CHAPTER 4
RESULTS AND DISCUSSION

This work includes a pilot run and an experimental study per the study's objectives. The pilot run was the basis of experimental work, included optimizing the extraction and dyeing process. The experimental work includes the dyeing in mixture and recipe prediction work. All the details of the results are mentioned in this section.

4.1 Pilot Study

The pilot study was done to find the optimum extraction of selected dyes and their optimum dyeing conditions on selected cotton fabric. The optimum extraction conditions were used to obtain the maximum color extraction for all samples to be dyed. In the second part of the pilot study, the optimum dyeing conditions for each dye were obtained on the cotton fabric. The obtained optimum dyeing conditions were then used in experimentation work. This section explains both the optimization processes.

4.1.1 Optimization of Extraction parameters for all the selected dyes

Dye material for Marigold, Pomegranate, Madder, Annatto, Babool, Sappanwood, Rhubarb, and Katha dye material was taken for extraction optimization. The optimization was done using a range of temperatures, time, and MLR as per Table 4.1. The extracted dyed solution was measured using a spectrophotometer to obtain the absorbance value / optical density. Optical density was used to find the maximum color extract from each dye; hence, the optimized parameters for extraction were found. The optimized parameters for respective dyes were then used to extract and further dye cotton fabric.

Table 4.1: Experimental setup for Extraction Optimization

| Parameter	Trail	Control Condition
MLR	1:10	Temperature -80°C, Time-60 mins
	1:20	
	1:30	
Temperature (°C)	60	MLR-1:20, Time - 60 mins
	80	
	100	
Time (min)	30	MLR-1:20, Temperature -80°C
	60	
	90	

4.1.1.1 Red/Orange tone dyes

(A)   Annatto

Annatto dye powder extraction was done as per the parameters mentioned above. The absorbance/optical density of the extracted solution was measured using a spectrophotometer in the visible region of spectra. The extracted solution was diluted at 2.5% to keep the absorbance value from zero to one. The absorbance values are shown in Table 4.2 at a wavelength of 380 nm (λ_{max}). The plot of absorption vs. MLR, temperature, and time are shown in Figure 4.1.

Table 4.2: Optical density/absorbance of aqueous extract of Annatto dye at various extraction conditions

| Parameter	Trail	Control Condition	Absorbance
MLR	1:10	Temperature -80°C, Time-60 mins	0.583
	1:20		0.496
	1:30		0.382
Temperature (°C)	60	MLR-1:20, Time - 60 mins	0.390
	80		0.437
	100		0.459
Time (min)	30	MLR-1:20, Temperature -80°C	0.407
	60		0.437
	90		0.440

The findings indicate that as MLR increases, absorbance decreases from 1:10 to 1:20 and then sharply declines till 1:30. This could be because there are more water molecules present per unit dye molecule in the case of higher MLR. The absorbance increases as the temperature rises from 60°C to 100°C, according to the absorbance vs. temperature plot. Compared to 60°C to 80°C, the increase in absorption from 80°C to 100°C was slower. Higher temperatures may cause more pigment molecules to disintegrate, which could explain the increase. Compared to other criteria, the impact of time was shown to be less important. A slight increase in absorbance from 30 to 60 minutes and a negligible increase from 60 to 90 minutes were discovered.

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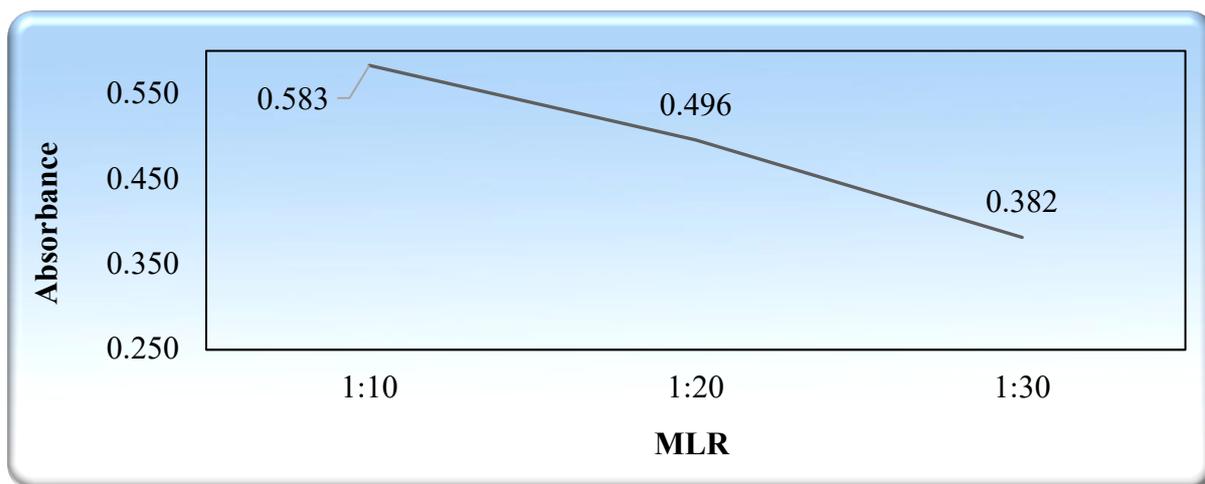
(a)
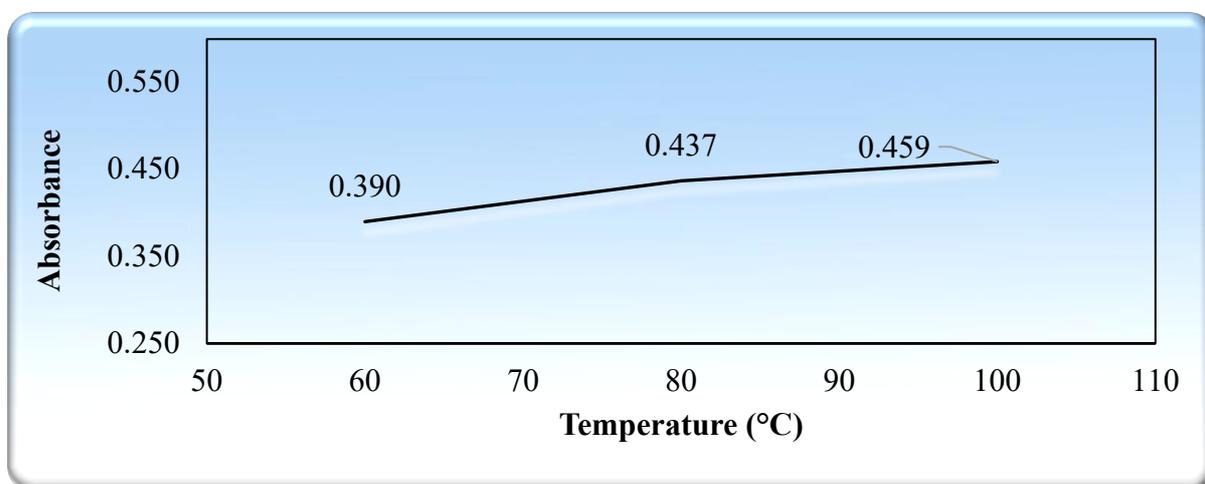
(b)
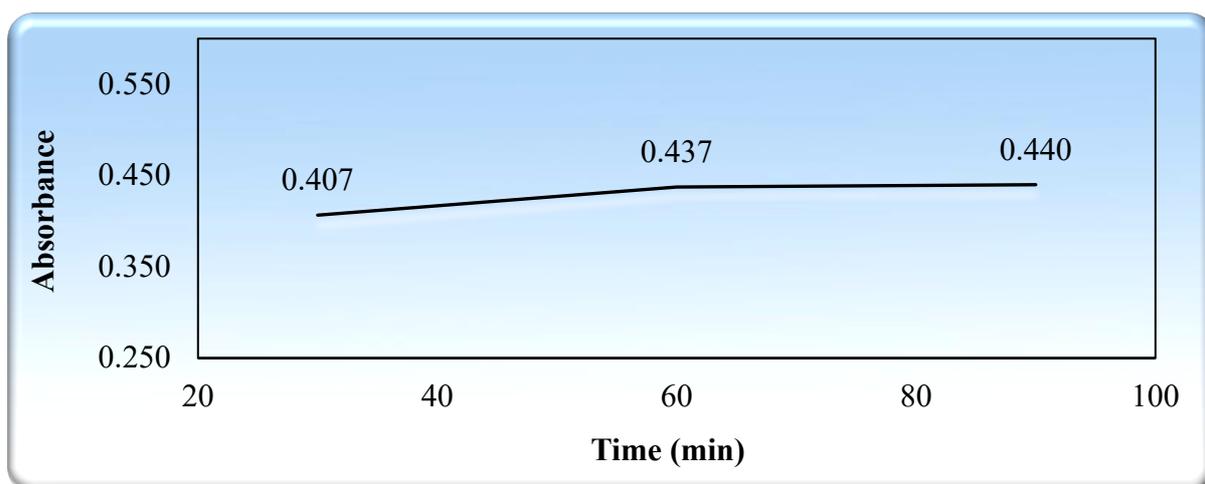
(c)

Figure 4.1: Plot of Absorption vs. MLR (a), Temperature (b), and Time (c) for aqueous extract of Annatto dye
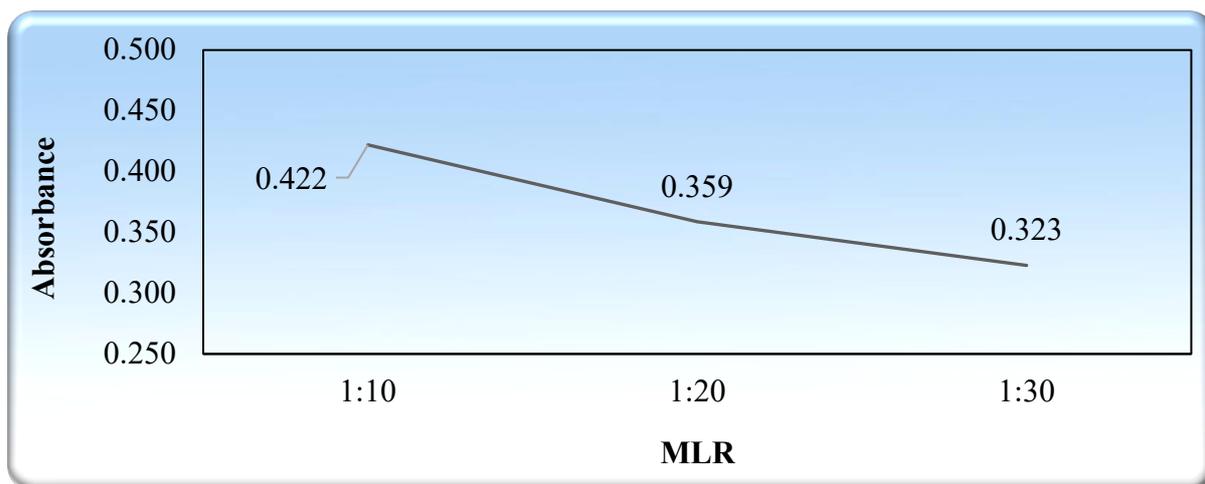
(B)   Madder

Extraction of Madder dye powder was performed according to the set conditions. The extracted solution's absorbance was measured using a spectrophotometer in the visible region of spectra. The extracted Madder solution was diluted to a concentration of 1.6% to maintain an absorbance value between zero and one. The absorbance values are shown in Table 4.3 at a wavelength of 430 nm (λ_{max}). The plot of absorption vs. MLR, temperature, and time are shown Figure 4.2.

Table 4.3: Optical density/absorbance of aqueous extract of Madder dye at various extraction conditions

| Parameter	Trail	Control Condition	Absorbance
MLR	1:10	Temperature -80°C, Time-60 mins	0.422
	1:20		0.359
	1:30		0.323
Temperature (°C)	60	MLR-1:20, Time - 60 mins	0.316
	80		0.359
	100		0.358
Time (min)	30	MLR-1:20, Temperature -80°C	0.334
	60		0.359
	90		0.366

According to the findings, the absorbance decreases as MLR increases from 1:10 to 1:20 and then continues to decline until 1:30. It may be said that the dye dissolution is better in the case of higher MLR. According to the absorbance vs. temperature plot, the absorbance increases as the temperature rises from 60°C to 80°C and stays nearly constant from 80°C to 100°C. The increase may be because more pigment molecules dissolve at higher temperatures and then attain saturation. The impact of time was discovered to be less important than other parameters. It was found that there was a small increase in absorbance from 30 minutes to 90 minutes.

(a)
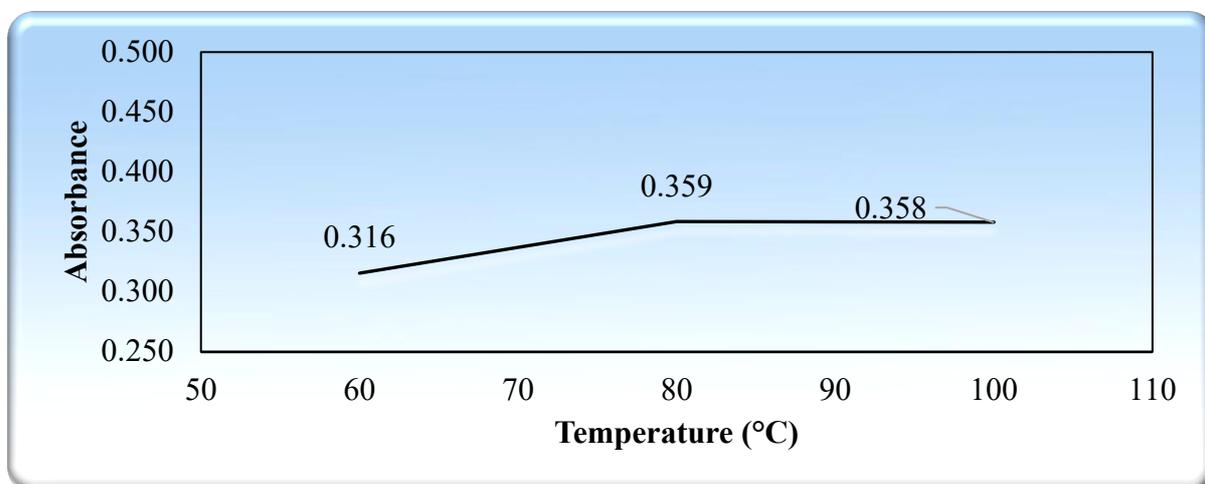
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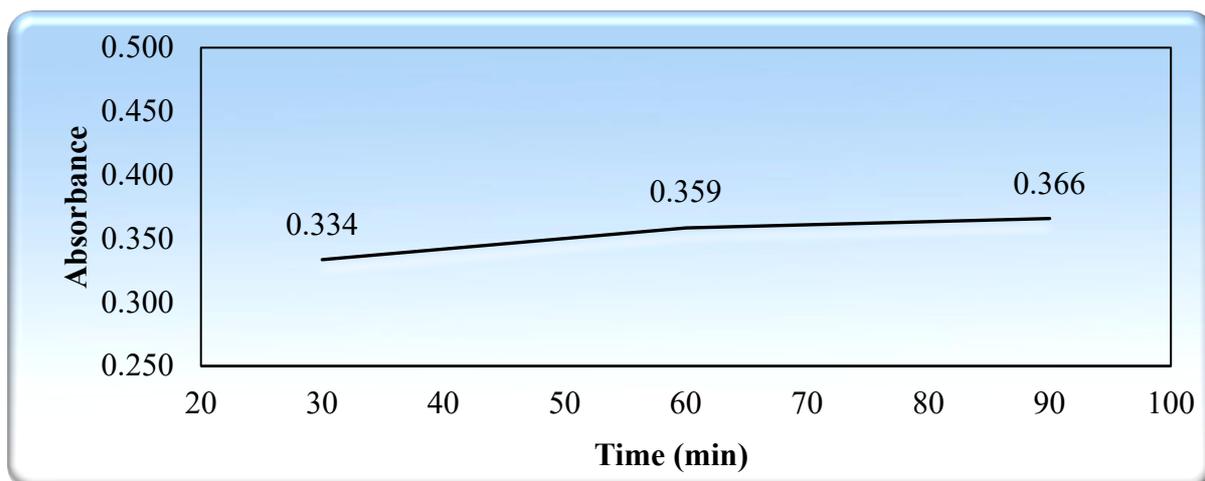
(c)

Figure 4.2: Plot of Absorption vs. MLR (a), Temperature (b), and Time (c) for aqueous extract of Madder dye
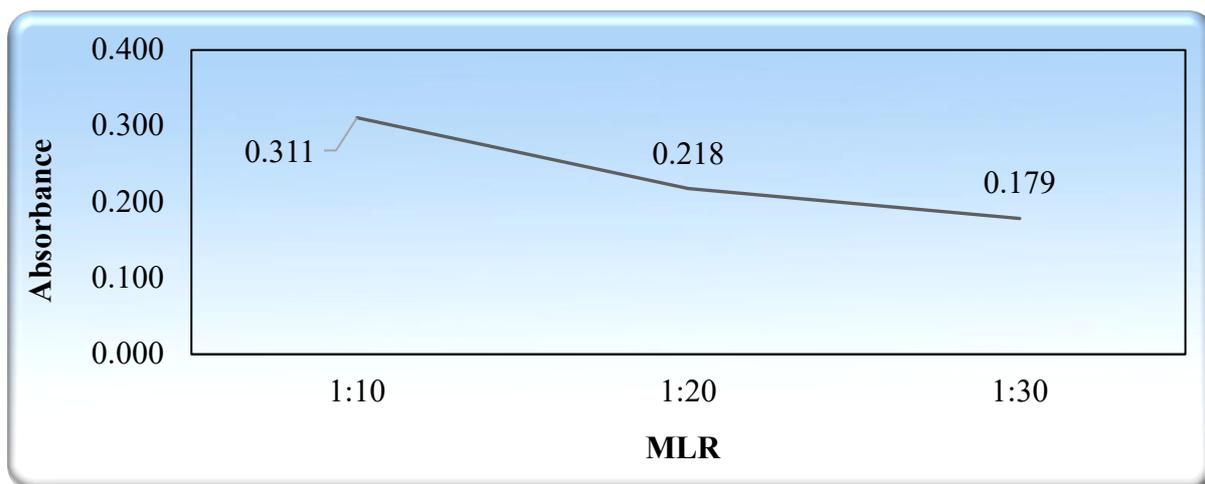
(C)   Sappanwood

Sappanwood dye powder extraction was done as per the selected parameters. The absorbance of the extracted solution was measured using a spectrophotometer in the visible region of spectra.   The extracted Sappanwood solution was diluted at 1 % to keep the absorbance value within the range of zero to one. The absorbance values are shown in Table 4.4 at a wavelength of 380 nm (λ_{max}). The plot of absorption vs. MLR, temperature, and time are shown Figure 4.3.

Table 4.4: Optical density/absorbance of aqueous extract of Sappanwood dye at various extraction conditions

Parameter	Trail	Control Condition	Absorbance
MLR	1:10	Temperature -80°C, Time-60 mins	0.311
	1:20		0.218
	1:30		0.179
Temperature (°C)	60	MLR-1:20, Time - 60 mins	0.161
	80		0.218
	100		0.242
Time (min)	30	MLR-1:20, Temperature -80°C	0.190
	60		0.218
	90		0.235

The findings indicate that absorbance diminishes as the MLR rises from 1:10 to 1:20, continuing to decrease until 1:30 but with a less pronounced slope. This might be attributed to a higher interaction of dye molecules with water. According to the graph depicting absorbance against temperature, absorbance rises as temperature increases from 60°C to 100°C, and slow increase was observed from 80°C to 100°C. This rise may result from the greater number of pigment molecules dissolving at elevated temperatures, reaching saturation eventually. Regarding the influence of time on absorbance, a notable increase was recorded from 30 minutes to 90 minutes.

(a)
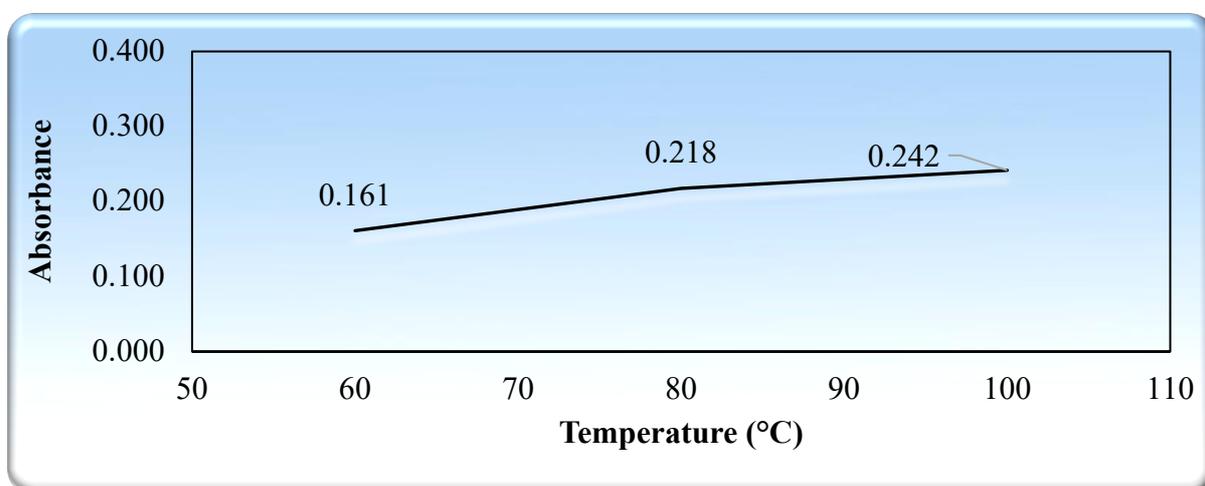
(b)
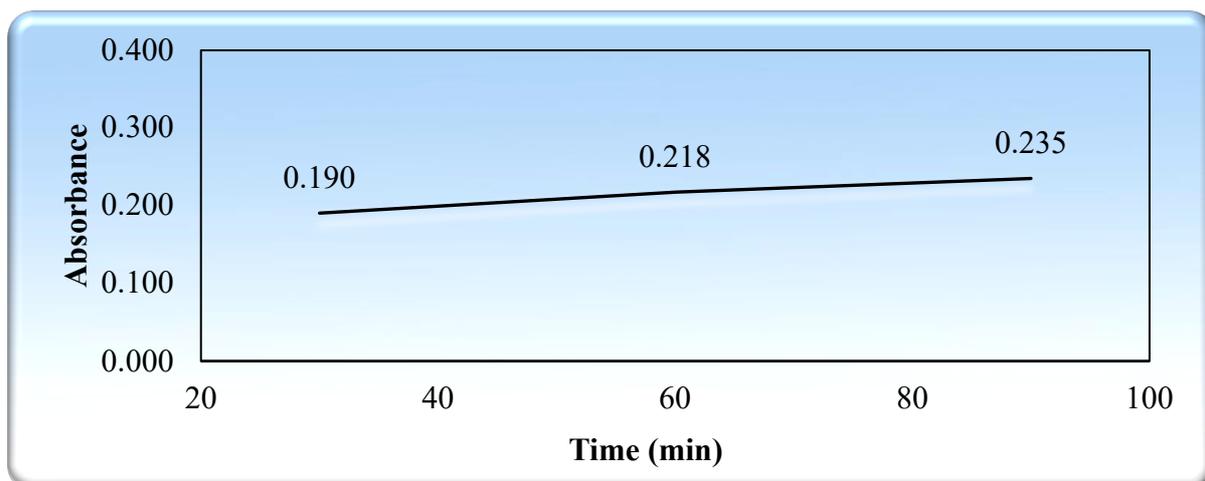
(c)

Figure 4.3: Plot of Absorption vs. MLR (a), Temperature (b), and Time (c) for aqueous extract of Sappanwood dye

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4.1.1.2 Brown dyes

(A)   Babool

Extraction of Babool dye powder was performed according to the set conditions. The extracted solution's absorbance was measured using a spectrophotometer in the visible region of spectra. The extracted Babool solution was diluted to a concentration of 1.6% to maintain an absorbance value between zero and one. The absorbance values are shown in Table 4.5 at a wavelength of 380 nm (λ_{max}). The plot of absorption vs. MLR, temperature, and time are shown Figure 4.4.
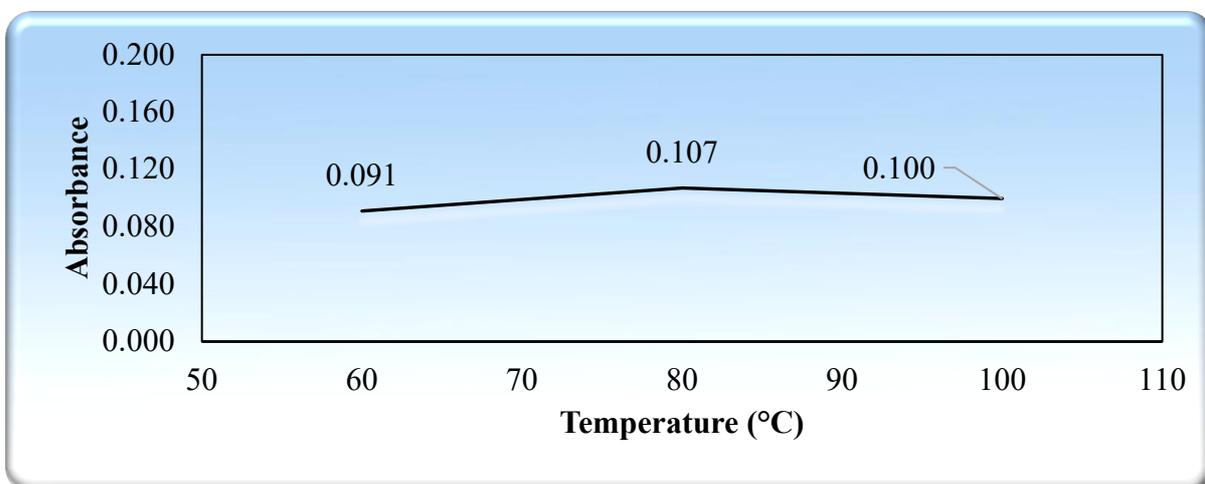
Table 4.5: Optical density/ absorbance of aqueous extract of Babool dye at various extraction conditions

Parameter	Trail	Control Condition	Absorbance
MLR	1:10	Temperature -80°C, Time-60 mins	0.119
	1:20		0.093
	1:30		0.081
Temperature (°C)	60	MLR-1:20, Time - 60 mins	0.091
	80		0.107
	100		0.100
Time (min)	30	MLR-1:20, Temperature -80°C	0.088
	60		0.107
	90		0.108

