max. = 660 nm, Shade – 1%

Calculated strength of all recovered dyed samples compared at with 0.5% shade of standard indigo has been presented in table 3.5. Maximum strength of 0.708 has been observed at pH 14 followed by 0.482 at pH 4.

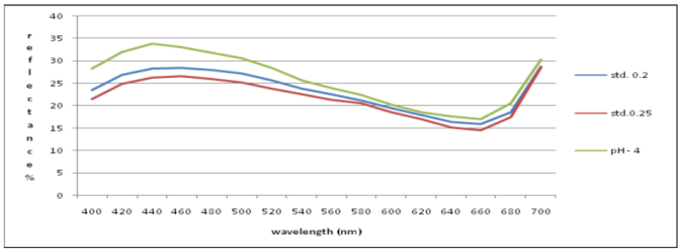


FIG.3.17 - COMPARISON BETWEEN INDIGO RECOVERED AT pH –4, 1% SHADE WITH 0.2 % & 0.25 % STANDARD INDIGO DYE

Dye recovered at pH 4, 1% has been compared with standard indigo 0.2%, 0.25% fig. 3.17.. Graph indicates slight tonal change in the recovered dye.

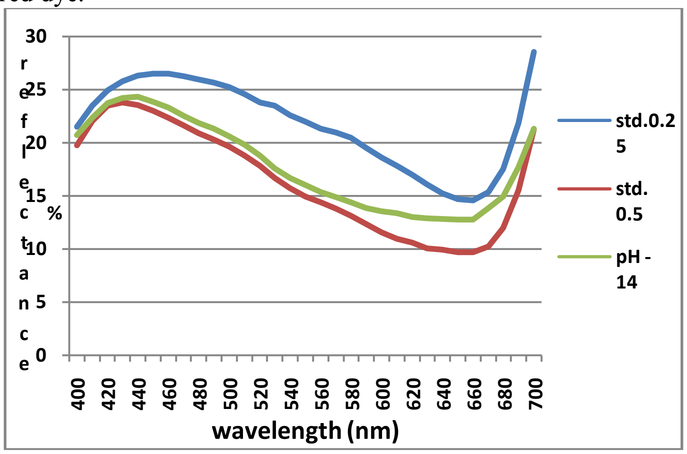


FIG.3.18 - COMPARISON BETWEEN INDIGO RECOVERED AT PH – 14, 1% SHADE AND INDIGO STANDARD DYE

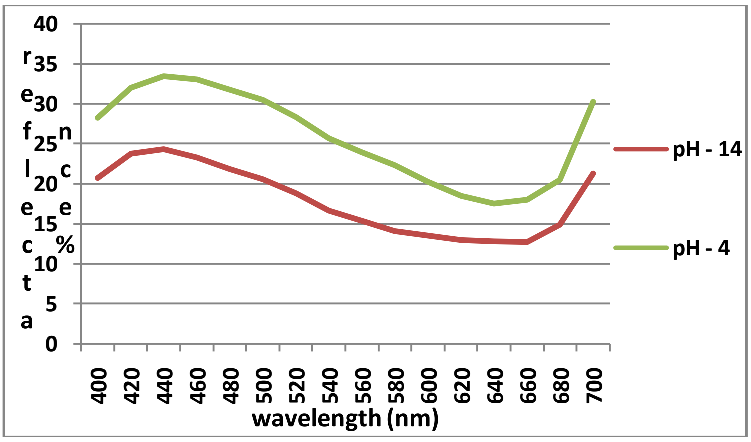


FIG.3.19 - REFLECTANCE CURVE OF RECOVERD INDIGO PH – 4 & PH – 14 AT 1% CONCENTRATION LEVEL

Reflectance curve of recovered dye at pH 4 and pH 14 has been shown in fig. 3.19. Both the curves have ƛ max. at 660 nm, but slope of the curve at pH 4 is more, indicating more dye purity and brightness of shade. Therefore the dye recovered at pH 4 gives more brighter shade than at pH 14, however the strength of dye recovered at pH 14 is greater than pH 4.

4. Conclusions

The present study on recovery and reuse of indigo from denim wash liquor by filteration using coagulants and variation in pH lead to the following conclusion.

- Indigo can be recoverd from the denim wash waste liquor by all the 7 methods using a nano filter and self made suction device.
- PAC and Fecl3 may be good coagulants, however produces dullness in shade. Therefore dye is not reusable.
- Concentration of Indigo in wash liquor determined by O.D. method, dissolving Indigo in DMSO is estimated to be 240 ppm. Therefore in one month 1080 Kg of Indigo/month can be recovered in the industry under study.
- TLC and IR studies of dye recovered at pH 4 and 14 reveals that structure of dye remains almost intact after recovery.
- Dispersing agent used in preparing stock solution of Indigo dye, increases the time of dye separation.
- light fastness of recovered Indigo is similar to standard Indigo.
- Filteration time is observed to be minimum at pH 14 followed by pH 4.
- Strength of dye recovered at pH 14 is maximum followed by pH 4.
- Shade of dye recovered at pH 4 has more brightness.
- Indigo recovered at pH 4 and 14 can be reused with partial replacement of pure Indigo.
- Indigo waste water after washing if used to prepare stock solution, will result in ultimate saving of 10-20%

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