According to the findings, the absorbance decreases as MLR increases from 1:10 to 1:20 and then continues to decline until 1:30. It was found that the decline was a sharp decline from 1:10 to 1:20. This absorbance decline trend can be because there are more water molecules present than extracted pigment molecules. According to the absorbance vs. temperature plot, the absorbance increases as the temperature rises from 60°C to 80°C and then decreases from 80°C to 100°C. The increase in absorbance from 60°C to 80°C may be because more pigment molecules get dissolved at higher temperatures. The decline in absorbance from 80°C to 100°C may be due to the unstable chromophore at higher temperatures. The impact of time was discovered to be less important than other parameters. It was found that there was a slight increase from 30 minutes to 60 minutes and then remained almost constant from 60 minutes to 90 minutes. The increase in absorbance may be due to more pigment release as time passes and then saturates.
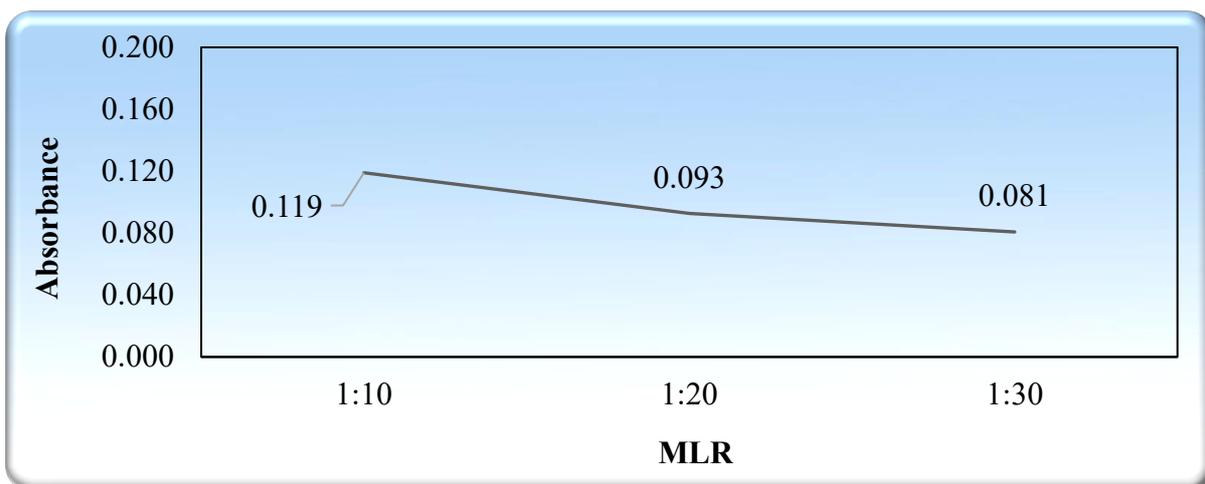
(a)

(b)
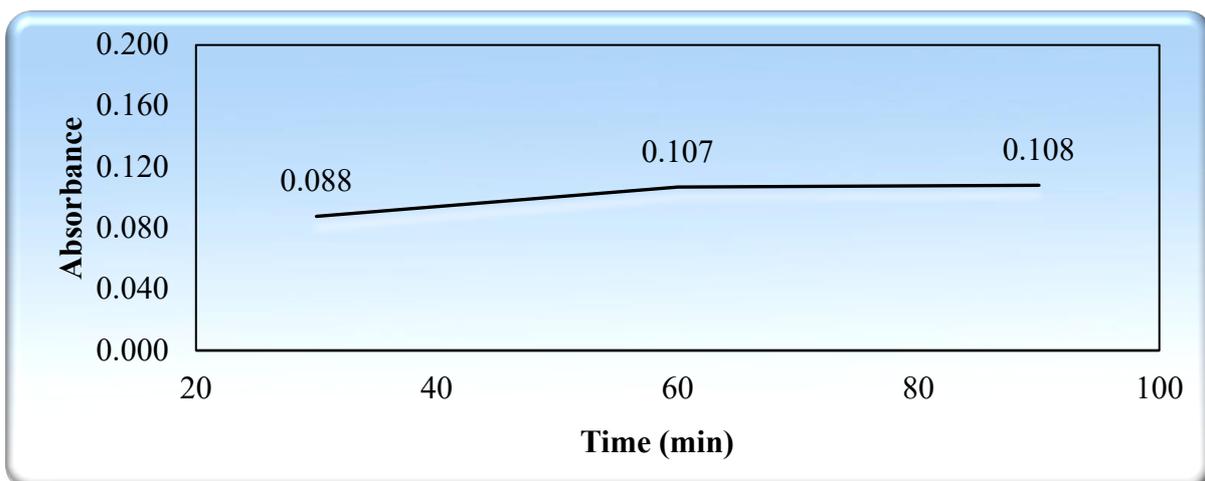
(c)

Figure 4.4: Plot of Absorption vs. MLR (a), Temperature (b), and Time (c) for aqueous extract of Babool dye
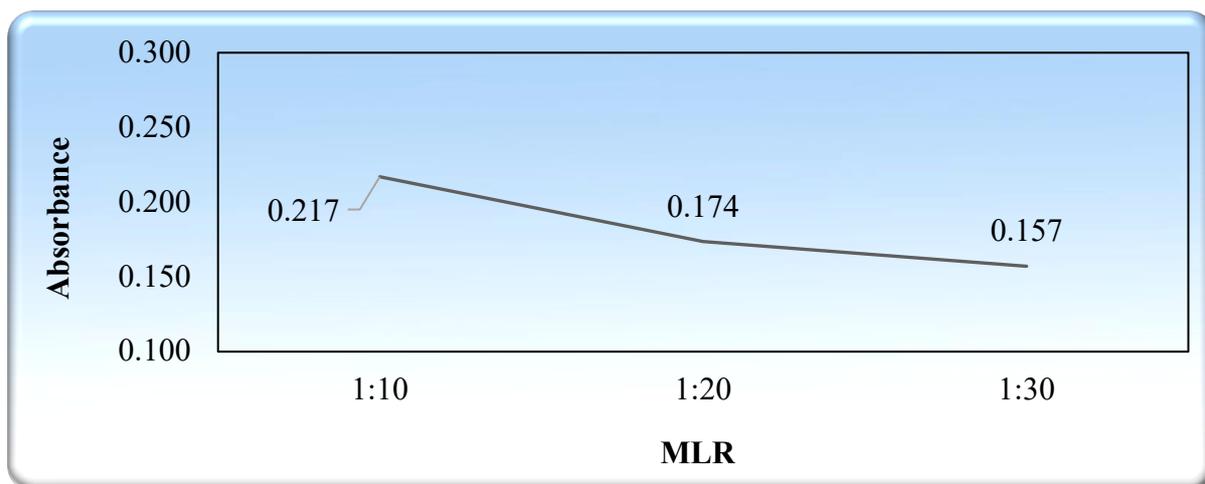
(B)   Katha

Katha dye powder extraction was done as per the parameters mentioned above. The absorbance/optical density of the extracted solution was measured using a spectrophotometer in the visible region of spectra. The extracted solution was diluted at 0.9 % to keep the absorbance value from zero to one. The absorbance values are shown in Table 4.6 at a wavelength of 380 nm (λ_{max}). The plot of absorption vs. MLR, temperature, and time are shown Figure 4.5.

Table 4.6: Optical density/ absorbance of aqueous extract of Katha dye at various extraction conditions

Parameter	Trail	Control Condition	Absorbance
MLR	1:10	Temperature -80°C, Time-60 mins	0.217
	1:20		0.174
	1:30		0.157
Temperature (°C)	60	MLR-1:20, Time - 60 mins	0.130
	80		0.174
	100		0.193
Time (min)	30	MLR-1:20, Temperature -80°C	0.156
	60		0.174
	90		0.184

The results show that absorbance decreases as the MLR increases from 1:10 to 1:30. This could be because there are more water molecules present per unit dye molecule in the case of higher MLR. The graph illustrating absorbance versus temperature reveals that as temperature rises from 60°C to 100°C, absorbance also increases. However, the rate of this increase diminishes from 80°C to 100°C when compared to the rise seen from 60°C to 80°C. This increase may be attributed to a higher kinetic energy at elevated temperature. In the graph of absorbance with time, absorbance increases as the duration extends from 30 to 90 minutes.

(a)
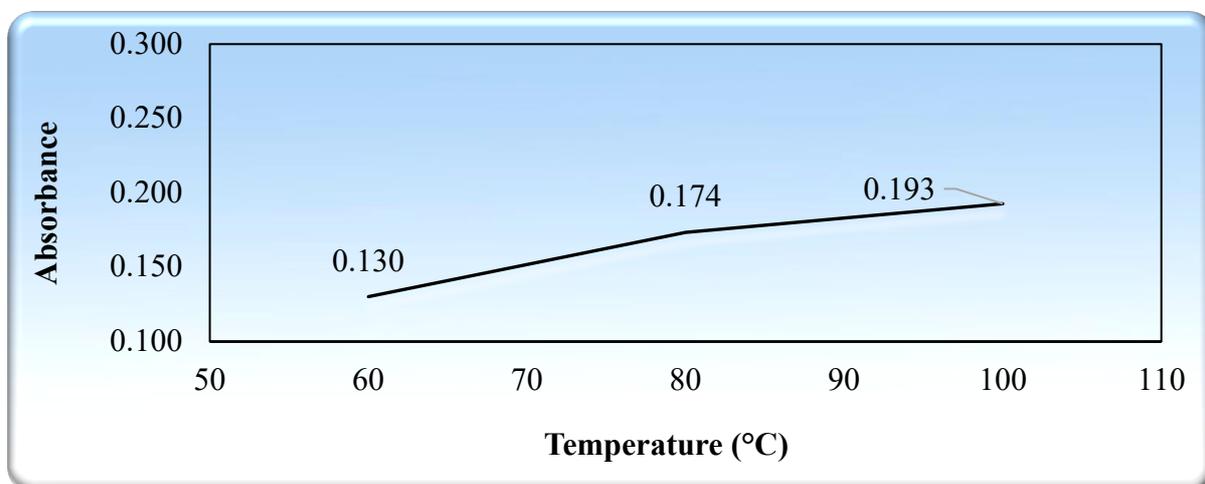
(b)
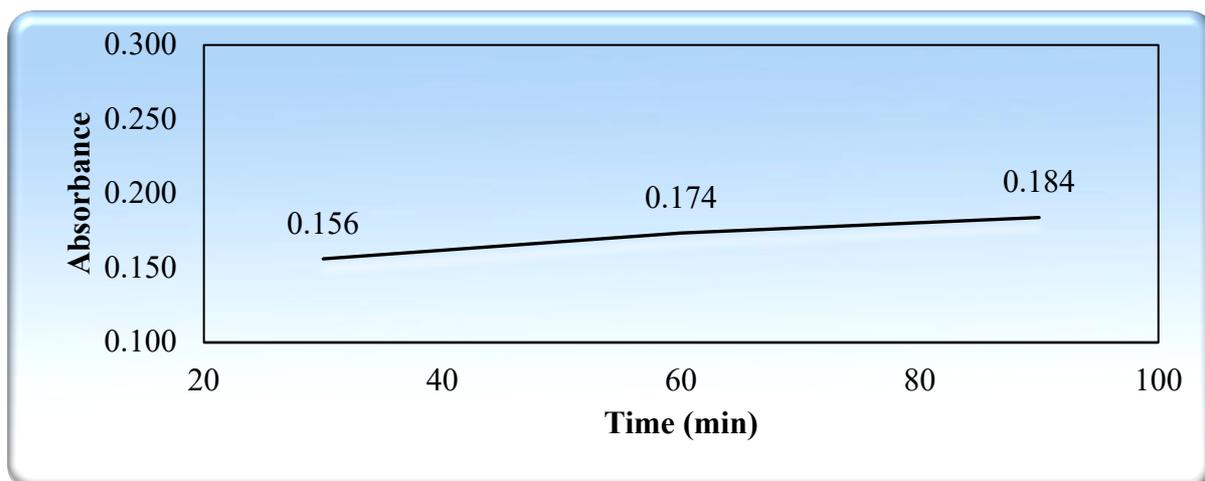
(c)

Figure 4.5: Plot of Absorption vs. MLR (a), Temperature (b), and Time (c) for aqueous extract of Katha dye

(C)   Rhubarb

The extraction of Rhubarb dye powder was conducted under the specified conditions. The absorbance of the extracted solution was measured using a spectrophotometer in the visible region of spectra. The extracted Rhubarb solution was diluted to a concentration of 0.4 percent to maintain an absorbance value between zero and one. The absorbance values are shown in Table 4.7 at a wavelength of 410 nm (λ_{max}). The plot of absorption vs. MLR, temperature, and time are shown Figure 4.6.

Table 4.7: Optical density/ absorbance of aqueous extract of Rhubarb dye at various extraction conditions

Parameter	Trail	Control Condition	Absorbance
MLR	1:10	Temperature -80°C, Time-60 mins	0.233
	1:20		0.200
	1:30		0.146
Temperature (°C)	60	MLR-1:20, Time - 60 mins	0.152
	80		0.203
	100		0.225
Time (min)	30	MLR-1:20, Temperature -80°C	0.177
	60		0.203
	90		0.219

According to the results, absorbance declines when MLR increases from 1:10 to 1:20 and then continues to fall until 1:30. The drop was determined to be a sharp decline from 1:10 to 1:20. This might be attributed to a higher interaction of dye molecules with water. The absorbance increases from 60°C to 80°C and then rises steadily from 80°C to 100°C, as indicated by the absorbance vs temperature graph. The increase in absorbance may be due to more pigment molecules being dissolved at higher temperatures. It was shown that absorbance increased from 30 minutes to 90 minutes. The rise in absorbance may result from increased pigment release over time.

(a)
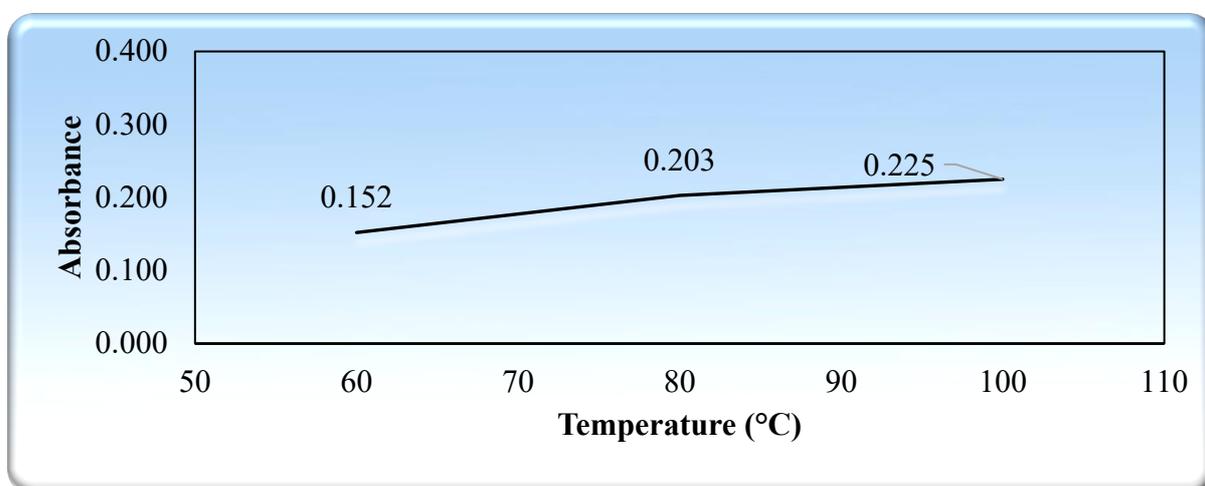
(b)
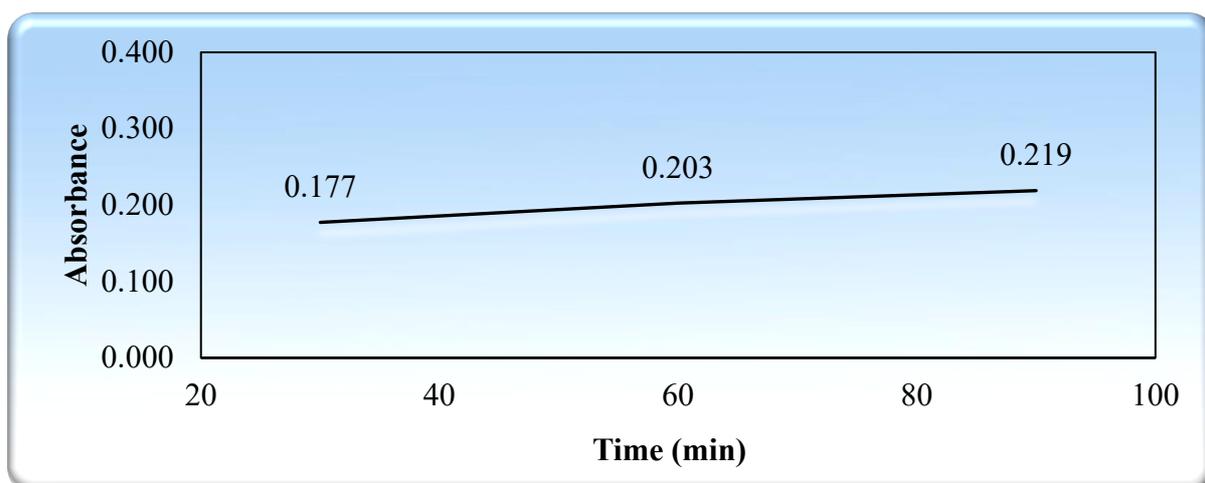
(c)

Figure 4.6: Plot of Absorption vs. MLR (a), Temperature (b), and Time (c) for aqueous extract of Rhubarb dye
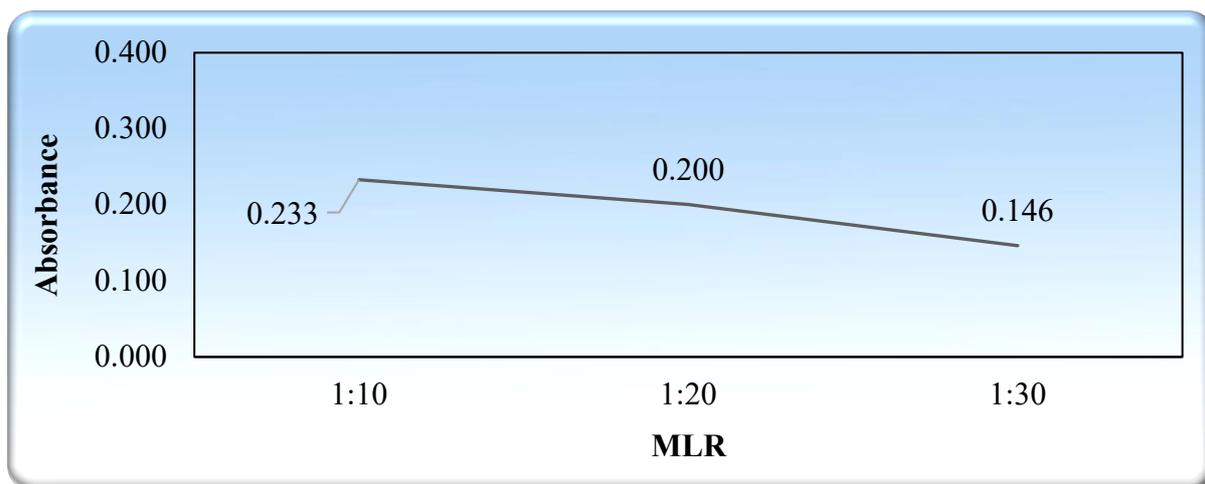
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4.1.1.3 Yellow Dyes

(A)   Marigold

The extraction of Marigold dye powder was conducted under the specified conditions. The absorbance of the extracted solution was measured using a spectrophotometer in the visible region of spectra. The extracted Marigold solution was diluted to a concentration of 1% to maintain an absorbance value between zero and one. The absorbance values are shown in Table 4.8 at a wavelength of 380 nm (λ_{max}). The plot of absorption vs. MLR, temperature, and time are shown Figure 4.7.

Table 4.8: Optical density/ absorbance of aqueous extract of Marigold dye at various extraction conditions

Parameter	Trail	Control Condition	Absorbance
MLR	1:10	Temperature -80°C, Time-60 mins	0.486
	1:20		0.431
	1:30		0.392
Temperature (°C)	60	MLR-1:20, Time - 60 mins	0.367
	80		0.431
	100		0.461
Time (min)	30	MLR-1:20, Temperature -80°C	0.401
	60		0.431
	90		0.440

The findings indicate that absorbance decreases as the MLR ratio rises from 1:10 to 1:20, continuing its decline until it reaches 1:30. A significant reduction was observed between 1:10 and 1:20. Higher quantity of water at higher MLR lead to increase in release of pigments . As shown in the absorbance versus temperature graph, absorbance increases from 60°C to 100°C. This increase may be attributed to a higher kinetic energy at elevated temperature. It was observed that absorbance notably increased between 30 and 60 minutes, with only a minimal increase from 60 to 90 minutes. The increase in absorbance is likely due to enhanced pigment release over time.

(a)
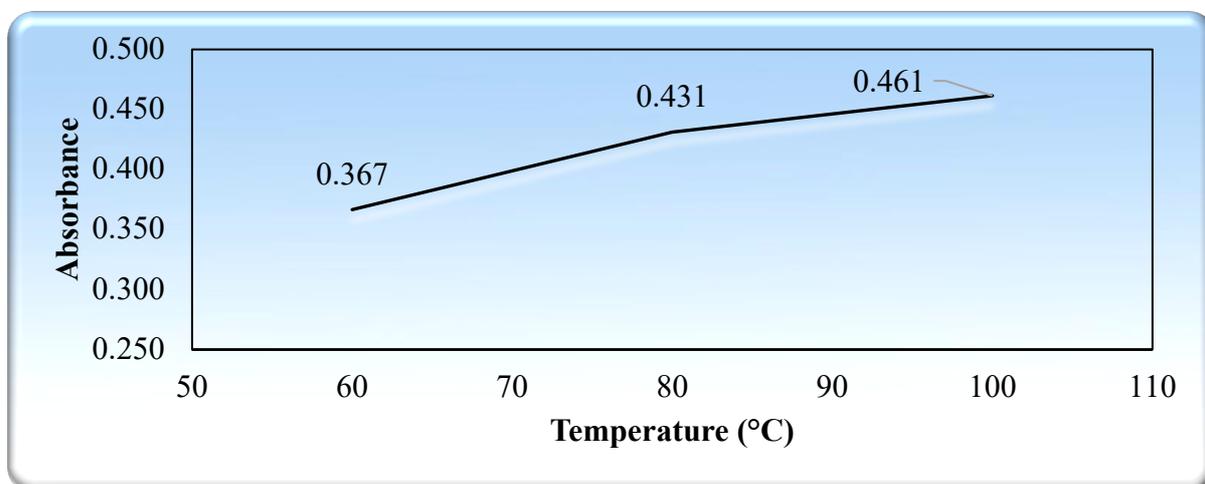
(b)
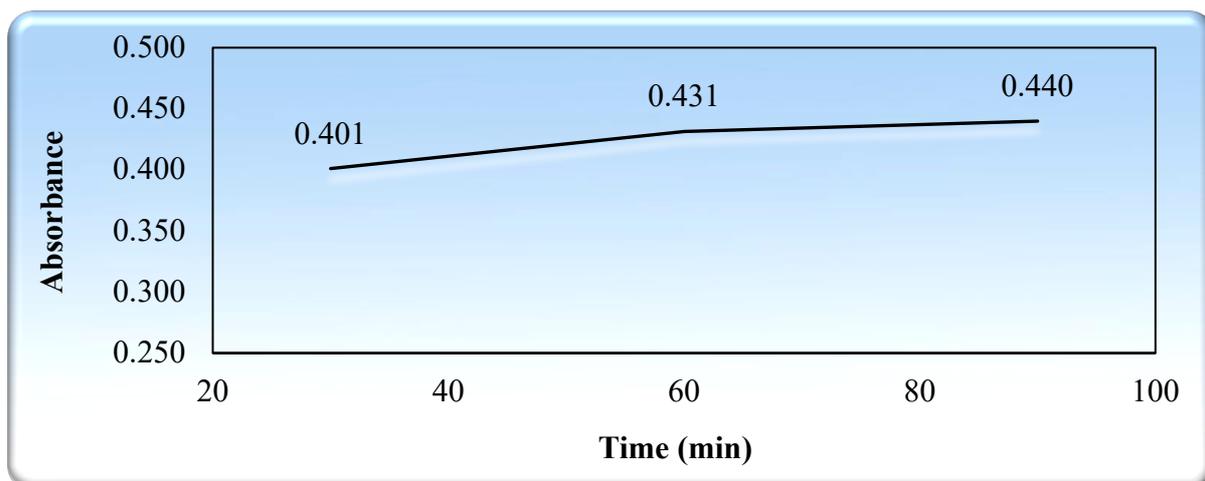
(c)

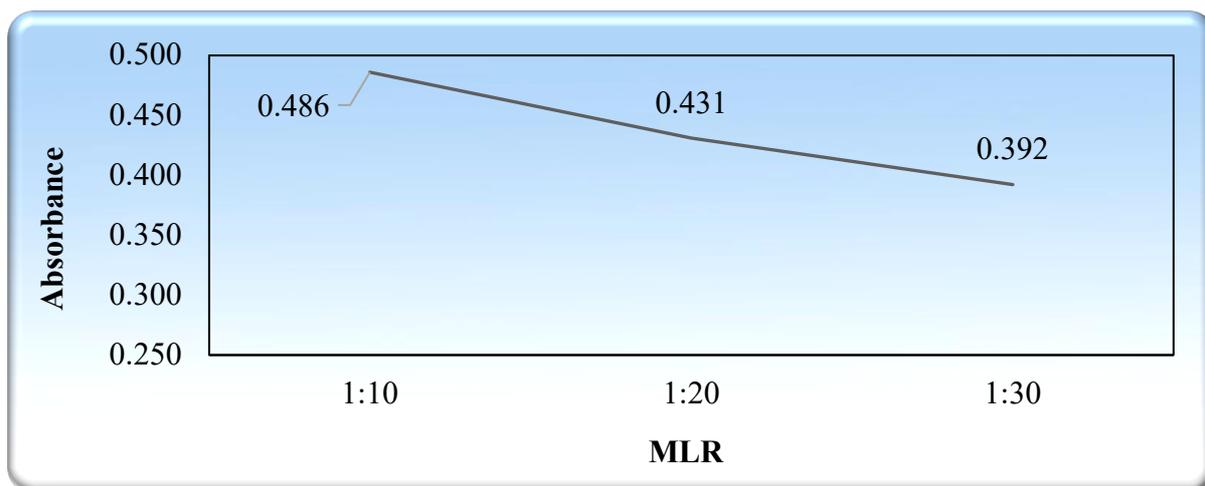**Figure 4.7: Plot of Absorption vs. MLR (a), Temperature (b), and Time (c) for aqueous extract of Marigold dye**

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(B)   Pomegranate

Extraction of Pomegranate dye powder was accomplished according to the set conditions. The absorbance of the extracted solution was measured using a spectrophotometer in the visible region of spectra. To maintain an absorbance value between zero and one, the solution extracted from the Pomegranate was diluted to a concentration of 2%. The absorbance values are shown in Table 4.9 at a wavelength of 380 nm (λ_{max}). Figure 4.8 depicts the plot of absorption versus MLR, temperature, and time.

Table 4.9: Optical density/absorbance of aqueous extract of Pomegranate dye at various extraction conditions

Parameter	Trail	Control Condition	Absorbance
MLR	1:10	Temperature -80°C, Time-60 mins	0.854
	1:20		0.743
	1:30		0.577
Temperature (°C)	60	MLR-1:20, Time - 60 mins	0.646
	80		0.726
	100		0.740
Time (min)	30	MLR-1:20, Temperature -80°C	0.675
	60		0.726
	90		0.711

As the MLR increases from 1:10 to 1:30, the absorbance falls, as seen by the findings. This pattern can be explained by the presence of high water quantity to extract the dye. According to the absorbance versus temperature graph, the absorbance increases from 60°C to 80°C and continues to rise until 100°C, albeit at a slower rate. It can happen because of higher temperature can lead to more interaction of dyes and water molecules. As a result of the influence of time on absorbance value, it was discovered that absorbance increased from 30 to 60 minutes and then dropped from 60 to 90 minutes. The rise in absorbance from 30 to 60 minutes may result from increased pigment release.

(a)
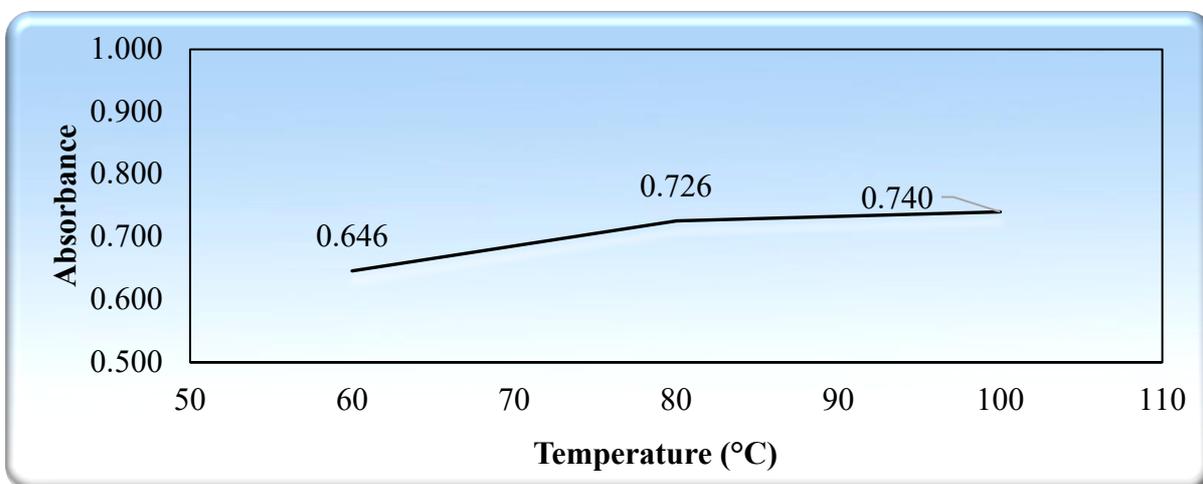
(b)
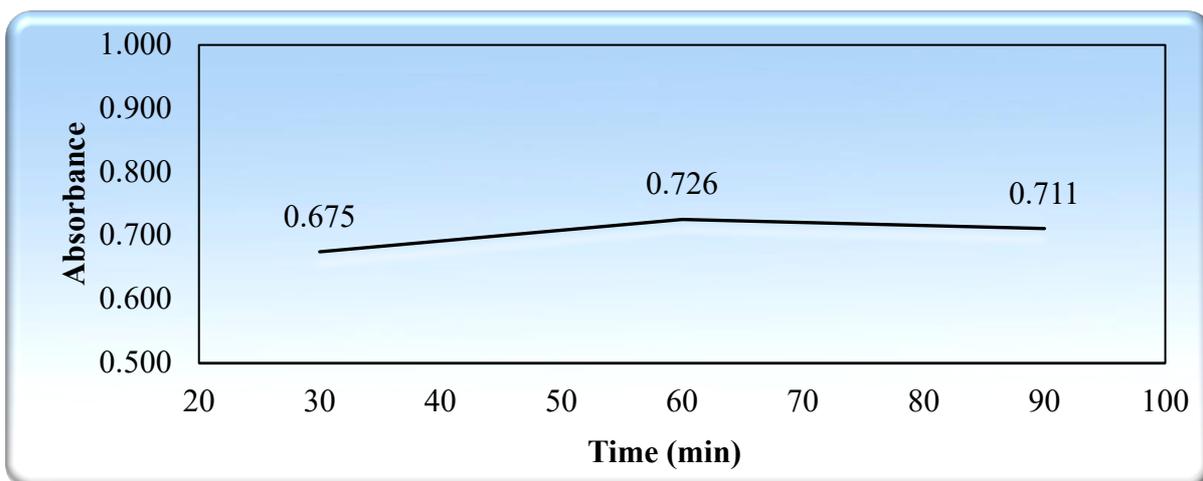
(c)

Figure 4.8: Plot of Absorption vs. MLR (a), Temperature (b), and Time (c) for aqueous extract of Pomegranate dye
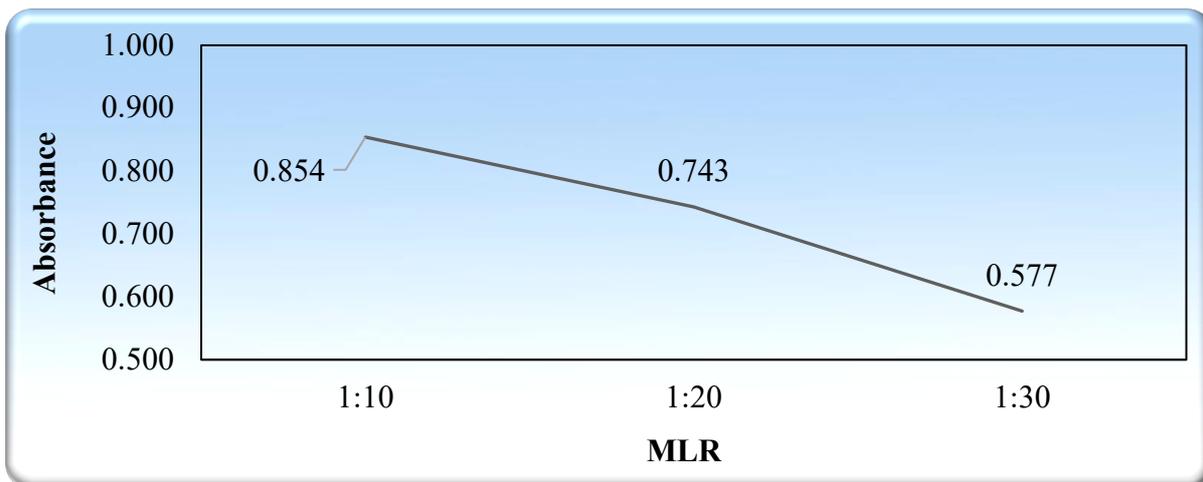
4.1.1.4 Optimized Extraction Parameters for dyes

Optimized extraction parameters for all the dyes are mentioned in Table 4.10. It shows that the optimized MLR in all the cases was 1:10. The optimized temperature for all the dyes was 100°C except for Babool dye at 80°C. The optimized extraction time for many dyes was 90 minutes, and it was 60 minutes for Annatto, Babool, and Pomegranate dyes. Beside the reasons given for individual dyes, the size and geometry of the dye molecule may impact the optimum extraction conditions. All the dyes were extracted using these conditions for all the dyeing purposes.

Table 4.10: Optimized extraction conditions for dyes

Dye	MLR	Temperature (°C)	Time (min)
Annatto	1:10	100	60
Madder	1:10	100	90
Sappanwood	1:10	100	90
Babool	1:10	80	60
Katha	1:10	100	90
Rhubarb	1:10	100	90
Marigold	1:10	100	90
Pomegranate	1:10	100	60

4.1.2 Optimization of Dyeing Parameters

Dyeing of cotton fabric was done using Marigold, Sappanwood, Pomegranate, Madder, Annatto, Babool, Himalyan Rhubarb, and Katha dyes. The color parameters were measured using Konica-Minolta Spectrophotometer, model-3600d. The measurement was done in Day light (D-65) illuminant with a 10° standard observer over the 400-700 nm range. CIE coordinates L*, a*, b*, C*, h, and K/S values were obtained with the help of relevant software for all the dyed samples. CIE L*, a*, and b* values signify the lightness/darkness, redder/greener tone, and yellower/bluer tone, respectively. K/S measures the surface color strength of dyed samples, and h is the hue angle.

Optimum dyeing conditions and graphs of K/S vs. pH, K/S vs. Temperature, and K/S vs. Time were obtained using the design expert software for all the dyes under analysis. L*, a*, and b* values determined the tonal variation and lightness/darkness for each highest K/S sample. One common set of dyeing conditions were found for all the dyes to dye the mixtures samples, primary dyed samples and shade matching samples.

4.1.2.1 Red/Orange tone dyes

Annatto, Madder, and Sappanwood dye materials produced orange, red, and pink colors, respectively. A detailed analysis of these dyes is mentioned in this section.

(A)   Annatto

CIEL*, a*,b*, C*, h, and K/S values of Annatto dyed samples are mentioned in Table 4.11. All the dyed samples obtained were orange in color with little change in hue. It is visible from the low variation in hue angle values obtained for all the samples. The range of K/S observed was 0.268 to 0.961 for all the samples. The samples at pH 3 show lower K/S values than pH 5 and 7. It is also observed that the samples at pH 5 with high temperature and time were reddish compared to samples at pH 7 and 3.

Table 4.11: CIEL*,a*,b*,C*, h and K/S values of Annatto dyed samples

Sample Number	pH	Temperature (°C)	Time (min)	L*	a*	b*	C*	h	K/S
A1	5	65	30	84.4	12.67	16.34	20.68	52.19	0.367
A2	3	65	60	85.58	9.43	15.29	17.97	58.32	0.268
A3	7	65	60	81.86	16.35	19.39	25.37	49.84	0.524
A4	5	65	90	82.77	15.58	19.34	24.84	51.12	0.512
A5	7	80	30	78.74	20.83	22.38	30.57	47.03	0.809
A6	3	80	30	83.07	13.46	18.22	22.65	53.52	0.427
A7	5	80	60	79	22.36	23.56	32.48	46.47	0.885
A8	5	80	60	78.82	21.87	23.36	32	46.87	0.886
A9	5	80	60	78.83	21.96	23.68	32.3	47.13	0.891
A10	5	80	60	79.11	22.11	23.72	32.43	46.99	0.877
A11	5	80	60	78.73	21.9	23.84	32.37	47.41	0.897
A12	3	80	90	80.88	15.6	20.59	25.84	52.83	0.573
A13	7	80	90	77.44	22.59	24.03	32.98	46.74	0.961
A14	5	95	30	78.78	21.35	20.94	29.9	44.42	0.791
A15	7	95	60	78.65	20.63	21.45	29.76	46.09	0.874
A16	3	95	60	81.07	15.79	19.81	25.34	51.43	0.557
A17	5	95	90	77.95	22.62	22.63	32	44.99	0.894

Effect of Dyeing variables on Color Strength

Response surface plots for K/S Vs. pH, temperature, and time were shown in Figure 4.9 (a, b & c). It was evident that the K/S value was increasing with the increase in pH (from 3 to nearly 7). At 80° C and 60 minutes, the K/S increased from pH 3 up to pH 6.5 and then decreased slightly up to pH 7. The K/S was also increasing with an increase in temperature and time. The effect was sharp in the case of temperature in comparison to time. At pH 5 and

time 60 minutes, the K/S increased sharply from temperature 65° C to 87°C and then decreased slightly up to 95° C. At pH 5 and temperature 80° C, the K/S increased slightly from time 30 minutes to 80 mins. The optimum dyeing conditions obtained from the experiment for Annatto dye were pH – 7 and temperature 84° C and time 84 mins.

The structural features of Annatto possibly resemble a direct dye (Haque et al., 2015). The effect of dye bath pH on color/tone and K/S of the dyed fabric can be attributed to the correlation between dye structure and the cellulose material. It is believed that increasing the temperature enhances the fiber swelling and the dye diffusion inside the fabric and hence, increased the color strength of the dyed fabric. Impact of time may be due to increased chances of more dye diffusion onto the fabric at 84 minutes.
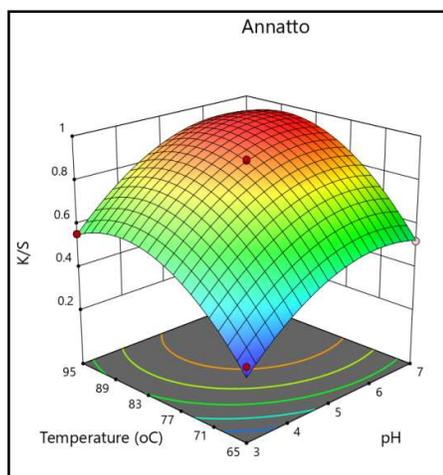
(a, at Time 60 mins)
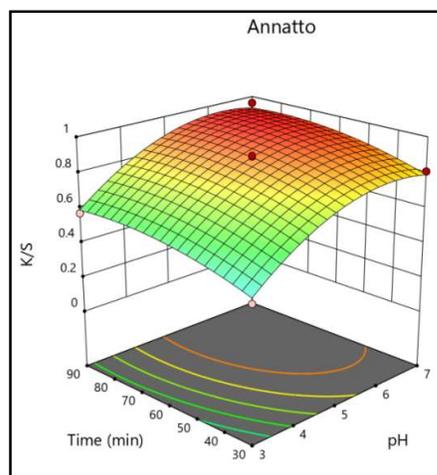
(b, at temperature 80° C)
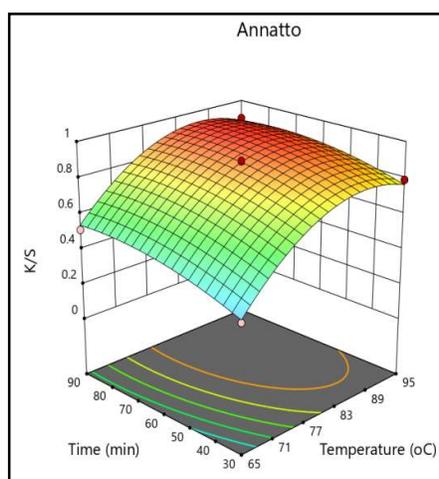
(c, at pH 5)

Figure 4.9: K/S Vs. pH, temperature, and time graph for Annatto (a, b & c)

(B)   Madder

CIEL*,a*,b*,C*, h and K/S values of Madder dyed samples are mentioned in Table 4.12. All the dyed samples that were obtained were visually checked and it was found that the Madder produced different colors/hues at different pH and other dye conditions. The samples at pH 3 were off-white with no red tint and almost no effect of time and temperature. At pH 5, the dye produced a peach color when the initial temp was 65°C for 30 minutes; it turned to light purple at 80°C for 60 minutes and then turned completely red at 95°C for 90 minutes. All red color samples were obtained at pH 7 with a small increment in color strength at higher temperature and time. The same behavior was observed with the hue angle, a*, b* values at different pH values. At pH 3, the hue angle varied from 38° to 77° and at pH 5, the hue angle varied from 11° to 43°. At pH 7, the hue angle was almost constant around 15°. A similar effect was observed for a*, b*, and C* values variation.

Table 4.12: CIEL*,a*,b*,C*, h and K/S values of Madder dyed samples

Sample Number	pH	Temperature (°C)	Time (min)	L*	a*	b*	C*	h	K/S
D1	5	65	30	75.83	14.62	13.93	20.19	43.59	0.533
D2	3	65	60	79.65	8.34	12.12	14.71	55.46	0.367
D3	7	65	60	48	28.42	8.1	29.55	15.9	3.41
D4	5	65	90	72.48	15.15	9.03	17.64	30.78	0.573
D5	7	80	30	46.18	28.36	8.12	29.5	15.98	3.613
D6	3	80	30	81.07	3.01	13.37	13.71	77.28	0.368
D7	5	80	60	62.27	18.22	3.84	18.62	11.9	1.167
D8	5	80	60	62.59	19.01	4.11	19.44	12.19	1.169
D9	5	80	60	62.83	17.78	4	18.23	12.66	1.115
D10	5	80	60	62.77	18.14	4.12	18.6	12.8	1.129
D11	5	80	60	62.66	17.75	3.86	18.16	12.26	1.124
D12	3	80	90	80.73	4.01	14.06	14.62	74.05	0.39
D13	7	80	90	49.87	28.76	8.11	29.88	15.73	3.58
D14	5	95	30	56.12	30.77	6.71	31.49	12.29	2.389
D15	7	95	60	47.18	28.09	6.82	28.9	13.63	4.075
D16	3	95	60	73.91	9.83	7.88	12.6	38.71	0.479
D17	5	95	90	54.82	32.05	6.71	32.74	11.82	2.672

Effect of Dyeing Variables on Color Strength

Response surface plots for K/S Vs. pH, temperature, and time are shown in Figure 4.10 (a, b, c). It was evident that the K/S value increased rapidly with the increase in pH from 3 to 7. At temperature of 80° C and time 60 minutes, the K/S value increased from 0.2 at pH 3 to 1.14 at pH 5 and then further increased to 3.47 at pH 7. The value of K/S increased significantly with an increase in temperature. At pH 5 and time 60 minutes, the K/S value

increased from 0.8 at 65° C to 1.98 at 95° C. It was also evident that there was a slight effect of an increase in time on the K/S value. At pH 5 and temperature 80° C, the K/S value was around 1.2, slightly increasing from 30 to 90 minutes. The optimum dyeing conditions obtained from the experiment for Madder dye were pH – 7, temperature 95° C, and time 60 minutes. Similar optimization results were by Mijas et al., (2022) in their study on cotton fabric.

The structural features of Madder possibly resemble a mordant dye (Gulrajani, 2001). The effect of dye bath pH on color/tone and K/S of the dyed fabric can be attributed to the correlation between dye structure and the cellulose material. It is believed that increasing the temperature enhances the fiber swelling and the dye diffusion inside the fabric and hence, increased the color strength of the dyed fabric. Impact of time may be due to increased chances of more dye diffusion onto the fabric at 60 minutes.
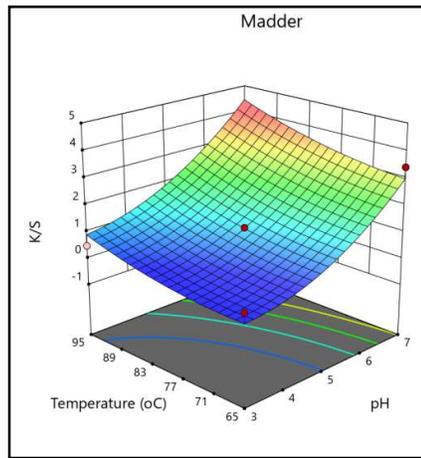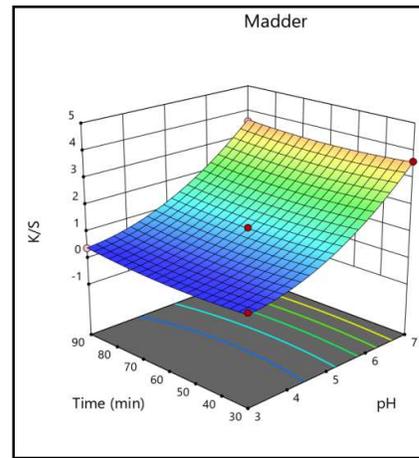
(a, at Time 60 mins)	(b, at temperature 80° C)
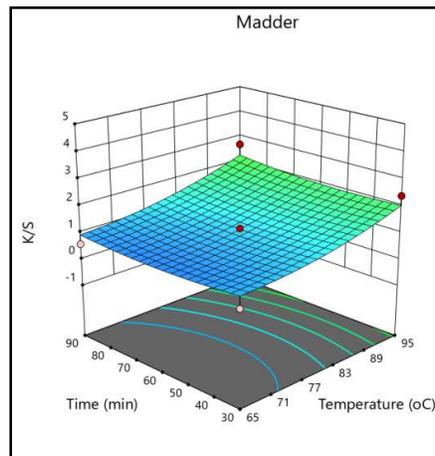
(c, at pH 5)

Figure 4.10: K/S Vs. pH, temperature, and time graph for Madder (a, b & c)

(C) Sappanwood

CIEL*,a*,b*,C*,h and K/S values of Sappanwood dyed samples are mentioned in **Table 4.13**. All the dyed samples obtained were checked visually, and found that the Sappanwood produces light pink color at pH 7 only. There was almost no color at pH 3 and 5. The color strength increased at pH 7 at higher temperature and time. Hue angle (h) at pH 3 and 5 was observed in the range of 43° to 57°. At pH 7, the hue angle was in the range of 11° to 26°. A similar effect was observed for a*, b*, h, and C* values variation.

Table 4.13: CIEL*,a*,b*,C*, h and K/S values of Sappanwood dyed samples

| Sample Number	pH	Temperature (°C)	Time (min)	L*	a*	b*	C*	h	K/S
S1	5	65	30	83.82	4.26	4.62	6.28	47.32	0.17
S2	3	65	60	84.87	3.63	4.9	6.1	53.5	0.154
S3	7	65	60	71.2	12.08	2.35	12.31	11.02	0.514
S4	5	65	90	82.36	4.79	4.55	6.61	43.52	0.195
S5	7	80	30	70.03	11.47	4.26	12.23	20.37	0.627
S6	3	80	30	83.42	3.63	5.5	6.59	56.54	0.19
S7	5	80	60	81.41	4.9	5.57	7.42	48.67	0.229
S8	5	80	60	82	4.62	5.45	7.14	49.69	0.214
S9	5	80	60	81.5	4.78	5.48	7.27	48.88	0.226
S10	5	80	60	82.05	4.49	5.4	7.02	50.25	0.212
S11	5	80	60	81.44	4.74	5.44	7.22	48.91	0.229
S12	3	80	90	83.78	3.67	5.67	6.76	57.07	0.185
S13	7	80	90	70.03	11.47	4.26	12.23	20.37	0.627
S14	5	95	30	79.13	5.14	5.7	12.45	47.93	0.279
S15	7	95	60	66.5	11.14	5.57	7.68	26.55	0.859
S16	3	95	60	80.01	4.89	6.41	8.06	52.63	0.278
S17	5	95	90	78.29	5.18	5.71	7.71	47.78	0.305

Effect of Dyeing variables on Color Strength

Response surface plots for K/S Vs. pH, temperature, and time are shown in Figure 4.11 (a, b & c). It was evident that the K/S value decreased to some extent above pH 3 and then increased up to pH 7. At a temperature of 80° C and a time of 60 minutes, the K/S value decreased from 0.2 at pH 3 to 0.15 at pH 4 and then increased to 0.64 till pH 7. The value of

K/S increased slightly with an increase in temperature. At pH 5 and time 60 minutes, the K/S increased from 0.165 to 0.33 with an increase in temperature from 65° C to 95° C. It was also evident that there was a slight increase in the K/S value with an increase in time. At pH 5 and temperature 80° C, the K/S value increased slightly from 30 to 90 minutes. The optimum dyeing conditions obtained from the experiment for Sappanwood dye were pH – 7, temperature 95° C, and time 67 minutes.

The structural features of Sappanwood possibly resemble a mordant dye(Samanta et al., 2009). The effect of dye bath pH on color/tone and K/S of the dyed fabric can be attributed to the correlation between dye structure and the cellulose material. The effect of temperature and time may be attributed to the fiber swelling and dye diffusion at optimum dyeing conditions.

(b, at temperature 80° C)   (a, at Time 60 mins)

(c, at pH 5)
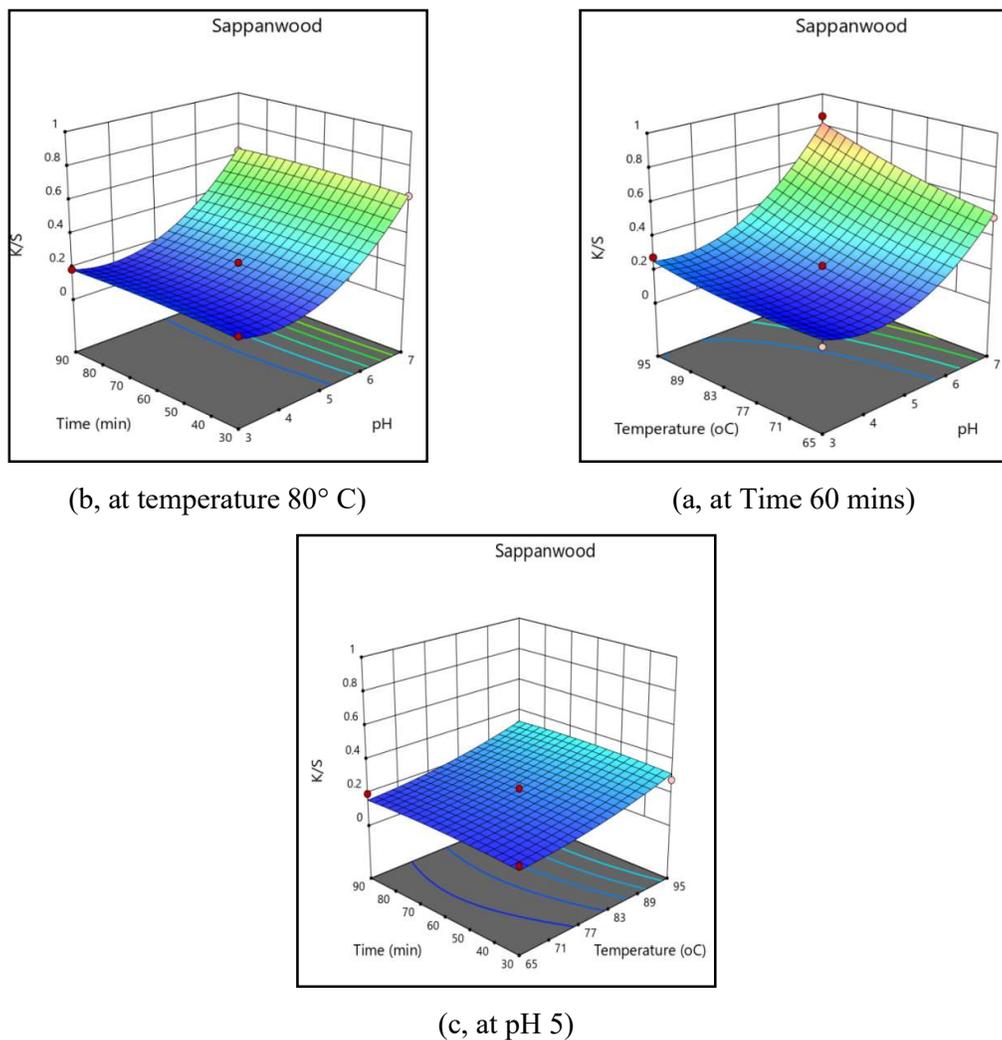
Figure 4.11: K/S Vs. pH, temperature, and time graph for Sappanwood (a, b & c)

Comparison of three dyes

The optimum dyeing conditions were compared to compare the three dyes, as mentioned in **Table 4.14**. It was visible that the optimum conditions were similar for pH and temperature with some difference in time parameters. The K/S for these dyes was in the order- Madder > Annatto > Sappanwood. The difference in K/S value between Madder and the other two dyes was very high.

Table 4.14: Optimum dyeing conditions and K/S for three Red/Orange tone dyes

Dye	pH	Temperature (°C)	Time (min)	K/S
Annatto	7	84	81	0.976
Madder	7	95	60	4.447
Sappanwood	7	95	67	0.86

Besides K/S, we need to compare the tone of the dye using colorimetric parameters h, a*, and b*. These values are analyzed for the A15, D15, and S15 (refer to Table 4.15), wherein the dyeing parameters were close to the optimized parameters. The h* values of 46.09°, 13.63°, and 26.55° for Annatto, Madder, and Sappanwood showed that all three dyes were having highly varied tones. The K/S value of Annatto and Sappanwood was in the same range, but Annatto had a much higher b* value and hence had a much higher yellow component. It is also observed that Madder had a low b* in comparison to Annatto despite high K/S and high a*, which shows more red than yellow.

Table 4.15: CIE a*, b*, and h values of three red/orange tone dyes at pH 7, temperature - 95° C, time – 60 min

Sample number	a*	b*	h	K/S
A15	20.63	21.45	46.09	0.874
D15	28.09	6.82	13.63	4.075
S15	11.14	5.57	26.55	0.859

With the above comparison, it was decided that the two dyes chosen were Madder and Annatto for experimentation purposes.

4.1.2.2 Brown Dyes

Babool, Katha, and Rhubarb dye materials produced a brown color. A detailed analysis of these dyes is mentioned in this section.

(A)   Babool

CIEL*,a*,b*,C*, h and K/S values of Babool dyed samples are mentioned in Table 4.16. All the dyed samples obtained were checked visually, and found that the samples at pH 3 and 5 had very low K/S. There was a significant increase in K/S at pH 7, and brown color was obtained. The dye was slightly pH sensitive and showed little change in hue, evident from the hue angle change range of 52° to 61°. It was also seen that the samples at pH 3 were yellower than those at pH 5.

Table 4.16: CIEL*,a*,b*,C*, h and K/S values of Babool dyed samples

Sample number	pH	Temperature (°C)	Time (min)	L*	a*	b*	C*	h	K/S
B1	5	65	30	80.19	5.76	10.45	11.93	61.13	0.4
B2	3	65	60	78.89	7.07	11.77	13.73	58.96	0.464
B3	7	65	60	61.46	11.86	16.71	20.49	54.61	2.083
B4	5	65	90	79.54	6.33	10.28	12.07	58.38	0.412
B5	7	80	30	61.05	11.46	15.65	19.4	53.78	2.04
B6	3	80	30	80.02	6.64	11.27	13.08	59.46	0.407
B7	5	80	60	79.44	6.64	9.98	11.98	56.32	0.397
B8	5	80	60	79.64	6.61	10	11.99	56.53	0.392
B9	5	80	60	79.63	6.63	9.95	11.96	56.31	0.391
B10	5	80	60	79.69	6.53	9.84	11.81	56.41	0.386
B11	5	80	60	79.99	6.47	9.86	11.79	56.69	0.38
B12	3	80	90	77.42	7.53	12.3	14.42	58.49	0.534
B13	7	80	90	60.08	11.93	16.11	20.05	53.47	2.246
B14	5	95	30	79.5	6.63	9.85	11.87	56.04	0.382
B15	7	95	60	58.85	12.2	15.96	20.09	52.58	2.411
B16	3	95	60	76.49	7.72	12.11	14.36	57.48	0.561
B17	5	95	90	77.7	7.15	9.91	12.22	54.17	0.44

Effect of Dyeing variables on Color Strength

Response surface plots for K/S Vs. pH, temperature, and time of Babool dye are shown in Figure 4.12 (a, b & c). It was evident that the K/S value decreased to some extent

from pH 3 to pH 4 and then increased sharply up to pH 7. At a temperature of 80° C and 60 minutes, the K/S value decreased from 0.5 at pH 3 to 0.2 at pH 4.2 and then increased to 2.18 until pH 7. The value of K/S slightly increased with an increase in time and temperature. The optimum dyeing conditions obtained from the experiment for Babool dye were pH – 7, temperature 95° C, and time 90 minutes.

The structural features of Babool dye possibly resemble a direct dye (Samanta et al., 2009). The effect of dye bath pH on color/tone and K/S of the dyed fabric can be attributed to the correlation between dye structure and the cellulose material. It is believed that increasing the temperature enhances the fiber swelling and the Babool dye diffusion inside the fabric and hence, increases the color strength of the dyed fabric. Impact of time may be due to increased chances of more dye diffusion onto the fabric.
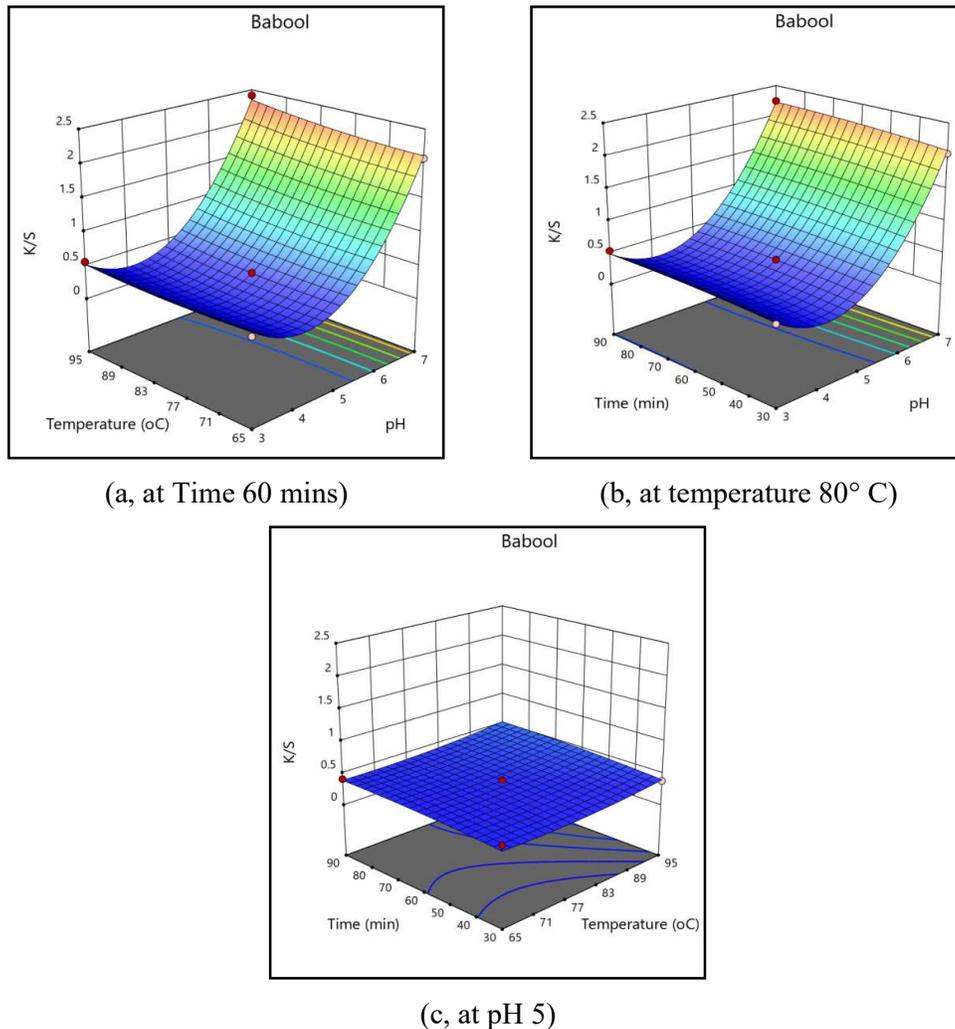
(a, at Time 60 mins) (b, at temperature 80° C)

(c, at pH 5)

Figure 4.12: K/S Vs. pH, temperature, and time graph for Babool (a, b & c)

(B)   Katha

CIEL*,a*,b*,C*, h and K/S values of Katha dyed samples are mentioned in Table 4.17. On visual examination, it was found that the samples at pH 3 were very light, then a little darker at pH 5, and very well dyed at pH 7. All the samples showed limited tonal variation, which is visible from the hue angle ranging from 40° to 51°. The effect of time and temperature was more profound on K/S at pH 7 compared to pH 3 & 5.

Table 4.17: CIEL*,a*,b*,C*, h and K/S values of Katha dyed samples

Sample number	pH	Temperature (°C)	Time (min)	L*	a*	b*	C*	h	K/S
K1	5	65	30	75.74	11.24	12.16	16.56	47.24	0.503
K2	3	65	60	77.47	10.19	11.76	15.56	49.06	0.428
K3	7	65	60	61.63	17.54	15.71	23.55	41.84	1.579
K4	5	65	90	72.31	12.42	12.2	17.41	44.47	0.649
K5	7	80	30	59.02	18.33	16.4	24.59	41.8	1.926
K6	3	80	30	77.61	9.16	11.68	14.85	51.86	0.422
K7	5	80	60	70.45	13.14	11.61	17.53	41.46	0.722
K8	5	80	60	69.09	13.75	11.84	18.15	40.71	0.806
K9	5	80	60	69.8	13.71	11.89	18.15	40.92	0.766
K10	5	80	60	67.14	15.24	12.8	19.91	40.01	0.964
K11	5	80	60	68.53	14.32	12.16	18.78	40.34	0.851
K12	3	80	90	74.95	10.63	11.58	15.71	47.42	0.524
K13	7	80	90	56.62	18.83	16.27	24.89	40.81	2.273
K14	5	95	30	73.83	11.45	11.46	16.2	45.03	0.556
K15	7	95	60	55.15	18.18	17.27	25.08	43.51	2.607
K16	3	95	60	76.33	10.03	12.57	16.08	51.41	0.503
K17	5	95	90	70.91	11.47	11.74	16.41	45.65	0.703

Effect of Dyeing variables on Color Strength

For Katha dyed samples, the response surface plots for K/S Vs. pH, temperature, and time are shown in Figure 4.13 (a, b & c). It was evident that the K/S value remained constant for some time and then increased up to pH 7. At a temperature of 80° C and 60 minutes, the K/S value was almost around 0.57 from pH 3 to pH 4 and then increased to 2.20 at pH 7. The K/S value increased slightly with an increase in temperature. At pH 5 and time 60 minutes, the K/S increases from 0.55 to 0.86 with an increase in temperature from 65° C to 95° C. It is also evident that there is a slight increase in K/S value with an increase in time. At pH 5 and

temperature 80° C, the K/S value increased slightly from 30 to 90 minutes. The optimum dyeing conditions obtained from the experiment for Katha dye were pH – 7, temperature 95° C, and time 82 minutes.

The structural features of Katha dye possibly resemble a direct dye(Samanta et al., 2009). The effect of dye bath pH on color/tone and K/S of the dyed fabric can be attributed to the correlation between dye structure and the cellulose material. The effect of temperature and time may be attributed to the fiber swelling and dye diffusion at optimum dyeing conditions.
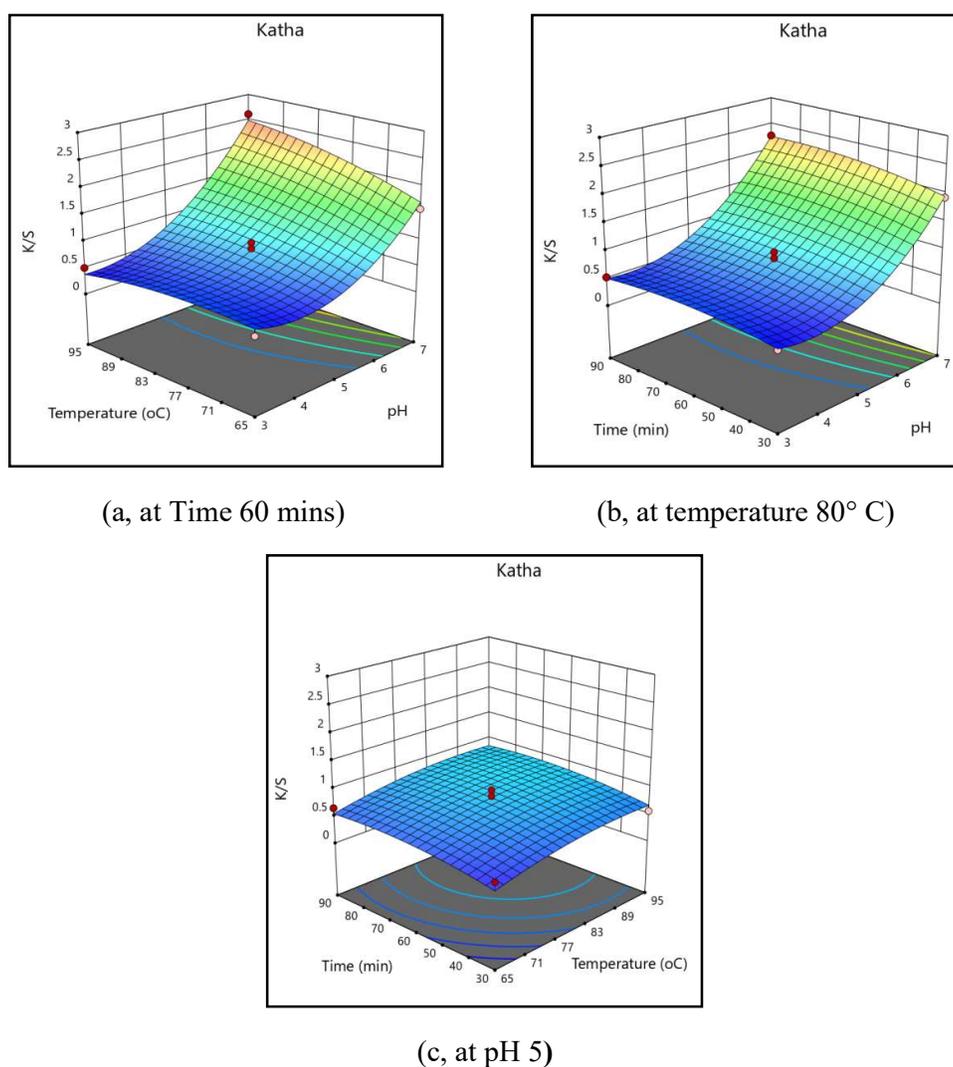

(a, at Time 60 mins)   (b, at temperature 80° C)

(c, at pH 5)

Figure 4.13: K/S Vs. pH, temperature and time graph for Katha (a, b & c)

Rhubarb

CIEL*,a*,b*,C*, h and K/S of Rhubarb dyed samples are mentioned in Table 4.18. On visual examination, it was found that all the samples had low color strength. The color strength was very low at pH 3 and 5 and then increased significantly at pH 7. Some tonal variation was also observed at pH 7 in comparison to pH 3 and 5, which was evident from the hue angle at the respective pH.

**Table 4.18: CIEL*,a*,b*,C*, h and K/S values of Rhubarb dyed samples**

Sample number	pH	Temperature (°C)	Time (min)	L*	a*	b*	C*	h	K/S
R1	5	65	30	83.48	3.33	11.8	12.26	74.2	0.263
R2	3	65	60	82.62	3.42	12.77	13.22	74.97	0.31
R3	7	65	60	71.35	9.54	14.2	17.11	56.08	0.886
R4	5	65	90	82.62	3.68	11.88	12.44	72.74	0.29
R5	7	80	30	70.1	9.42	14.35	17.17	56.7	0.974
R6	3	80	30	81.11	3.35	13.33	13.74	75.85	0.361
R7	5	80	60	80.15	4.09	11.88	12.56	70.98	0.355
R8	5	80	60	78.71	4.79	11.52	12.48	67.4	0.394
R9	5	80	60	80.69	3.74	12.35	12.9	73.12	0.344
R10	5	80	60	79.86	3.89	12.02	12.63	72.05	0.367
R11	5	80	60	80.06	4.04	11.91	12.58	71.25	0.355
R12	3	80	90	78.93	4.03	13.8	14.38	73.7	0.447
R13	7	80	90	68.26	10.05	15.18	18.21	56.46	1.155
R14	5	95	30	81.16	4.18	11.95	12.66	70.7	0.323
R15	7	95	60	67.79	9.67	14.53	17.46	56.34	1.182
R16	3	95	60	78.67	4.16	13.6	14.22	72.95	0.438
R17	5	95	90	79.18	4.69	12.33	13.19	69.17	0.389

Effect of Dyeing variables on Color Strength

For Rhubarb dyed samples, the response surface plots for K/S Vs. pH, temperature, and time are shown in Figure 4.14 (a, b & c). It was evident that the K/S value decreased to some extent and then increased up to pH 7. At a temperature of 80° C and a time of 60 minutes, the K/S value decreased from 0.41 at pH 3 to 0.29 at pH 4 and then increased to 1.07 at pH 7. The K/S value increased slightly with an increase in temperature. At pH 5 and time 60 minutes, the K/S risen from 0.25 to 0.39 with an increase in temperature from 65° C to 95° C. It was also evident that there was a slight increase in K/S value with an increase in

time. The optimum dyeing conditions obtained from the experiment for Rhubarb dye were pH – 7, temperature 94° C, and time 85 minutes.

The dye is pH sensitive, and changes color with pH, mordant type, and mordant concentration (M. A. Khan et al., 2017; S. A. Khan et al., 2012). The effect of dye bath pH on color/tone and K/S of the dyed fabric can be attributed to the correlation between dye structure and the cellulose material. It is believed that increasing the temperature enhances the fiber swelling and the Rhubarb dye diffusion inside the fabric and hence, increases the color strength of the dyed fabric. Impact of time may be due to increased chances of more dye diffusion onto the fabric.
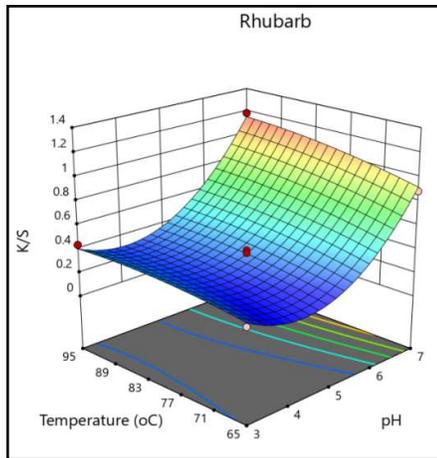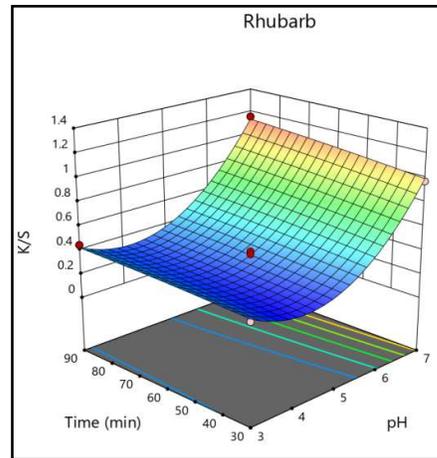
(a, at Time 60 mins)   (b, at temperature 80° C)
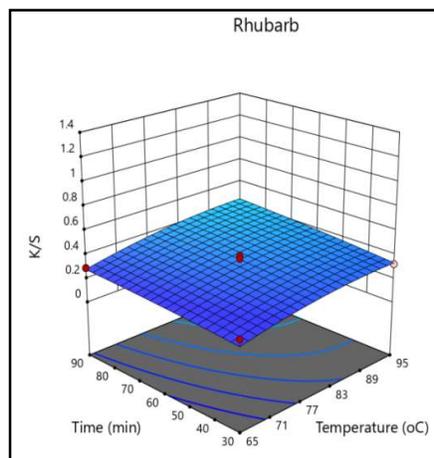
(c, at pH 5)

Figure 4.14: K/S Vs. pH, temperature, and time graph for Rhubarb (a, b & c)

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Comparison of Brown tone dyes

The optimum dyeing conditions were compared to compare the three dyes, as mentioned in Table 4.19. It was visible that the optimum conditions were similar for pH and temperature with some difference in time parameters. The K/S for these dyes was in the order: Katha > Babool > Rhubarb. The K/S for Babool and Katha were in the same range, but Rhubarb had very low K/S in similar conditions.

Table 4.19: Optimum dyeing conditions and K/S for three brown dyes

Dye	pH	Temperature (°C)	Time (min)	K/S
Babool	7	95	90	2.395
Katha	7	95	82	2.538
Rhubarb	7	94	85	1.185

Besides K/S, we need to compare the tone of the dye using colorimetric parameters h, a*, and b*. These values were analyzed for the B15, K15, and R15 (refer to Table 4.20), wherein the dyeing parameters were close to the optimized parameters. For the analysis of the tone of three dyes, there was some change in hue, which was evident from h values. The Katha showed a maximum a* value and a redder tone than the other two dyes. In the case of the b* value analysis, the Katha dye shows the maximum value and is yellower than other dyes. The visual examination of the samples also aligns with the results obtained that Katha samples were redder and yellowish (i.e., more orangish).

Table 4.20: CIE a*, b*, and h values of three brown dyes at pH 7, temperature - 95° C, time – 60 min

Sample number	a*	b*	h	K/S
B15	12.2	15.96	52.58	2.411
K15	18.18	17.27	43.51	2.607
R15	9.67	14.53	56.34	1.182

With the above comparison, it was decided that the two dyes chosen were Katha and Babool for experimentation purpose.

4.1.2.3 Yellow Dyes

Marigold and Pomegranate dye materials produced a yellow color. A detailed analysis of these dyes is mentioned in this section.

(A)   Marigold

CIEL*,a*,b*,C*, h and K/S values of Marigold dyed samples are mentioned in Table 4.21. All the dyed samples obtained were checked visually, and all the samples were bright yellow dyed with minor changes in color strength with changes in dyeing parameters. It was visible from the K/S values ranging from 0.548 to 0.886, which was very low compared to other dyes in experimentation. The dye is not pH sensitive and shows negligible change in hue, which is evident from the hue angle change range of 87.5° to 91.6°.

Table 4.21: CIEL*,a*,b*,C*, h and K/S values of Marigold dyed samples

Sample number	pH	Temperature (°C)	Time (min)	L*	a*	b*	C*	h	K/S
M1	5	65	30	86.57	0.51	35.57	35.57	89.14	0.704
M2	3	65	60	85.19	0.75	34.64	34.65	88.72	0.766
M3	7	65	60	85.23	1.6	38.04	38.08	87.56	0.886
M4	5	65	90	87.23	0.47	35.44	35.45	89.2	0.672
M5	7	80	30	85.33	0.83	36.2	36.21	88.65	0.807
M6	3	80	30	86.51	0.67	35.52	35.52	88.88	0.706
M7	5	80	60	86.81	0.35	34.11	34.11	89.38	0.649
M8	5	80	60	86.93	0.43	34.85	34.85	89.26	0.666
M9	5	80	60	86.87	0.39	34.48	34.48	89.32	0.679
M10	5	80	60	86.84	0.34	34.47	34.48	89.4	0.661
M11	5	80	60	86.81	0.54	35.04	35.04	89.09	0.677
M12	3	80	90	87.23	-0.87	30.79	30.8	91.66	0.548
M13	7	80	90	87.76	-0.28	33.03	33.03	90.52	0.579
M14	5	95	30	87.03	0.97	36.57	36.58	88.44	0.71
M15	7	95	60	84.26	2.21	28.47	28.56	85.53	0.604
M16	3	95	60	85.5	0.04	31.41	31.41	89.89	0.657
M17	5	95	90	87.18	-0.41	32.82	32.82	90.76	0.599

Effect of Dyeing variables on Color Strength

For Marigold dyed samples, the response surface plots for K/S Vs. pH, temperature, and time are shown in Figure 4.15 (a, b & c). As mentioned in the above section, the dyed samples had a small change in color strength with a change in dyeing parameters, which was from the K/S values ranging from 0.548 to 0.886. The influence of the dyeing variable on color strength was not very high, and some trends could not be established. At a temperature of 65° C and 60 minutes, the K/S value was almost the same, around 0.65 from pH 3 to pH

4.5, then increased to 0.84 at pH 7. At a temperature of 95° C and 60 minutes, the K/S value decreased from 0.65 at pH 3 to 0.55 at pH 5.2 and then increased back to 0.65 at pH 7.

In relation to the value of K/S with temperature, at pH 3 and time 60 minutes, the K/S increased slightly from 65° C to 80° C and then came back to its initial value at 95° C. At pH 7 and time 60 minutes, the K/S decreases continuously from 0.88 at 65° C to 0.64 at 95° C. The effect of time on K/S value at pH 7 and temperature 65° C, the value increased from 0.8 at 30 minutes to 0.86 at 90 minutes. The optimum dyeing conditions obtained from the experiment for Marigold dye were pH – 7, temperature 65° C, and time 90 minutes.

The effect of dye bath pH on color/tone and K/S of the dyed fabric can be attributed to the correlation between dye structure and the cellulose material. The effect of temperature and time may be attributed to the fiber swelling and dye diffusion at optimum dyeing conditions.
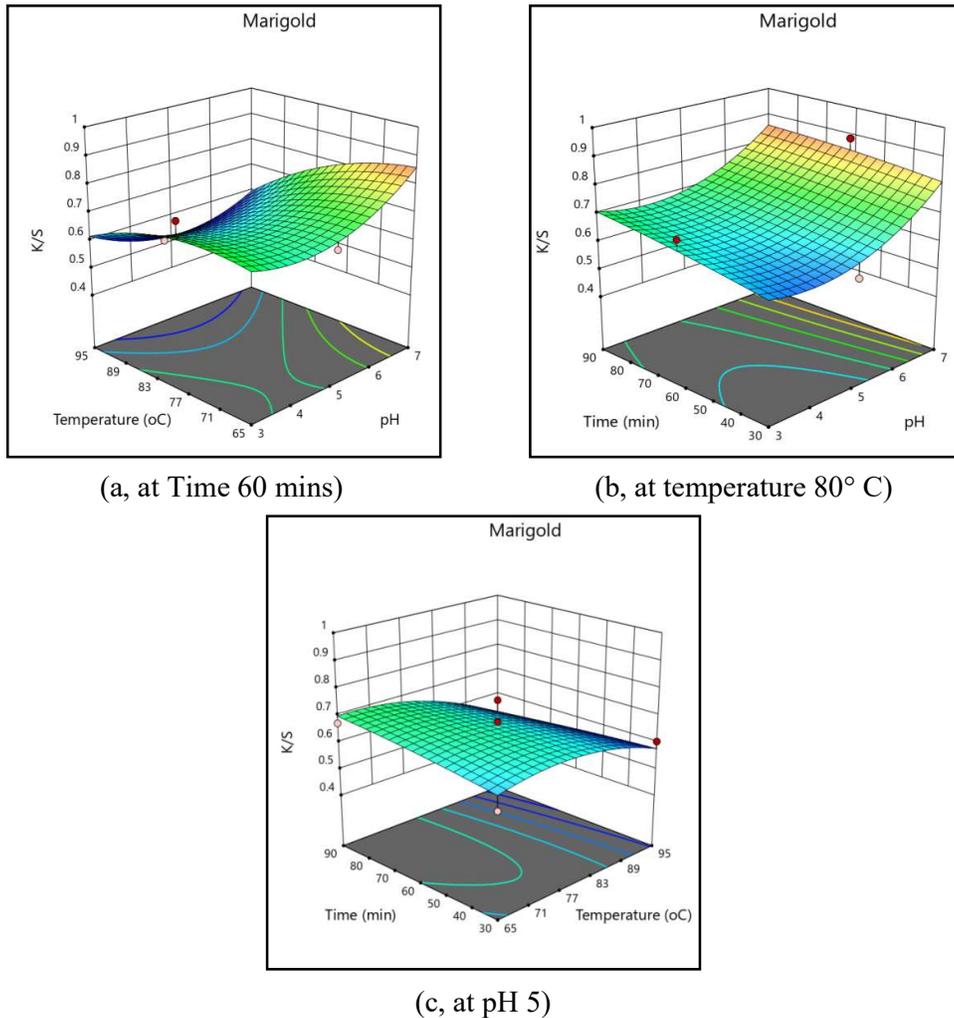

(a, at Time 60 mins)   (b, at temperature 80° C)

(c, at pH 5)

Figure 4.15: K/S Vs. pH, temperature, and time graph for Marigold (a, b & c)

(B)   Pomegranate

CIEL*,a*,b*,C*, h and K/S values of Pomegranate dyed samples are mentioned in Table 4.22. All the dyed samples obtained were checked visually, and found that samples at pH 3 were light brownish in tone, and samples at pH 5 were light yellow. All the samples at pH 3 and pH 5 had low to medium color strength. The samples dyed at pH 7 were observed to be average to dark yellow.

**Table 4.22: CIEL*,a*,b*,C*, h and K/S values of Pomegranate dyed samples**

Sample number	pH	Temperature (°C)	Time (min)	L*	a*	b*	C*	h	K/S
P1	5	65	30	86.34	-2.26	19.93	20.06	96.52	0.869
P2	3	65	60	82.39	0.74	19.63	19.65	87.81	0.791
P3	7	65	60	73.87	1.44	33.93	33.96	87.53	3.744
P4	5	65	90	85.85	-2.08	20.4	20.51	95.86	0.953
P5	7	80	30	77.03	0.59	31.44	31.44	88.89	2.614
P6	3	80	30	86.68	-0.22	9.21	9.21	91.41	0.254
P7	5	80	60	85.34	-1.95	19.58	19.68	95.73	0.877
P8	5	80	60	85.1	-1.92	20.18	20.27	95.47	0.928
P9	5	80	60	84.84	-2	20.23	20.32	95.69	0.97
P10	5	80	60	84.16	-1.8	20.81	20.89	94.97	1.061
P11	5	80	60	84.24	-1.86	21.27	21.35	95.02	1.118
P12	3	80	90	78.86	1.84	21.35	21.43	85.04	1.101
P13	7	80	90	74.07	1.64	32.96	32.17	87.03	3.678
P14	5	95	30	84.06	-1.31	19.26	19.31	93.94	0.888
P15	7	95	60	77.36	0.41	31.14	31.15	89.22	2.523
P16	3	95	60	79.13	2.03	18.85	18.96	83.82	0.915
P17	5	95	90	83.81	-1.03	19.37	19.4	93.07	0.912

**Effect of Dyeing variables on Color Strength**

For Pomegranate dyed samples, the response surface plots for K/S Vs. pH, temperature, and time are shown in Figure 4.16 (a, b & c). It is evident that the K/S value remained constant for some time and then increased up to pH 7. At a temperature of 80° C and time 60 minutes, the K/S value was slightly dropped from 0.80 at pH 3 to 0.64 at pH 4 and then increased to 3.18 at pH 7. For the K/S value with respect to temperature, the trend changes with pH change. At pH 7 and time 60 minutes, the K/S value decreased from 3.65 at 65° C and 2.70 at 95° C. In contrast, at pH 3 and time 60 minutes, the K/S value increased from 0.60 at 65° C and 1.0 at 95° C. It is also evident that there was an increase in K/S value

with an increase in time. At pH 5 and temperature 80° C, the K/S value increased from 0.65 at 30 minutes to 1.15 at 90 minutes. The optimum dyeing conditions obtained from the experiment for Pomegranate dye were pH – 6.93, temperature 65° C, and time 89 minutes.

The structural features of Pomegranate possibly resemble a direct dye (Samanta et al., 2009). The effect of dye bath pH on color/tone and K/S of the dyed fabric can be attributed to the correlation between dye structure and the cellulose material. It is believed that increasing the temperature enhances the fiber swelling and the Pomegranate dye diffusion inside the fabric and hence, increases the color strength of the dyed fabric. Impact of time may be due to increased chances of more dye diffusion onto the fabric.
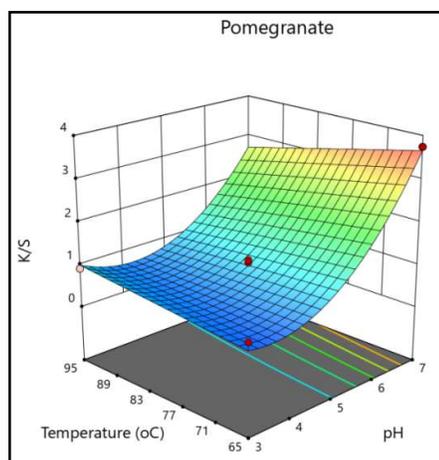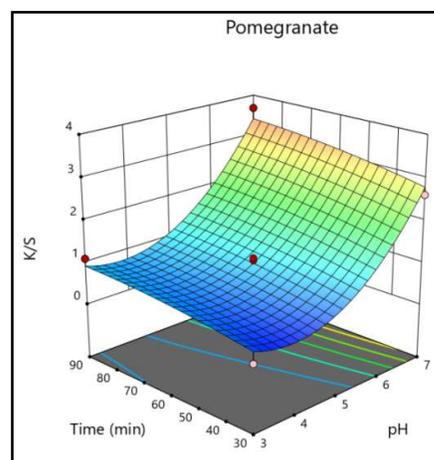
(a, at Time 60 mins) (b, at temperature 80° C)
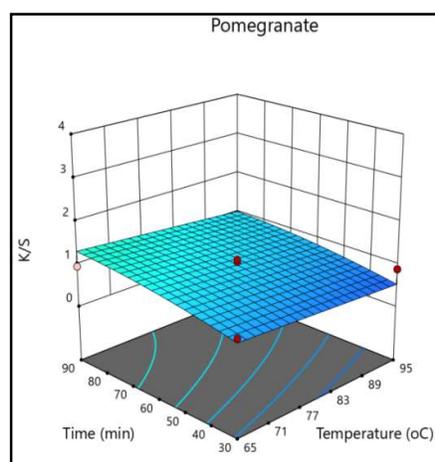
(c, at pH 5)

Figure 4.16: K/S Vs. pH, temperature and time graph for Pomegranate (a, b & c)

Comparison of Yellow tone dyes

To compare the two dyes, the optimum dyeing conditions were compared as mentioned in Table 4.23. It was clearly visible that the optimum conditions were similar. The K/S for Pomegranate was much higher than Marigold dye.

Table 4.23: Optimum dyeing conditions and K/S for two Yellow dyes

Dye	pH	Temperature (°C)	Time (min)	K/S
Marigold	7	65	90	0.861
Pomegranate	6.93	65	89	3.774

Besides K/S, we need to compare the tone of the dye using colorimetric parameters h, a*, and b*. These values were analyzed for the M3 and P3 samples (refer to Table 4.24), wherein the dyeing parameters were close to the optimized parameters. It shows that both the dyed samples showed similar values of h, a*, and b* with high difference in K/S. The visual examination also showed that M3 was brighter than P3.

Table 4.24: CIE a*, b*, and h values of three Brown dyes at pH 7, temperature - 95° C, time – 60 min

Sample number	a*	b*	h	K/S
M3	1.6	38.04	87.56	0.886
P3	1.44	33.93	87.53	3.744

4.1.2.4 Common dyeing conditions for dye mixtures

As per the study's objective, the dyes were mixed as binary and tertiary mixtures for dyeing. For this objective to be accomplished, one common set of dyeing conditions must be found for all the dyes. All the binary and tertiary mixtures were dyed using the standard set of dyeing conditions.

Table 4.25 shows the data predicted by design expert software using the Box-Behnken method. It shows each dye's predicted optimum dyeing conditions with K/S (Individual maximum). The common dyeing conditions for all the dyes were also obtained using the software, keeping the condition for maximum K/S for all the dyes. The common dyeing conditions were used for binary and tertiary mixtures. The common conditions obtained were pH – 7, temperature- 82.8°C, and time – 88 mins. The nearest dyeing

conditions were used for ease in practical dyeing: pH – 7, temperature- 85°C, and time – 90 mins.

Table 4.25: Optimum and common dyeing conditions for all dyes (Predicted)

Dye Name	pH	Temperature (°C)	Time (min)	K/S (Individual Maximum)	K/S (at common dyeing condition)
Katha	7.00	95.00	81.84	2.538	2.327
Marigold	7.00	65.00	90.00	0.861	0.756
Rhubarb	7.00	94.00	85.00	1.185	1.152
Pomegranate	6.94	65.09	89.38	3.774	3.303
Madder	7.00	95.00	60.00	4.447	3.786
Annatto	6.99	84.34	81.39	0.976	0.961
Babool	7.00	95.00	90.00	2.395	2.253
Sappanwood	7.00	95.00	67.75	0.821	0.671
Common conditions by Design expert software	7.00	82.86	88.07		
Dyeing conditions used	7.00	85.00	90.00		

K/S (at common dyeing conditions) was also predicted for all the dyes. It showed the predicted K/S when common dyeing conditions were taken, and it was found that there was a slight decrease in K/S due to a change in optimum dyeing conditions.

It was also observed that there is significant decrease in K/S for Madder, Marigold and Pomegranate dyes at common dyeing conditions. It may be due to the significant temperature and time difference in optimum dye conditions for these dyes as individual and common dyeing conditions. The optimum temperature for Marigold and Pomegranate is 65°C as compared to 85°C (common temperature) and optimum time for Madder is 60 mins as compared to 90 mins (common time).

4.1.2.5 Effect of Alkaline pH

It was found from Table 4.25 that the maximum K/S was coming around pH 7 for all the dyes. Experiments were conducted to check the color and K/S at alkaline pH 9 & 11 using optimum common dyeing conditions. The CIEL*,a*,b*, C*, h and K/S values of samples dyed at pH 9 and 11 are shown in Table 4.26.

Table 4.26: CIEL*, a*, b*, C*, h and K/S values of samples dyed at pH 9 & 11

Code	Dye	pH	L*	a*	b*	C*	h	K/S
PA1	Annatto	9	76.55	24.23	26.34	35.79	47.37	1.13
PA2		11	78.37	21.98	29.33	36.65	53.12	1.14
PD1	Madder	9	59.88	25.93	6.89	26.83	14.88	1.67
PD2		11	77.11	4.76	13.31	14.14	70.29	0.54
PB1	Babool	9	80.91	4.65	9.8	10.84	64.61	0.46
PB2		11	85.39	3.06	8.33	8.87	69.8	0.32
PK1	Katha	9	71.49	13.48	12.3	18.25	42.37	0.79
PK2		11	75.28	8.44	10.73	13.65	51.77	0.67
PM1	Marigold	9	87.69	-2.86	27.27	27.42	96.01	0.48
PM2		11	86.04	-1.36	28.95	28.98	92.73	0.59
PP1	Pomegranate	9	88.84	-1.28	11.84	11.91	96.19	0.30
PP2		11	86	0.11	13.63	13.63	89.51	0.48

The values of K/S for Annatto were 0.961, 1.13, and 1.14 at pH 7, 9, and 11, respectively. It was evident that the samples dyed at pH 9 and 11 had a slightly higher color strength than those dyed at pH 5 or 7, with substantial tonal variation towards yellow. It was observed that the yellow tone increased with an increase in pH from 3 to 11.

The values of K/S for Madder were 3.786, 1.67, and 0.54 at pH 7, 9, and 11, respectively. It was evident that the samples dyed at pH 9 and 11 had a much lower color strength than samples at pH 7. The sample at pH 9 was light pink, and the sample at pH 11 had almost no color.

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The values of K/S for Babool were 2.253, 0.46, and 0.32 at pH 7, 9, and 11, respectively. It was evident that the samples dyed at pH 9 and 11 had a much lower color strength than samples at pH 7. The samples at alkaline pH showed almost no color.

The values of K/S for Katha were 2.327, 0.79, and 0.67 at pH 7, 9 and 11 respectively. It was evident that the samples dyed at pH 9 and 11 had a much lower color strength than samples at pH 7. The samples at alkaline pH showed almost no color.

The values of K/S for Marigold were 0.756, 0.48, and 0.59 at pH 7, 9, and 11, respectively. It was evident that the samples dyed at pH 9 and 11 had lower color strength than samples at pH 7. Samples at alkaline pH turned a little greenish also.

The values of K/S for Pomegranate were 3.303, 0.3, and 0.48 at pH 7, 9, and 11, respectively. It was evident that the samples dyed at pH 9 and 11 had much lower color strength than samples at pH 7.

With the analysis of all the samples dyed at alkaline pH, the K/S is highest in the case of neutral pH only, except in the case of annatto dye. Since the dyeing conditions have to be common for mixtures of dyes, the conditions mentioned in Table 4.25 were chosen as the optimum dyeing conditions.

4.2 Experimental Study

The common dyeing conditions for all the dyes obtained from the pilot study were used for the experimentation study. The following samples were dyed in the experimental study.

- Dyeing using binary and tertiary dye mixtures
- Dyeing of Primary dyes at various percentages for spectral data
- Prediction of recipe and dyeing of samples as per standard

The following will be discussed in this part of study:
- Dyeing results and compatibility assessment for dye mixtures
- Dyeing results of Primary dyes
- Prediction of recipe and dyeing of samples as per standard

4.2.1 Dyeing Results and Compatibility Assessment for dye mixtures

Set I & II dyed samples were obtained using binary and tertiary dyes mixture for each mixture. Both sets have six samples each for the respective mixture. The color parameters were measured for all the dyed samples using the Konica-Minolta Spectrophotometer, model-3600d. CIE coordinates L*, a*, b*, C*, h, and K/S values were obtained with the help of relevant software for all the dyed samples. The undyed white fabric was used as standard, and the color difference values dL*, da*, db*, and dC* were also determined. The CIE color coordinate values were used to find the compatibility in the dye mixture.

The following compatibility assessment methods were used:

A. Method based on -dL vs. dC and -dL vs. K/S plot

B. Method based on da vs. K/S and db vs. K/S plot

C. Based on change in Hue angle (h°)

    (i)   Using graphical analysis

    (ii)   Using coefficient of variation (CV)

D. Compatibility factor method

E. Visual rating

4.2.1.1 Dyeing results and Compatibility Assessment for binary mixtures

The binary mixtures were used to dye the cotton material using equal proportions at various concentrations and time/temperature, denoted as set I and II. The detailed dyeing conditions are mentioned in section 3.2.2.

CIE coordinates L*, a*, b*, C*, h, and K/S values were obtained for all Set I & II dyed samples. Both sets have six samples each for binary mixture. The undyed white fabric (RFD) was used as standard, and the color difference values dL*, da*, db*, and dC* were also determined. The CIE coordinates L*, a*, b*, C*, h, and K/S values of RFD fabric are given in Table 4.27.

The colorimetric parameters L*, a*, b*, C*, h, K/S, dL*, da*, db*, and dC* are mentioned in Table 4.27 to Table 4.38 for all 12 binary mixtures. These parameters were used in the compatibility check methods. The dyeing outcome and color coordinates of the

mixtures may be attributed to the interaction of dyes (with or without alum) and their respective complex formation. This may also be attributed to the comparative affinity of dyes, diffusion rate and effect of dyeing conditions in mixture.

Table 4.27: Colorimetric parameters for the fabric dyed with a binary mixture of Babool and Annatto dyes (BA)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I (Increasing Concentration samples)	1	85.19	8.84	10.06	13.39	48.67	0.21	7.29	8.92	9.17	12.50
	2	83.03	12.19	12.71	17.61	46.19	0.33	9.45	12.27	11.82	16.72
	3	80.24	13.8	15.19	20.52	47.72	0.45	12.24	13.88	14.30	19.63
	4	77.06	15.01	16.89	22.60	48.35	0.67	15.42	15.09	16.00	21.71
	5	74.1	15.45	17.95	23.68	49.25	0.96	18.38	15.53	17.06	22.79
	6	71.71	16.15	18.6	24.63	49.01	1.21	20.77	16.23	17.71	23.74
Set II (Increasing Time Temperature samples)	7	76.35	10.56	17.11	20.11	58.3	1.12	16.13	10.64	16.22	19.22
	8	75.32	12.16	16.91	20.83	54.25	1.03	17.16	12.24	16.02	19.94
	9	74.9	13.84	17.84	22.58	52.17	1.03	17.58	13.92	16.95	21.69
	10	71.57	16.18	19.39	25.25	50.14	1.38	20.91	16.26	18.50	24.36
	11	71.86	16.08	18.78	24.72	49.4	1.25	20.62	16.16	17.89	23.83
	12	71.66	16.29	19.11	25.11	49.54	1.31	20.82	16.37	18.22	24.22

Table 4.28: Colorimetric parameters for the fabric dyed with a binary mixture of Babool and Madder dyes (BD)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I (Increasing Concentration samples)	1	70.54	18.44	8.28	20.21	24.17	0.73	21.94	18.52	7.39	19.32
	2	63.75	24.05	10.87	26.39	24.32	1.3	28.73	24.13	9.98	25.50
	3	59.64	24.31	10.75	26.58	23.84	1.64	32.84	24.39	9.86	25.69
	4	54.28	26.22	10.72	28.33	22.22	2.24	38.20	26.30	9.83	27.44
	5	51.95	28.77	10.56	30.65	20.15	2.33	40.53	28.85	9.67	29.76
	6	51.57	29.9	10.96	31.85	20.13	2.37	40.91	29.98	10.07	30.96
Set II (Increasing Time Temperature samples)	7	60.31	27.38	10.64	29.37	21.22	1.29	32.17	27.46	9.75	28.48
	8	53.52	29.41	10.89	31.36	20.31	2.02	38.96	29.49	10.00	30.47
	9	52.4	30.15	11.41	32.24	20.73	2.24	40.08	30.23	10.52	31.35
	10	51.91	29.09	10.69	30.99	20.17	2.25	40.57	29.17	9.80	30.10
	11	51.57	29.9	10.96	31.85	20.13	2.37	40.91	29.98	10.07	30.96
	12	51.57	29.9	10.96	31.85	20.13	2.37	40.91	29.98	10.07	30.96

Table 4.29: Colorimetric parameters for the fabric dyed with a binary mixture of Katha and Annatto dyes (KA)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I (Increasing Concentration samples)	1	73	12.73	13.57	18.61	46.82	0.71	19.48	12.81	12.68	17.72
	2	68.51	15.68	15.33	21.93	44.33	0.97	23.97	15.76	14.44	21.04
	3	66.51	17.95	16.96	24.70	43.36	1.12	25.97	18.03	16.07	23.81
	4	63.36	19.35	18.27	26.61	43.33	1.42	29.12	19.43	17.38	25.72
	5	63.35	19.27	18.11	26.44	43.21	1.39	29.13	19.35	17.22	25.55
	6	61.03	19.01	17.66	25.95	42.88	1.59	31.45	19.09	16.77	25.06
Set II (Increasing Time Temperature samples)	7	70.72	17.13	15.3	22.97	41.74	0.7	21.76	17.21	14.41	22.08
	8	67.24	18.88	16.14	24.84	40.51	0.89	25.24	18.96	15.25	23.95
	9	64.05	20.63	17.1	26.80	39.64	1.13	28.43	20.71	16.21	25.91
	10	63.1	20.13	17.81	26.88	41.48	1.33	29.38	20.21	16.92	25.99
	11	63.26	20	18.08	26.96	42.1	1.36	29.22	20.08	17.19	26.07
	12	62.24	20.93	18.14	27.70	40.89	1.37	30.24	21.01	17.25	26.81

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Table 4.30: Colorimetric parameters for the fabric dyed with a binary mixture of Katha and Madder dyes (KD)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	68.14	18.65	10.54	21.42	29.47	0.81	24.34	18.73	9.65	20.53
	2	60.32	23.30	11.65	26.05	26.57	1.31	32.16	23.38	10.76	25.16
	3	57.52	25.76	12.94	28.83	26.66	1.62	34.96	25.84	12.05	27.94
	4	53.10	27.15	13.17	30.18	25.87	2.08	39.38	27.23	12.28	29.29
	5	51.80	27.18	13.62	30.40	26.60	2.27	40.68	27.26	12.73	29.51
	6	47.29	27.48	13.71	30.71	26.51	2.72	45.19	27.56	12.82	29.82
Set II **(Increasing Time Temperature samples)**	7	58.19	27.12	10.83	29.20	21.75	1.14	34.29	27.20	9.94	28.31
	8	51.26	27.30	11.57	29.65	22.97	1.86	41.22	27.38	10.68	28.76
	9	49.89	27.37	11.99	29.88	23.65	2.30	42.59	27.45	11.10	28.99
	10	49.25	27.50	12.77	30.32	25.07	2.30	43.23	27.58	11.88	29.43
	11	49.32	28.19	13.03	31.06	24.79	2.30	43.16	28.27	12.14	30.17
	12	49.13	28.30	12.98	31.13	24.65	2.46	43.35	28.38	12.09	30.24

Table 4.31: Colorimetric parameters for the fabric dyed with a binary mixture of Marigold and Annatto dyes (MA)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	86.28	7.35	16.04	17.64	65.35	0.18	6.20	7.43	15.15	16.75
	2	83.85	9.99	20.9	23.16	64.44	0.33	8.63	10.07	20.01	22.27
	3	82.32	11.87	23.48	26.31	63.16	0.4	10.16	11.95	22.59	25.42
	4	80.79	13.12	26.13	29.24	63.31	0.57	11.69	13.20	25.24	28.35
	5	80.25	13.98	27.1	30.49	62.68	0.53	12.23	14.06	26.21	29.60
	6	79.54	15.17	28.77	32.52	62.17	0.61	12.94	15.25	27.88	31.63
Set II **(Increasing Time Temperature samples)**	7	84.79	7	29.73	30.54	76.73	0.45	7.69	7.08	28.84	29.65
	8	83.47	9.12	28.86	30.27	72.43	0.44	9.01	9.20	27.97	29.38
	9	80.83	13.59	30.8	33.66	66.17	0.6	11.65	13.67	29.91	32.77
	10	79.76	15.17	29.74	33.39	62.95	0.57	12.72	15.25	28.85	32.50
	11	79.16	15.94	29.77	33.77	61.8	0.63	13.32	16.02	28.88	32.88
	12	79.34	15.95	28.37	32.55	60.64	0.54	13.14	16.03	27.48	31.66

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Table 4.32: Colorimetric parameters for the fabric dyed with a binary mixture of Marigold and Babool dyes (MB)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	81.7	4.06	16.79	17.27	76.37	0.58	10.78	4.14	15.90	16.38
	2	77.36	6.16	20.34	21.25	73.13	0.98	15.12	6.24	19.45	20.36
	3	72.88	7.64	20.85	22.21	69.83	1.44	19.60	7.72	19.96	21.32
	4	71.27	8.09	21.71	23.17	69.54	1.62	21.21	8.17	20.82	22.28
	5	68.17	9.08	22.14	23.93	67.67	2.07	24.31	9.16	21.25	23.04
	6	66.62	9.49	22.4	24.33	67.01	2.28	25.86	9.57	21.51	23.44
Set II **(Increasing Time Temperature samples)**	7	72.33	8.6	22.89	24.45	69.39	1.53	20.15	8.68	22.00	23.56
	8	69.02	9.67	24.84	26.66	68.71	1.9	23.46	9.75	23.95	25.77
	9	68.57	9.42	23.12	24.97	67.81	1.96	23.91	9.50	22.23	24.08
	10	67.08	9.55	22.91	24.82	67.34	2.2	25.40	9.63	22.02	23.93
	11	66.02	9.63	22.51	24.48	66.81	2.43	26.46	9.71	21.62	23.59
	12	65.27	9.93	22.7	24.78	66.35	2.57	27.21	10.01	21.81	23.89

Table 4.33: Colorimetric parameters for the fabric dyed with a binary mixture of Marigold and Madder dyes (MD)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	72.22	19.84	9.96	22.20	26.65	0.48	20.26	19.92	9.07	21.31
	2	65.45	24.47	11.19	26.91	24.57	0.82	27.03	24.55	10.30	26.02
	3	62.24	26.45	12.15	29.11	24.66	1.07	30.24	26.53	11.26	28.22
	4	58.98	27.66	12.23	30.24	23.84	1.34	33.50	27.74	11.34	29.35
	5	57.29	28.39	13.44	31.41	25.31	1.57	35.19	28.47	12.55	30.52
	6	53.85	29.33	14.34	32.65	26.06	2.07	38.63	29.41	13.45	31.76
Set II **(Increasing Time Temperature samples)**	7	61.85	25.42	14.24	29.14	29.25	1.2	30.63	25.50	13.35	28.25
	8	54.83	29.09	13.76	32.18	25.3	1.87	37.65	29.17	12.87	31.29
	9	53.85	29.62	13.69	32.63	24.8	2.08	38.63	29.70	12.80	31.74
	10	52.94	29.8	13.94	32.90	25.06	2.18	39.54	29.88	13.05	32.01
	11	53.15	28.6	13.87	31.79	25.87	2.06	39.33	28.68	12.98	30.90
	12	53.15	28.6	13.87	31.79	25.87	2.06	39.33	28.68	12.98	30.90

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Table 4.34: Colorimetric parameters for the fabric dyed with a binary mixture of Marigold and Katha dyes (MK)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I (Increasing Concentration samples)	1	74.37	10.54	16.84	19.87	57.94	0.730	18.11	10.62	15.95	18.98
	2	67.93	13.05	19.14	23.17	55.71	1.210	24.55	13.13	18.25	22.28
	3	68.15	13.64	19.46	23.76	54.94	1.170	24.33	13.72	18.57	22.87
	4	65.05	14.60	20.82	25.43	54.95	1.450	27.43	14.68	19.93	24.54
	5	64.36	14.87	20.86	25.62	54.50	1.490	28.12	14.95	19.97	24.73
	6	62.53	15.81	21.44	26.64	53.58	1.740	29.95	15.89	20.55	25.75
Set II (Increasing Time Temperature samples)	7	71.91	13.13	22.80	26.31	60.05	0.810	20.57	13.21	21.91	25.42
	8	67.50	15.60	22.25	27.17	54.95	1.110	24.98	15.68	21.36	26.28
	9	64.44	16.30	21.52	27.00	52.21	1.420	28.04	16.38	20.63	26.11
	10	62.52	16.48	20.74	26.49	51.51	1.560	29.96	16.56	19.85	25.60
	11	61.41	16.61	20.24	26.18	50.60	1.760	31.07	16.69	19.35	25.29
	12	61.41	16.61	20.24	26.18	50.60	1.760	31.07	16.69	19.35	25.29

Table 4.35: Colorimetric parameters for the fabric dyed with a binary mixture of Pomegranate and Annatto dyes (PA)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I (Increasing Concentration samples)	1	80.02	10.11	18.82	21.36	61.74	1.04	12.46	10.19	17.93	20.47
	2	78.09	11.73	26.06	28.58	65.74	1.33	14.39	11.81	25.17	27.69
	3	78.09	11.73	26.06	28.58	65.74	1.33	14.39	11.81	25.17	27.69
	4	76.18	12.37	27.88	30.50	66.04	1.67	16.30	12.45	26.99	29.61
	5	74.31	13.04	30.9	33.54	67.09	2.35	18.17	13.12	30.01	32.65
	6	72.97	13.52	31.51	34.29	66.74	2.55	19.51	13.60	30.62	33.40
Set II (Increasing Time Temperature samples)	7	80.18	4.11	28.39	28.69	81.74	1.73	12.30	4.19	27.50	27.80
	8	76.77	6.8	30.78	31.52	77.5	2.39	15.71	6.88	29.89	30.63
	9	75.41	10.02	30.32	31.93	71.68	2.25	17.07	10.10	29.43	31.04
	10	74.31	12.45	30.65	33.08	67.86	2.24	18.17	12.53	29.76	32.19
	11	73.6	12.73	30.54	33.09	67.35	2.31	18.88	12.81	29.65	32.20
	12	73.85	13.13	30.89	33.56	65.9	2.35	18.63	13.21	30.00	32.67

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Table 4.36: Colorimetric parameters for the fabric dyed with a binary mixture of Pomegranate and Babool dyes (PB)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	81.37	2.96	14.60	14.90	78.49	0.79	11.11	3.04	13.71	14.01
	2	75.03	5.30	19.07	19.79	74.44	1.58	17.45	5.38	18.18	18.90
	3	71.17	6.56	20.47	21.50	72.20	2.18	21.31	6.64	19.58	20.61
	4	69.09	6.93	21.61	22.69	72.18	2.65	23.39	7.01	20.72	21.80
	5	66.36	7.76	21.98	23.31	70.53	3.18	26.12	7.84	21.09	22.42
	6	64.33	8.05	22.20	23.61	70.03	3.59	28.15	8.13	21.31	22.72
Set II **(Increasing Time Temperature samples)**	7	74.58	5.13	20.88	21.50	76.17	1.77	17.90	5.21	19.99	20.61
	8	68.81	6.96	23.70	24.70	73.66	3.10	23.67	7.04	22.81	23.81
	9	68.80	7.27	22.66	23.80	72.19	3.09	23.68	7.35	21.77	22.91
	10	65.30	8.01	22.75	24.12	70.56	3.58	27.18	8.09	21.86	23.23
	11	64.44	8.29	21.70	23.23	69.05	3.62	28.04	8.37	20.81	22.34
	12	64.67	8.34	22.06	23.58	69.27	3.58	27.81	8.42	21.17	22.69

Table 4.37: Colorimetric parameters for the fabric dyed with a binary mixture of Pomegranate and Madder dyes (PD)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	71.21	20.85	11.28	23.71	28.40	0.78	21.27	20.93	10.39	22.82
	2	65.12	23.92	13.58	27.51	29.58	1.35	27.36	24.00	12.69	26.62
	3	60.31	26.55	14.69	30.34	28.94	1.95	32.17	26.63	13.80	29.45
	4	56.57	28.61	14.07	31.88	26.17	2.25	35.91	28.69	13.18	30.99
	5	54.46	28.79	14.08	32.05	26.06	2.60	38.02	28.87	13.19	31.16
	6	53.08	27.75	15.19	31.64	28.68	2.77	39.40	27.83	14.30	30.75
Set II **(Increasing Time Temperature samples)**	7	61.71	26.10	16.19	30.71	31.79	1.82	30.77	26.18	15.30	29.82
	8	57.28	25.90	13.53	29.22	27.47	2.07	35.20	25.98	12.64	28.33
	9	53.62	26.97	13.40	30.12	26.40	2.59	38.86	27.05	12.51	29.23
	10	52.25	27.80	13.63	30.96	26.10	2.77	40.23	27.88	12.74	30.07
	11	52.60	28.05	13.93	31.32	26.41	2.78	39.88	28.13	13.04	30.43
	12	52.66	28.24	14.02	31.53	26.38	2.81	39.82	28.32	13.13	30.64

Table 4.38: Colorimetric parameters for the fabric dyed with a binary mixture of Pomegranate and Katha dyes (PK)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I (Increasing Concentration samples)	1	76.36	9.00	14.43	17.01	58.02	0.80	16.12	9.08	13.54	16.12
	2	69.44	11.92	17.66	21.31	55.95	1.50	23.04	12.00	16.77	20.42
	3	65.36	13.61	18.90	23.29	54.21	1.99	27.12	13.69	18.01	22.40
	4	61.94	14.56	20.24	24.93	54.26	2.91	30.54	14.64	19.35	24.04
	5	60.40	14.89	20.28	25.16	53.69	2.90	32.08	14.97	19.39	24.27
	6	59.45	14.80	20.08	24.94	53.60	3.07	33.03	14.88	19.19	24.05
Set II (Increasing Time Temperature samples)	7	70.79	10.70	22.35	24.78	64.40	1.87	21.69	10.78	21.46	23.89
	8	67.21	12.97	21.20	24.85	58.51	2.06	25.27	13.05	20.31	23.96
	9	62.50	15.18	21.05	25.95	54.17	2.62	29.98	15.26	20.16	25.06
	10	59.37	15.70	19.98	25.41	51.84	3.05	33.11	15.78	19.09	24.52
	11	59.20	15.72	20.77	26.05	52.87	3.16	33.28	15.80	19.88	25.16
	12	58.36	15.80	20.02	25.50	51.71	3.19	34.12	15.88	19.13	24.61

4.2.1.1.1 Compatibility Assessment Methods

(A) Method based on -dL vs. dC and -dL vs. K/S Plot

Samanta et al., (2015) worked on compatibility check by plotting ΔL versus K/S or ΔC versus K/S. It is generally used for compatibility assessment of two dyes for two sets of the progressive depth of shade developed for a binary mixture of dyes. It is done by varying the temperature and time of dyeing for one set and varying the total dye concentrations of the binary mixtures of dyes in another set to judge whether the two sets of curves for shade buildup run alike or not. A plot of ΔL versus ΔC and ΔL versus K/S gives better results than other methods because they assume that there is no interaction between dyes and no change in the rate of dyeing in the presence of another dyestuff, which is not true. A plot of ΔL versus ΔC and ΔL versus K/S would require a precise temperature-controlled machine for progressive shade buildup. This method is time-consuming and subjective.

Plots for -dL vs. dC and -dL vs. K/S for each mixture are shown in Figure 4.17 to Figure 4.28. It was visible from the plots that both the curves of set I and set II were not represented by a single curve. Generally, both curves were distinct, and the set II curve joined the set I curve. Both curves took the common path toward the end of the curves.

In -dL vs. dC plots for all mixtures, it was observed that the mixture of Marigold/Madder (MD) showed a good overlap of set I and set II curves. This mixture was considered as highly compatible mixture. Some mixtures showed small deviation in overlapping but can be regarded as compatible mixtures as per observation using this method, which includes Katha/Madder (KD), Babool/Annatto (BA), Katha/Annatto (KA), and Pomegranate/Annatto (PA).

Certain mixtures had significant variations between both curves, which include Pomegranate/Madder (PD), Marigold/Katha (MK), Pomegranate/Babool (PB), Pomegranate/Katha (PK), Babool/Madder (BD), Marigold/Annatto (MA) and Marigold/Babool (MB). These mixtures were considered incompatible mixtures as per the study using this method.

It was also observed that most incompatible mixtures contain either Pomegranate or Marigold, where the sample no. 7 and 8 of set II (low time/temperature was given) were yellower than other samples in set II. This was considered as the reason for the deviated chroma in these cases.

The sets showed better overlap in -dL vs. K/S plots for all mixtures than -dL vs. dC plots, and showed more compatibility amongst mixtures. It was observed that the mixture of Pomegranate/Madder (PD), Marigold/Katha (MK), Pomegranate/ Babool (PB), Marigold/Babool (MB), and Marigold/Madder (MD) showed good overlap of set I and set II curves. These mixtures were considered as highly compatible mixtures.

Some mixtures showed some deviation in overlapping but can be regarded as compatible mixtures as per observation using this method, which includes Katha/Madder (KD), Pomegranate/Katha (PK), Babool/Madder (BD), Marigold/ Annatto (MA), and Katha/Annatto (KA) mixtures. Mixtures Babool/Annatto (BA) and Pomegranate/Annatto (PA) showed significant deviations in curves and were considered incompatible mixtures.

(a)

(b)
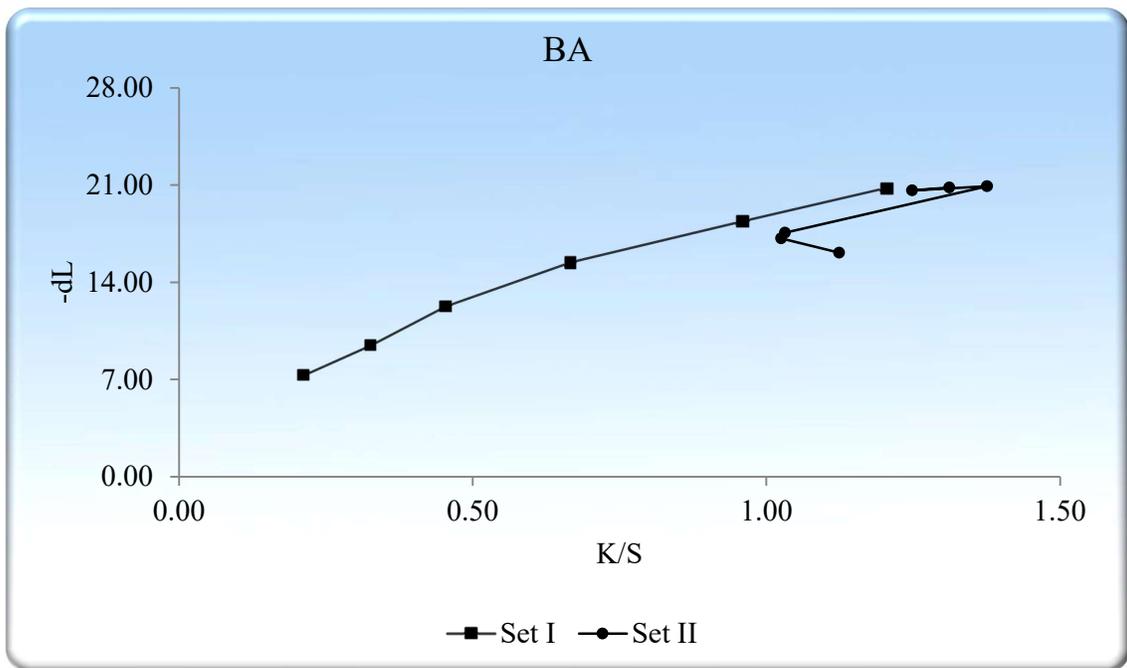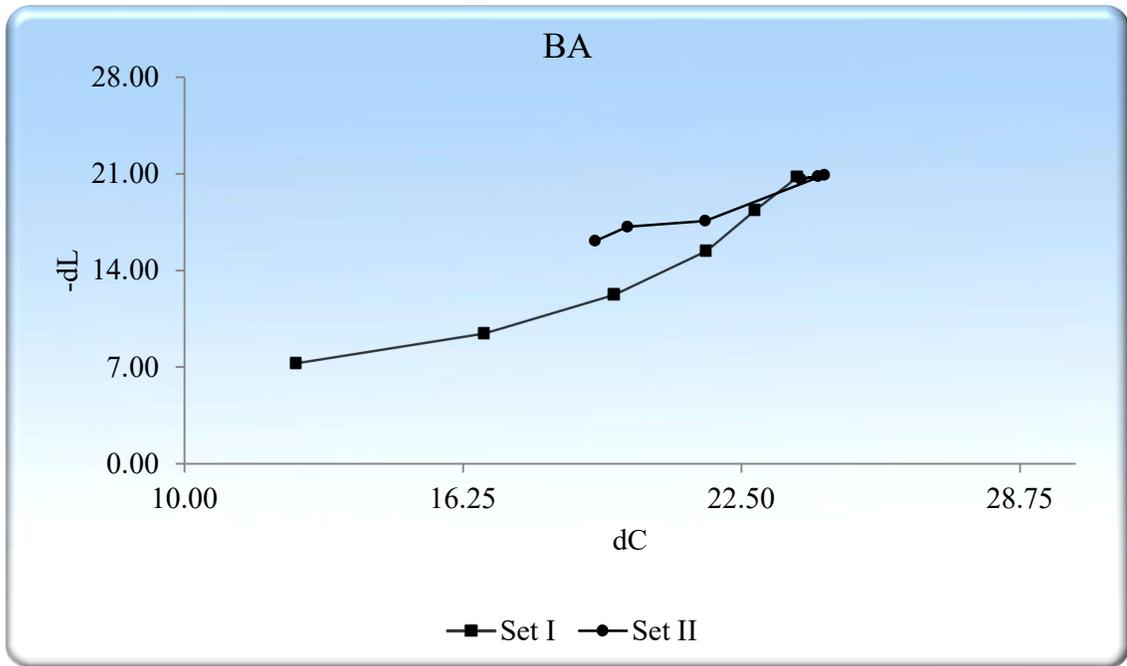
Figure 4.17: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Babool/Annatto (BA) dye mixture
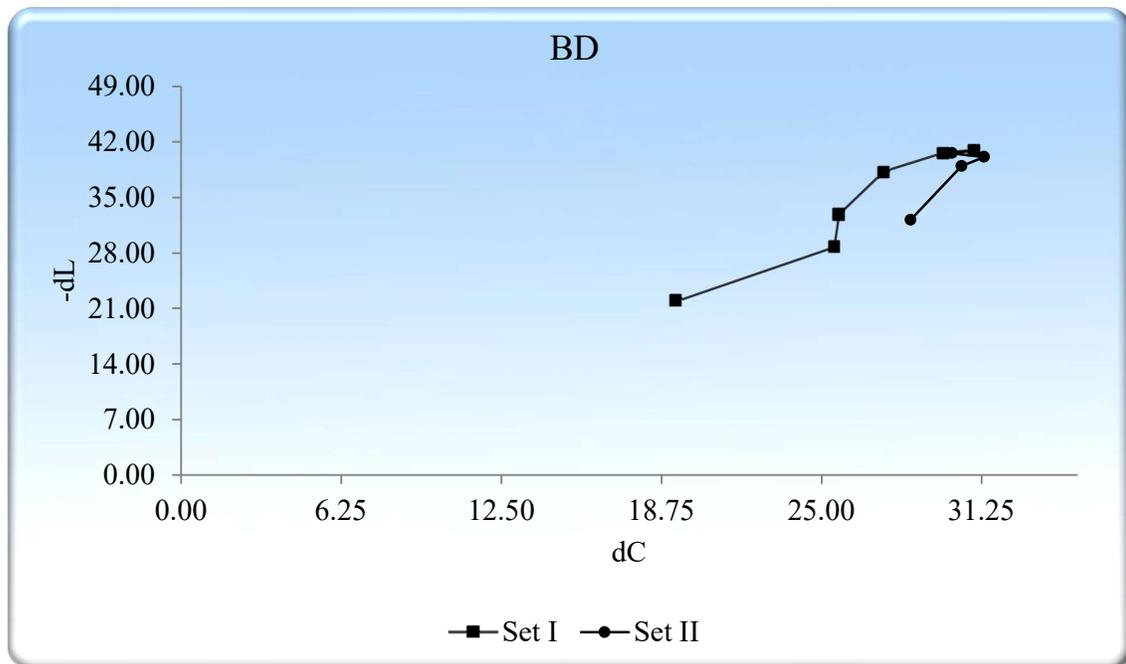
(a)
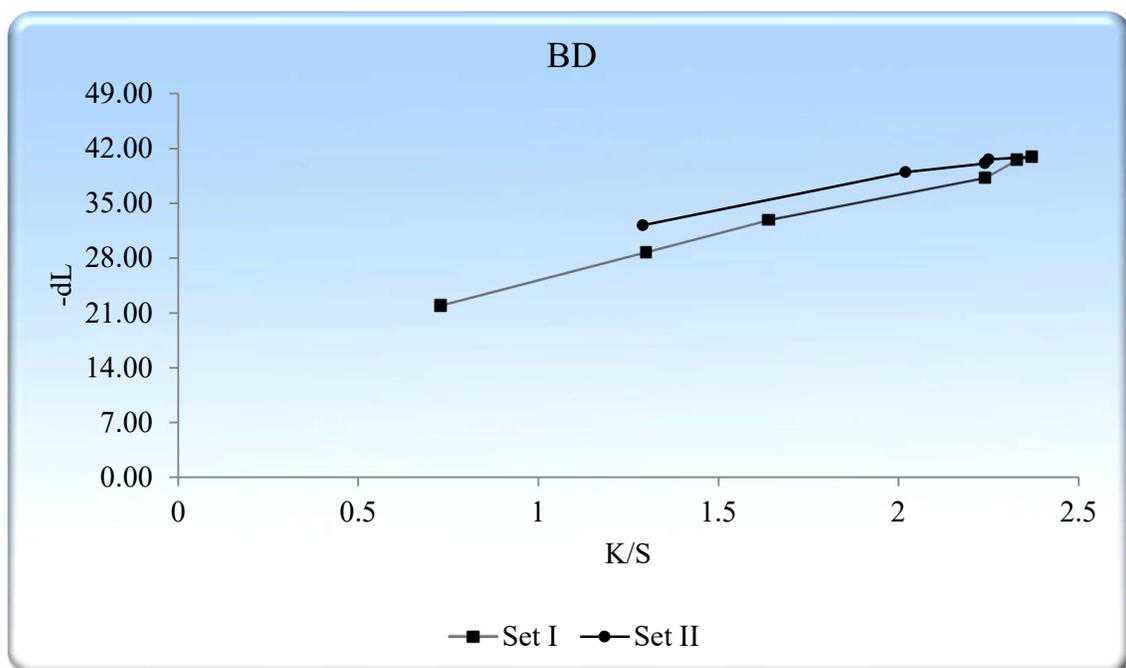
(b)

Figure 4.18: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Babool/Madder (BD) dye mixture
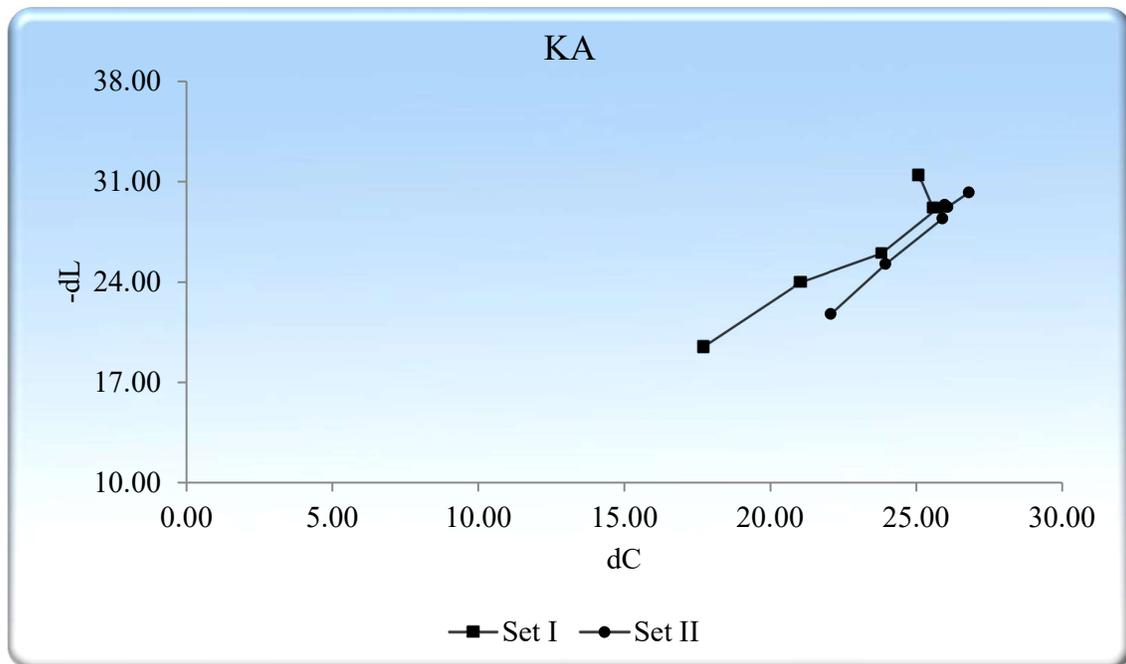
(a)
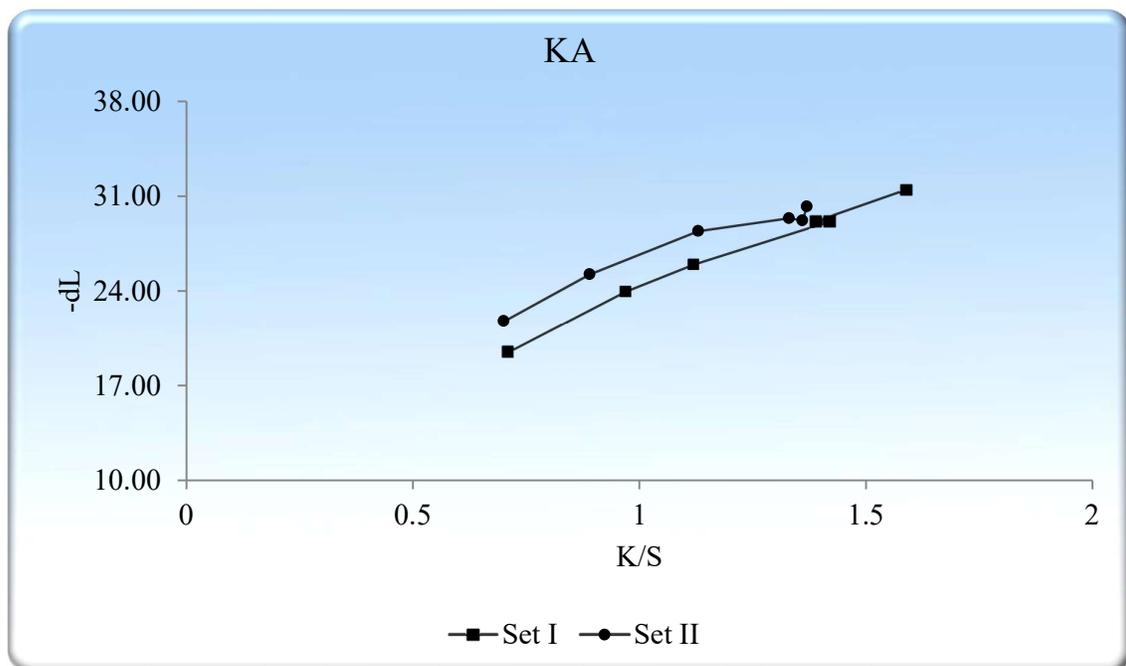
(b)

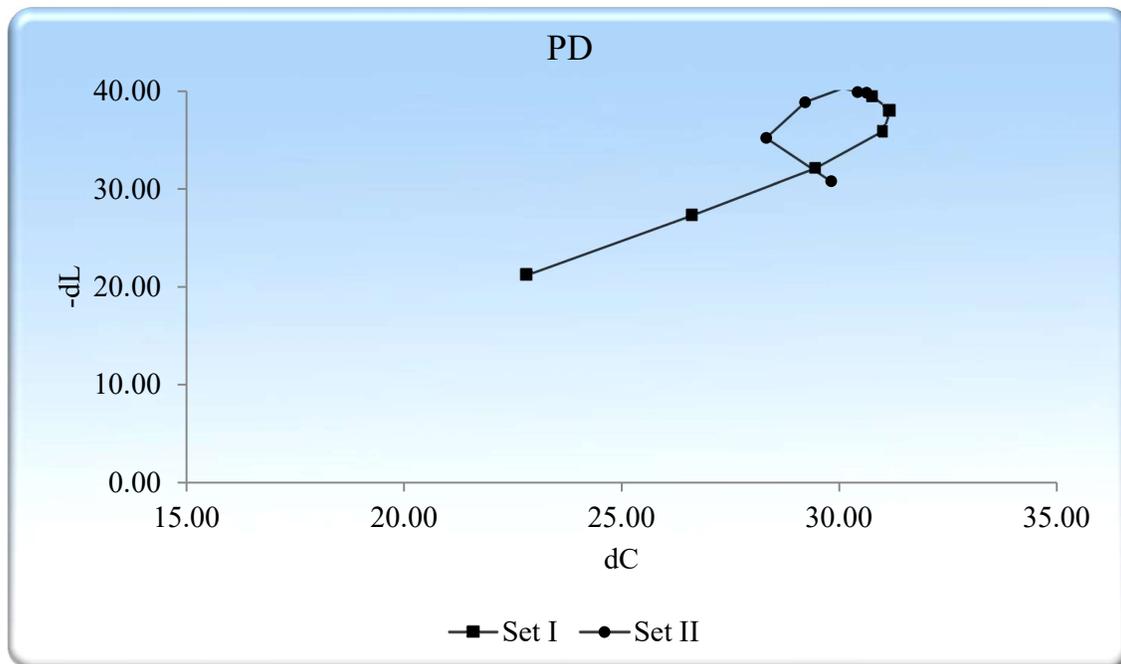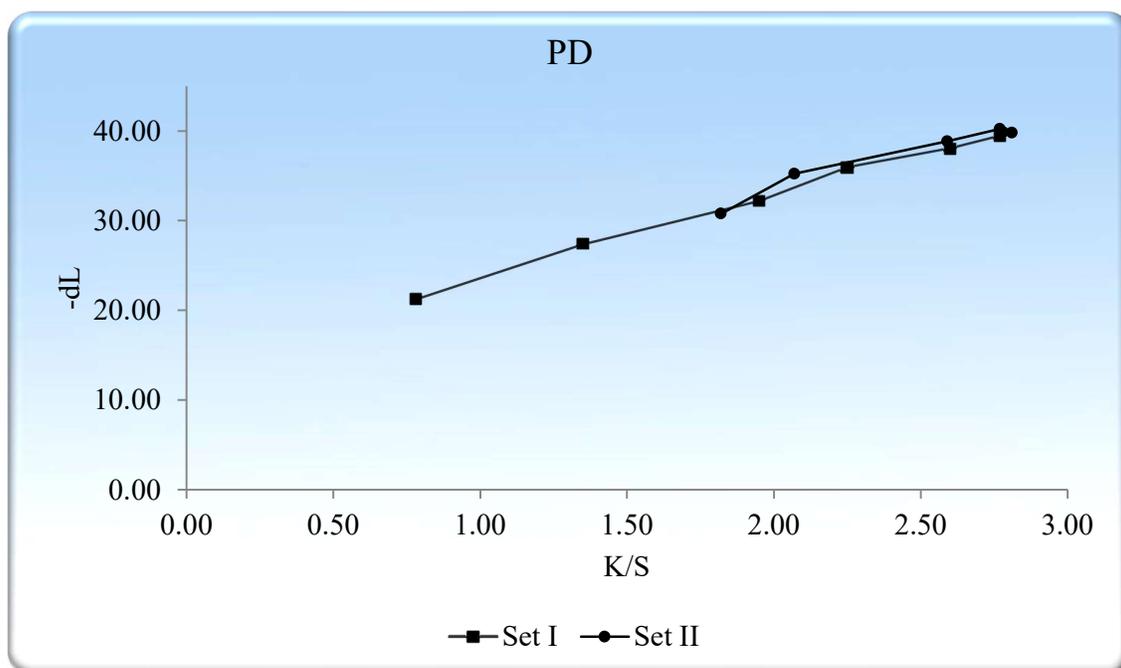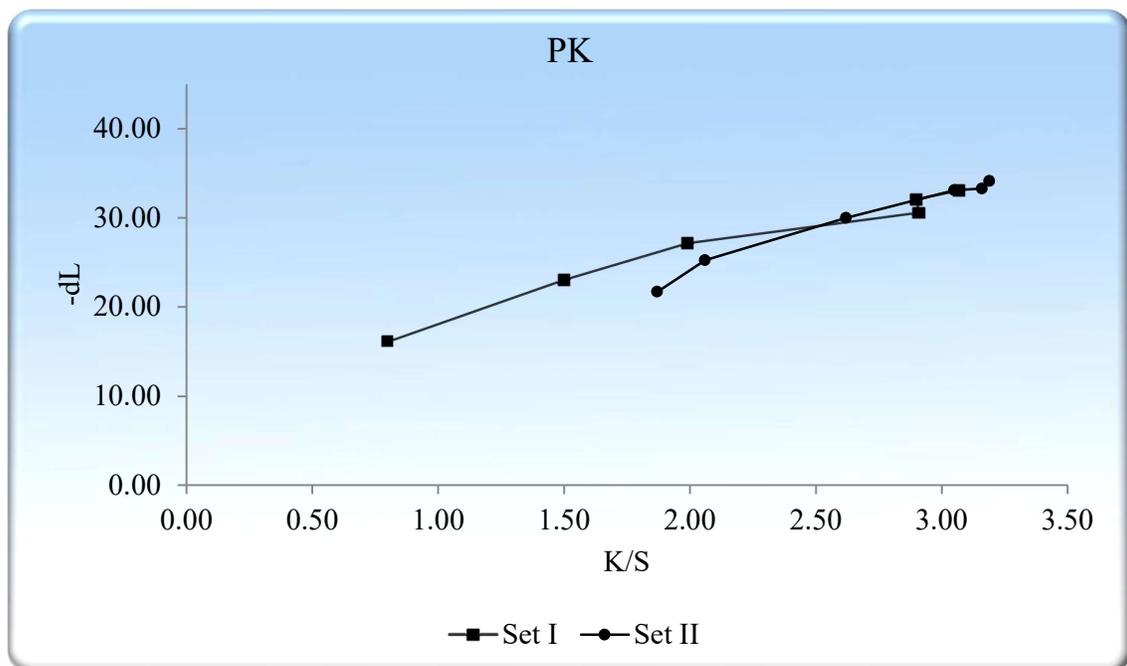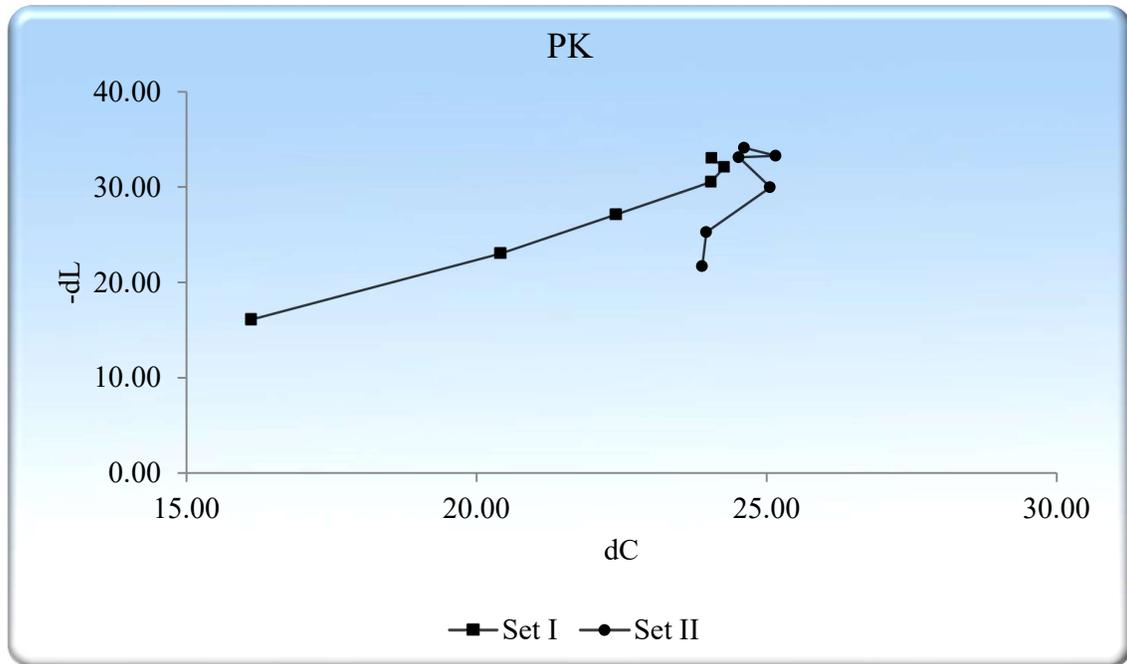**Figure 4.19: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Katha/Annatto (KA) dye mixture**
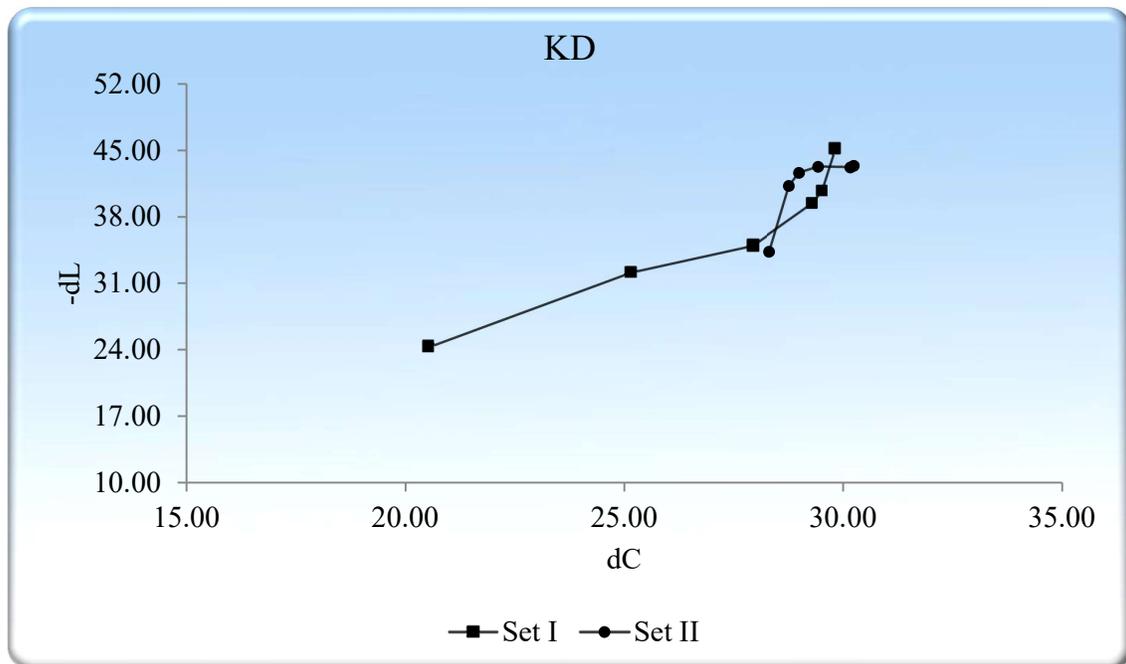
(a)
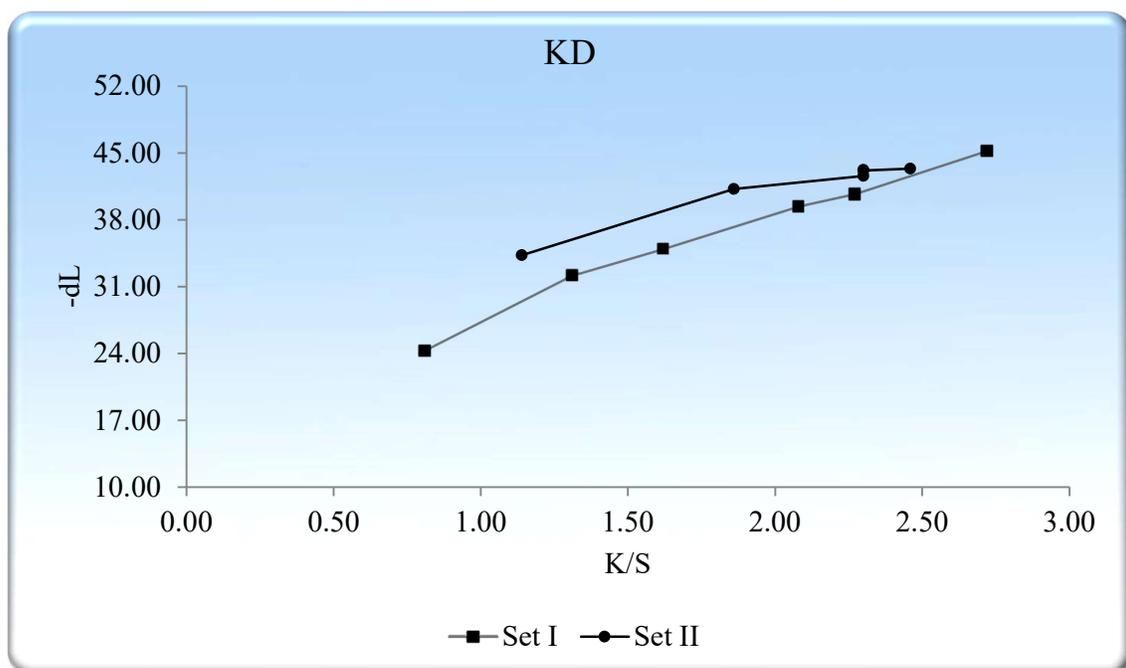
(b)

Figure 4.20: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Katha/Madder (KD) dye mixture
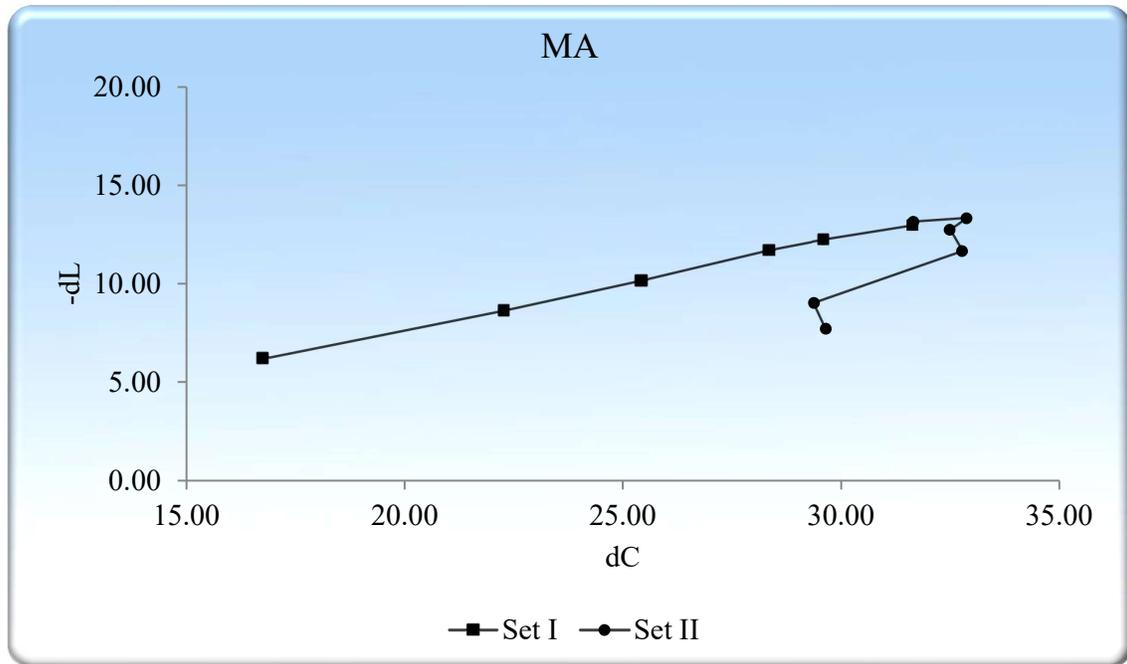
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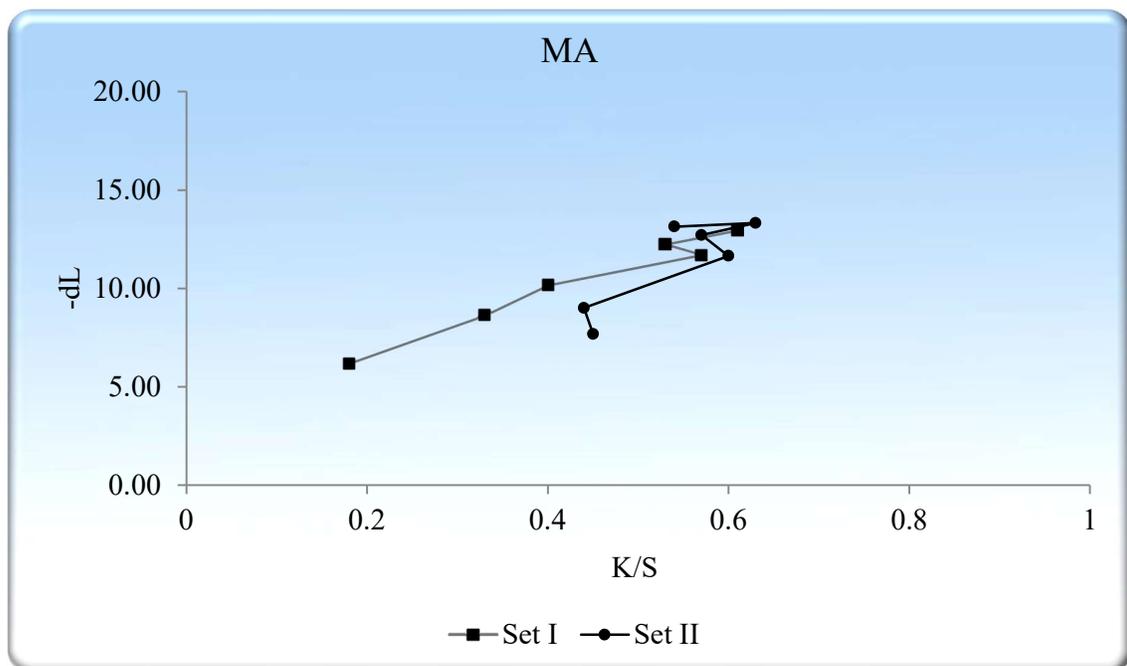
(b)

Figure 4.21: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Marigold/Annatto (MA) dye mixture
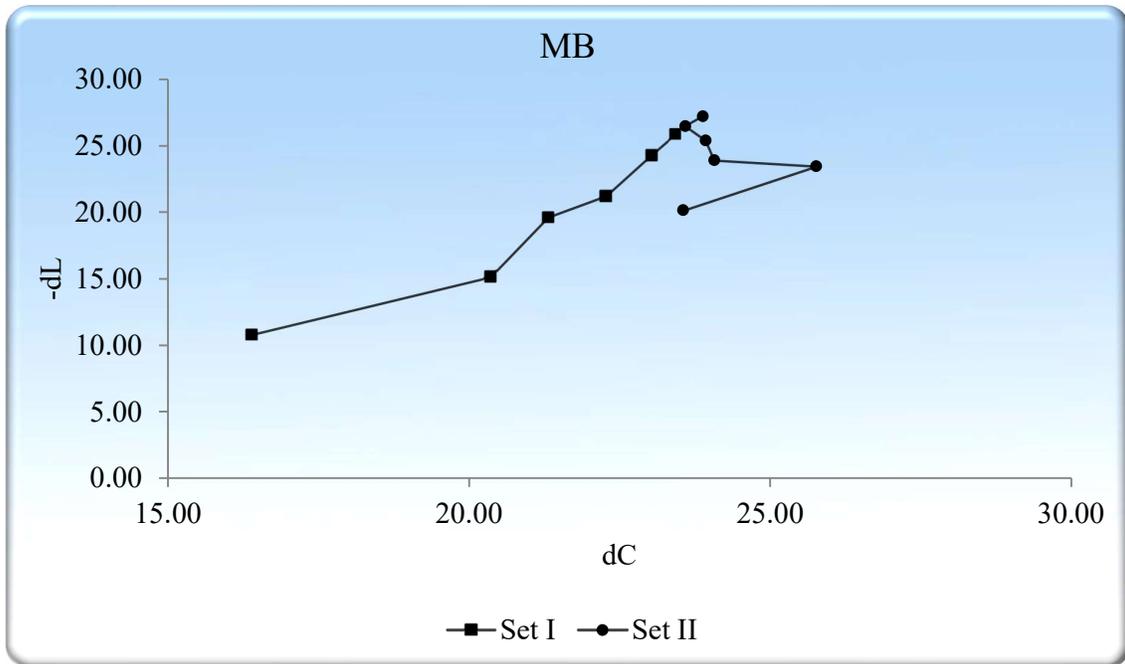
(a)
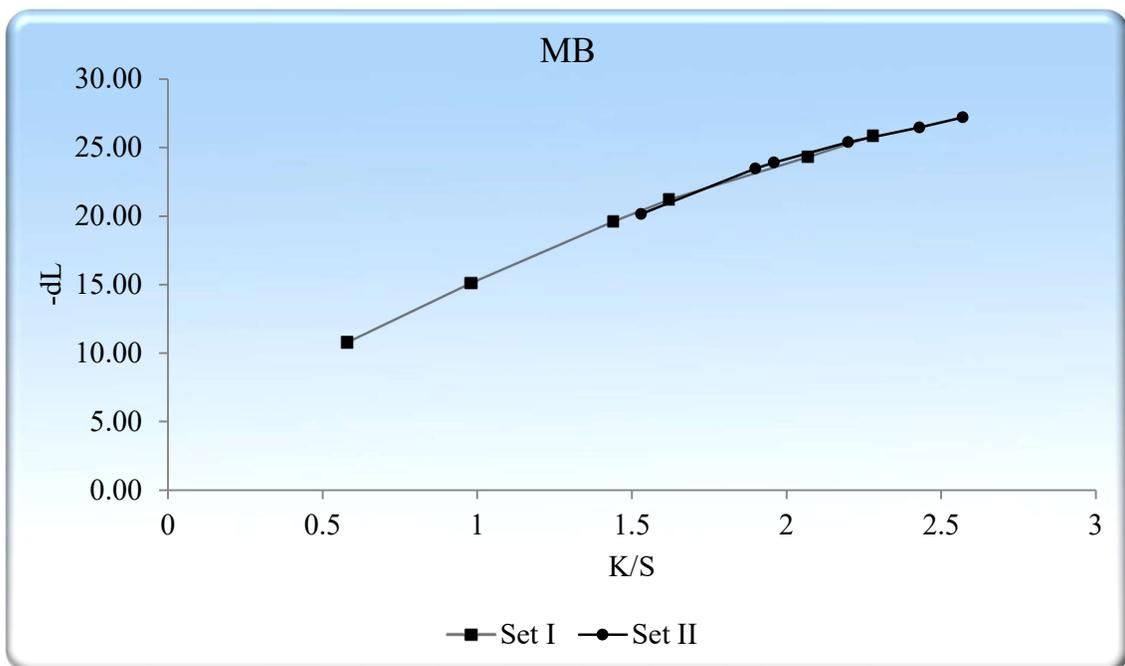
(b)

Figure 4.22: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Marigold/Babool (MB) dye mixture
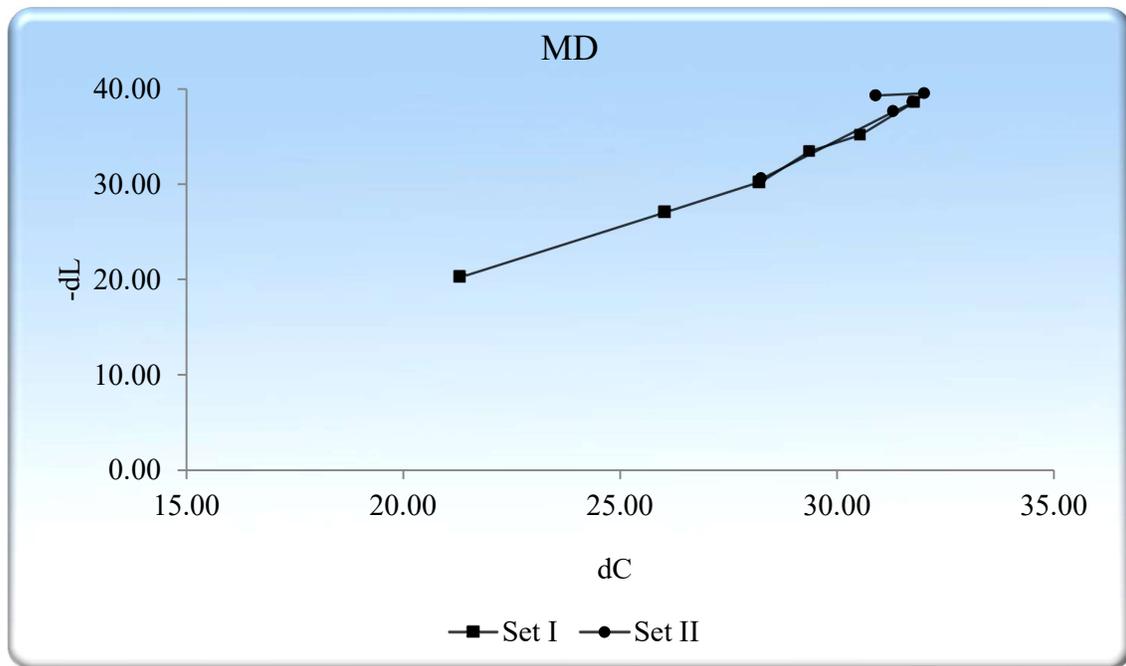
(a)
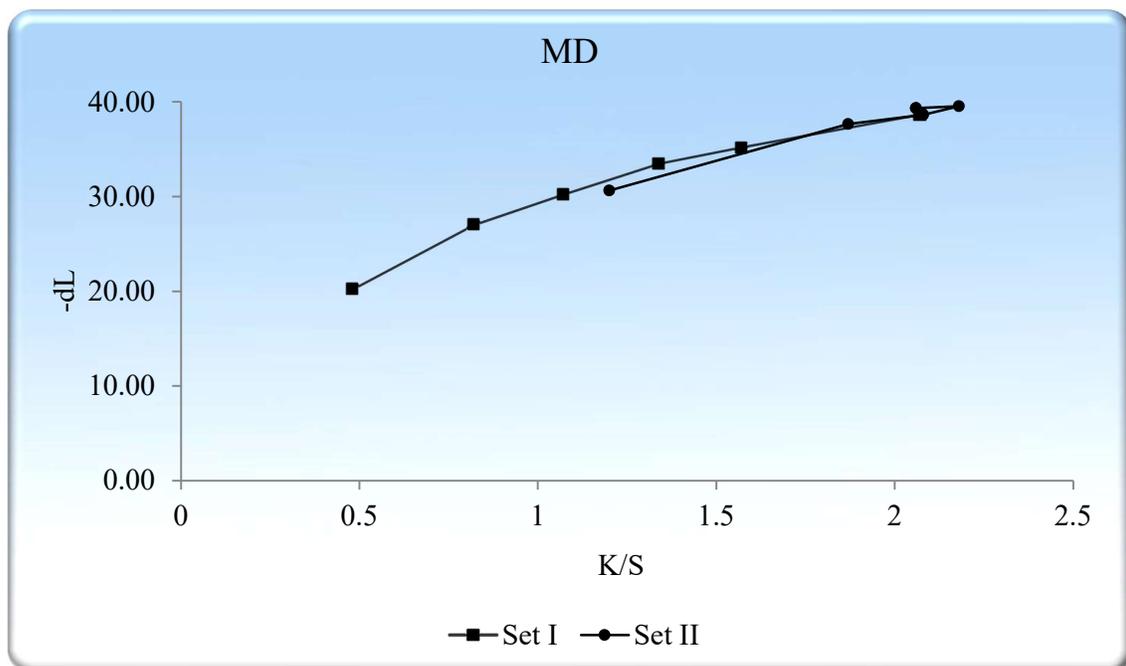
(b)

Figure 4.23: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Marigold/Madder (MD) dye mixture
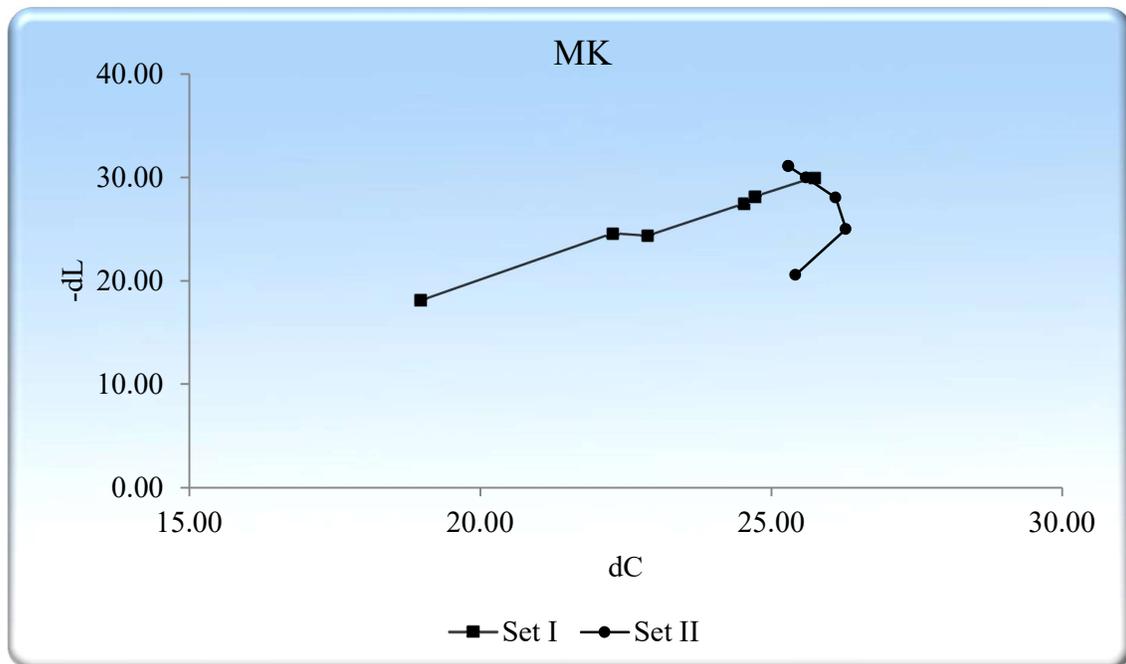
(a)
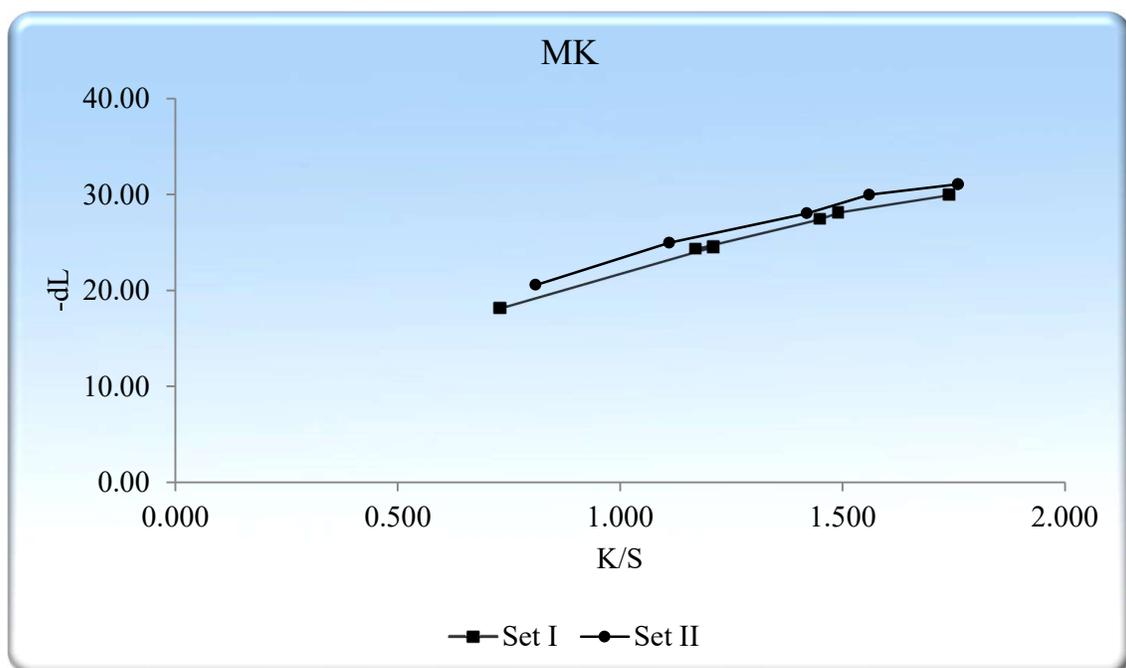
(b)

Figure 4.24: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Marigold/Katha (MK) dye mixture
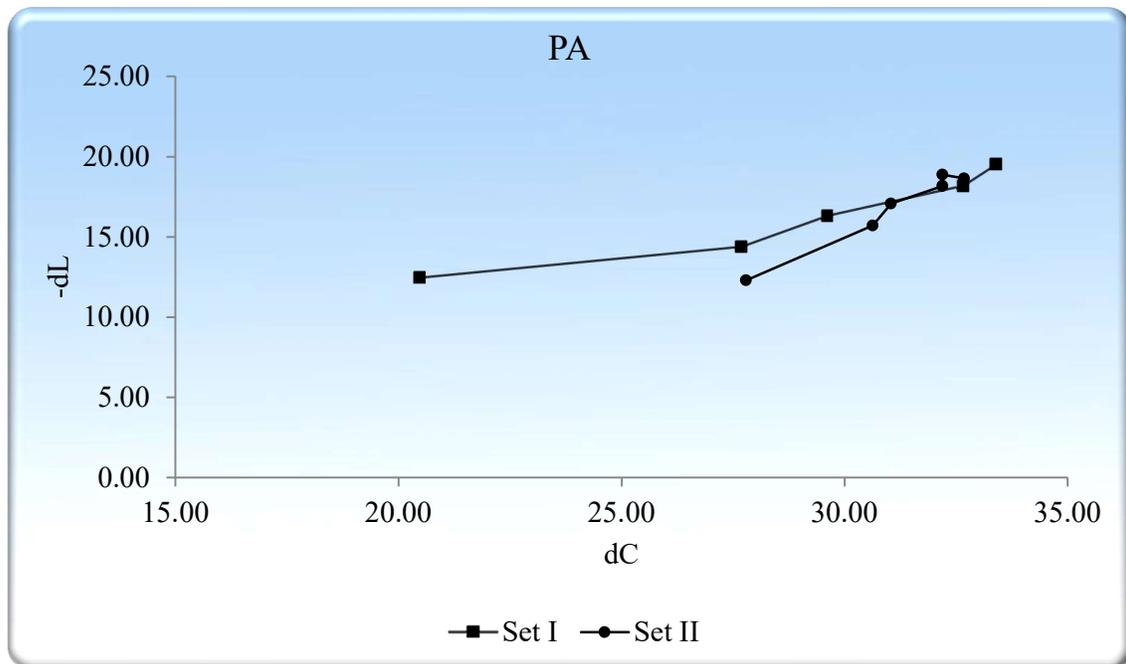
(a)
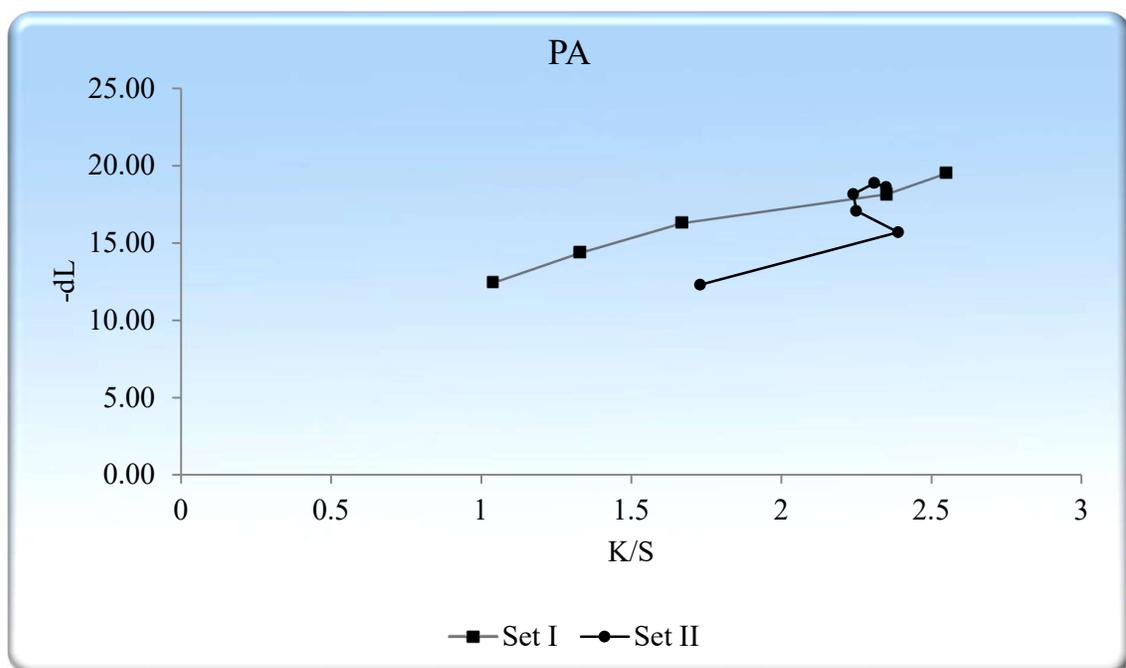
(b)

Figure 4.25: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Pomegranate/Annatto (PA) dye mixture
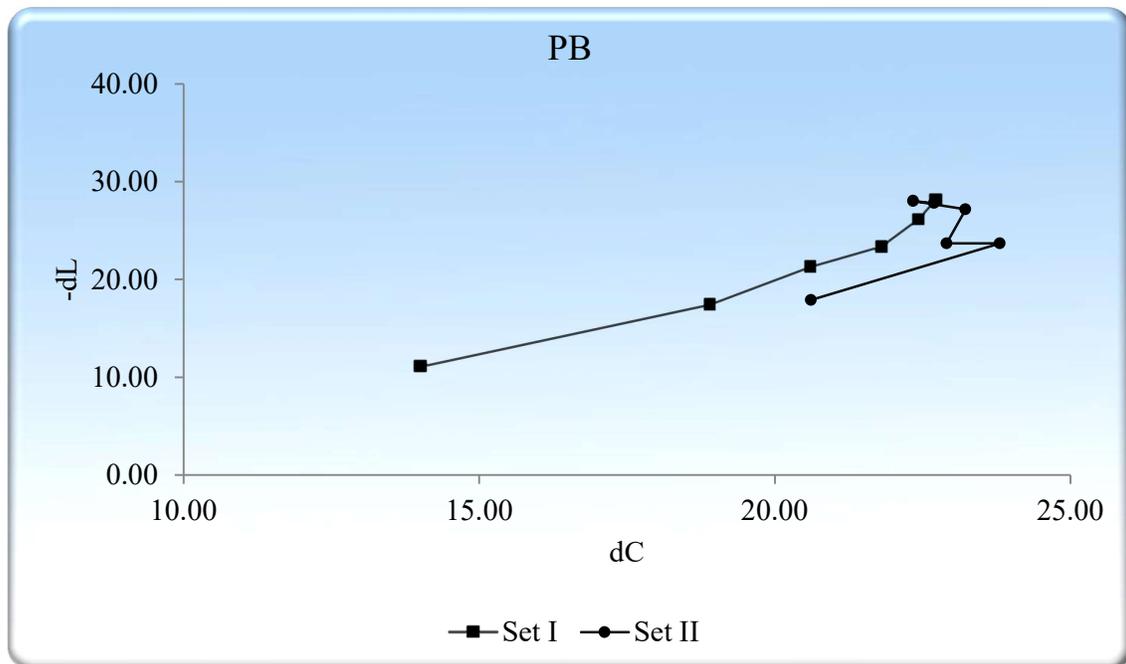
(a)
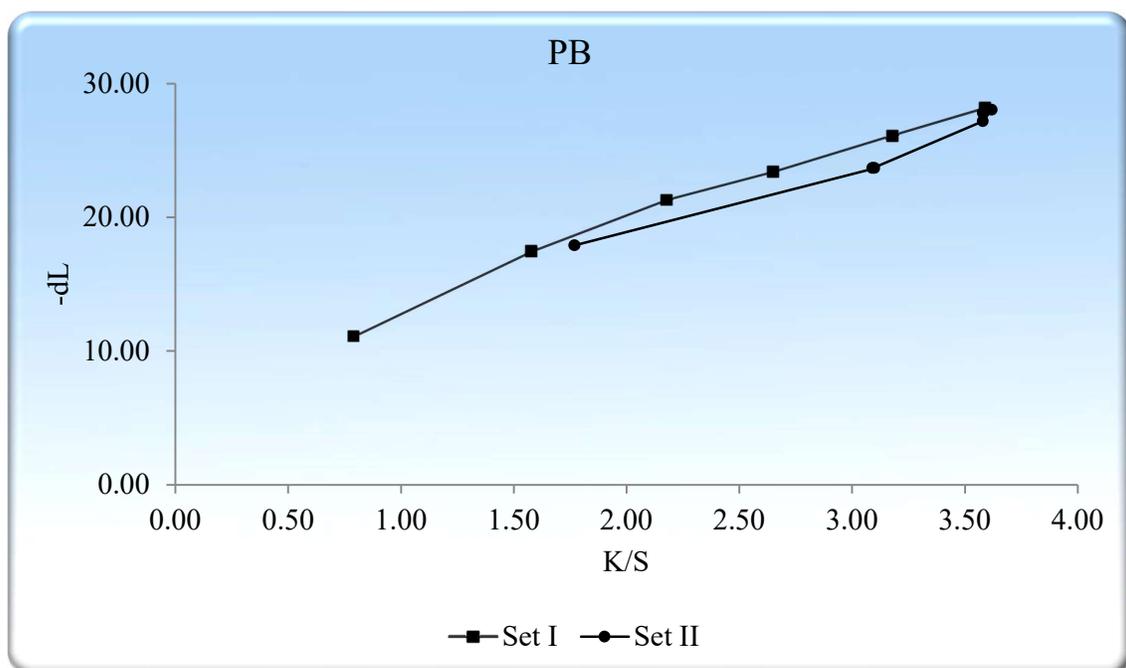
(b)

Figure 4.26: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Pomegranate/Babool (PB) dye mixture

(a)

(b)

Figure 4.27: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Pomegranate/Madder (PD) dye mixture

(a)

(b)

Figure 4.28: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Pomegranate/Katha (PK) dye mixture

(B)   Method based on da vs. K/S and db vs. K/S Plot

Shukla & Dhuri, (1993) used the plots of da vs. K/S and db vs. K/S to check the compatibility of dyes. It was desired that the redness or yellowness buildup should be in accordance with K/S for both sets. In the case of compatible mixtures, the curves for set I and II in plots of da vs. K/S and db vs. K/S should coincide. The compatibility is assessed by observing the curves for both sets.

Plots for da vs. K/S and db vs. K/S for each mixture are shown in Figure 4.29 to Figure 4.40. It was visible from the plots that both the curves of set I and set II are not represented by a single curve. Generally, both curves were distinct, and the set II curve joined the set I curve. Both curves took the common path toward the end of the curves.

In da vs. K/S plot for all mixtures, it was observed that the mixture of Pomegranate/Babool (PB), Marigold/Babool (MB), and Marigold/Madder (MD) showed good overlap of set I and set II curves. This mixture was considered as highly compatible mixture.

Some mixtures showed slight deviation in overlapping but can be regarded as compatible mixtures as per observation using this method, which includes Pomegranate/Madder (PD), Marigold/Katha (MK), Katha/Madder (KD), Katha/Annatto (KA), and Pomegranate/Katha (PK).

As per the plot for Babool/Madder (BD) and Marigold/Annatto (MA), they were considered partially compatible mixtures. Certain mixtures had significant variations between both curves, which included Babool/Annatto (BA) and Pomegranate/Annatto (PA). These mixtures were considered incompatible mixtures as per the study using this method.

In the db vs. K/S plot for all mixtures, as mentioned earlier, it was observed that in some cases, initial samples (no. 7 and 8) of set II samples were yellower than others. It seems that Pomegranate and Marigold have higher affinity than few other dyes.

It was also observed in the db value of set II for the binary mixture of Marigold. In the case of the Marigold/Annatto (MA) mixture, the db value of sample 7 was 28.84 and then decreased to 27.48 for sample 12 after some intermediate increase. It showed that the

Marigold absorption was very fast at the beginning of the process and then reduced towards the end. Similar behavior was exhibited by Marigold/Babool (MB), Marigold/Madder (MD), and Marigold/Katha (MK) mixtures. In the case of the binary mixture of Pomegranate, Pomegranate/Madder (PD) and Pomegranate/Katha (PK) showed similar behavior.

As per plots of db vs. K/S, it was observed that the mixture of Pomegranate/Babool (PB), Pomegranate/Annatto (PA), Pomegranate/Madder (PD), Katha/Madder (KD), Babool/Annatto (BA), Babool/ Madder (BD), Katha/Annatto (KA), Marigold/Babool (MB), and Marigold/Madder (MD) showed average or slight overlap of set I and set II curves. These mixtures were considered as compatible mixture.

As per the plot for Marigold/Katha (MK), Pomegranate/Katha (PK), and Marigold/Annatto (MA), they were considered partially compatible mixtures.
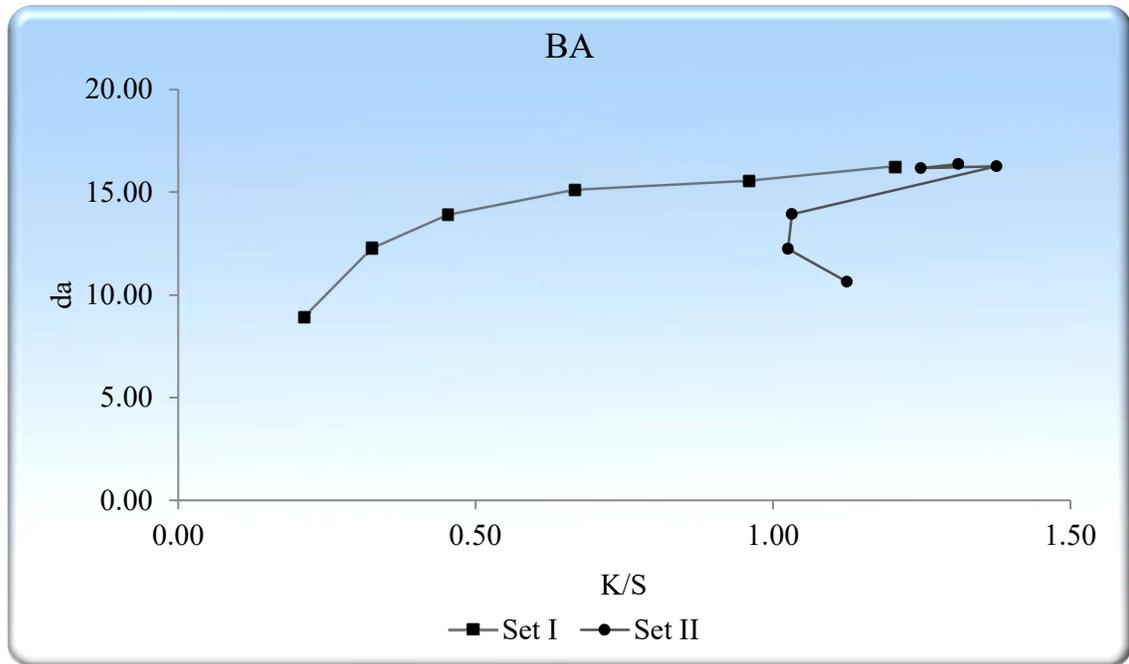
(a)
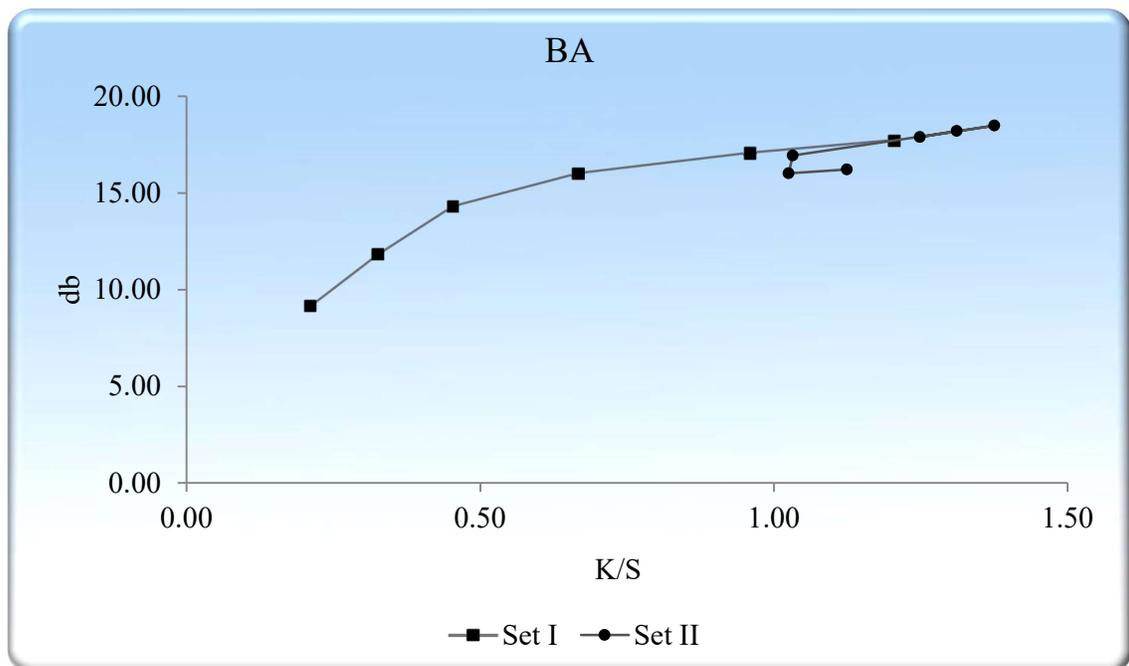
(b)

Figure 4.29: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Babool/Annatto (BA) dye mixture
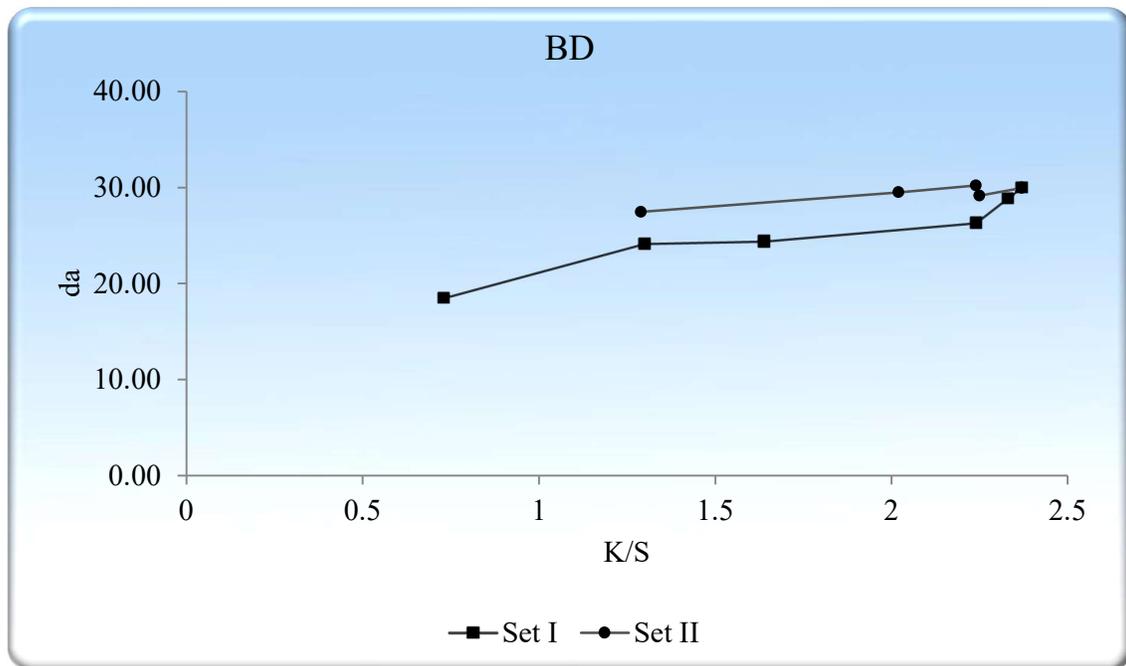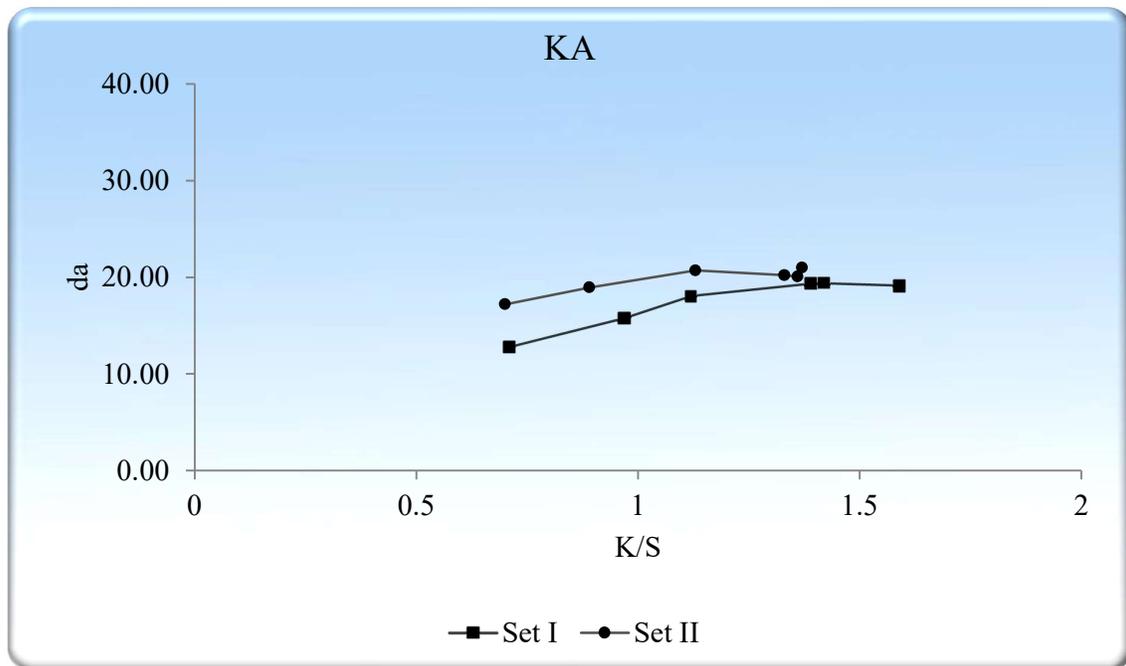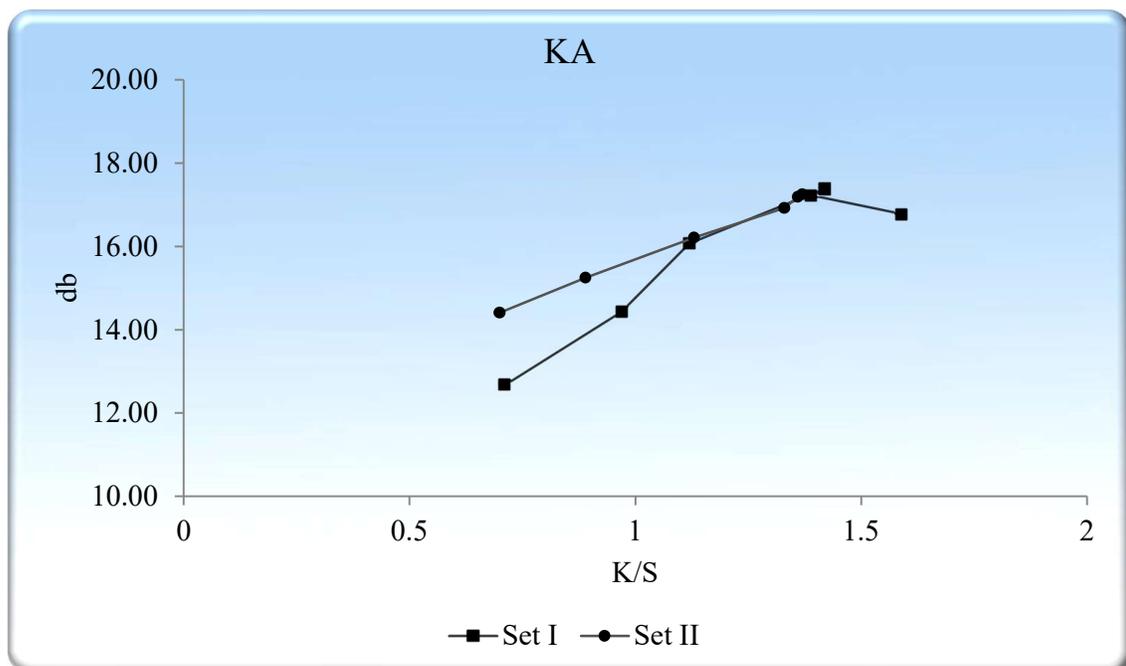
(a)
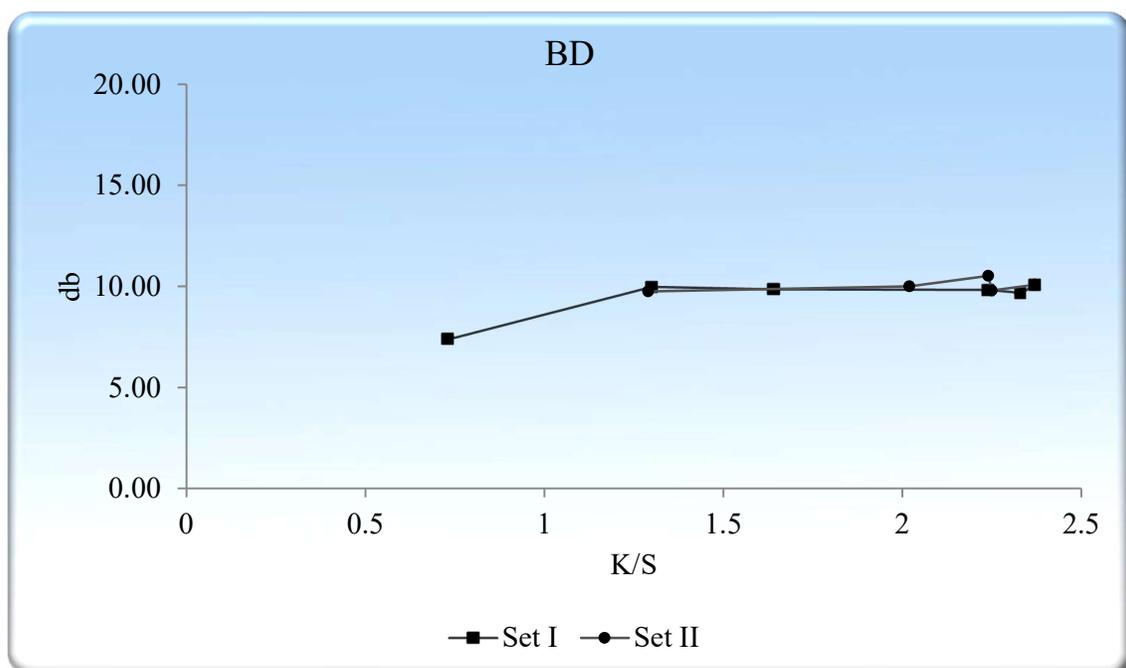
(b)

Figure 4.30: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Babool/Madder (BD) dye mixture
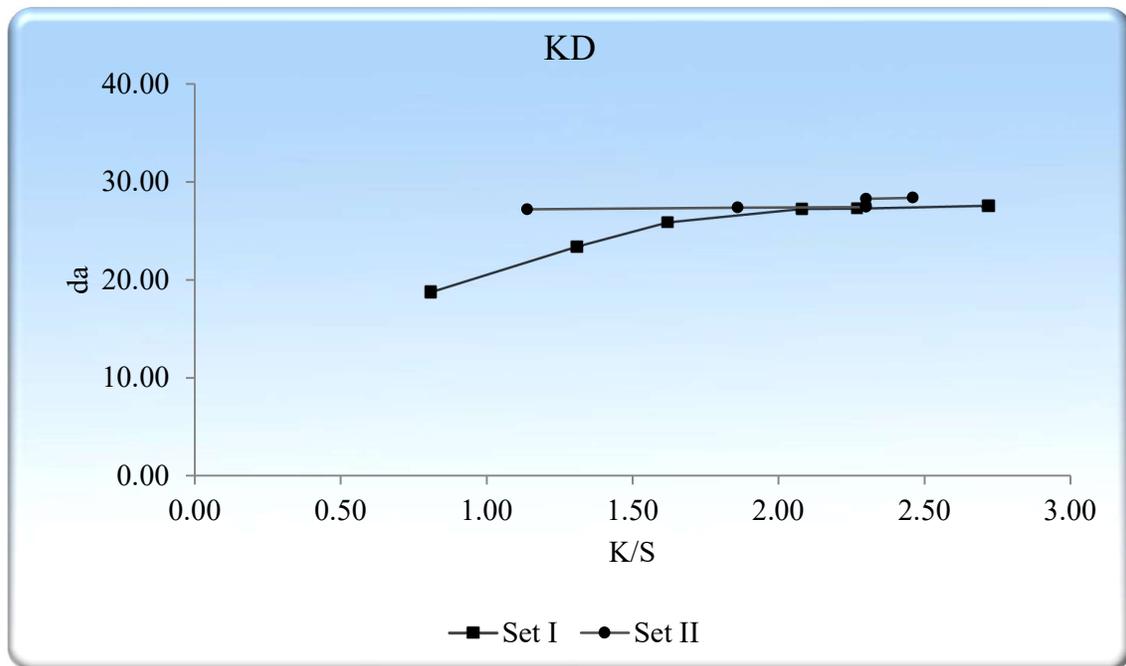
(a)

(b)

Figure 4.31: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Katha/Annatto (KA) dye mixture
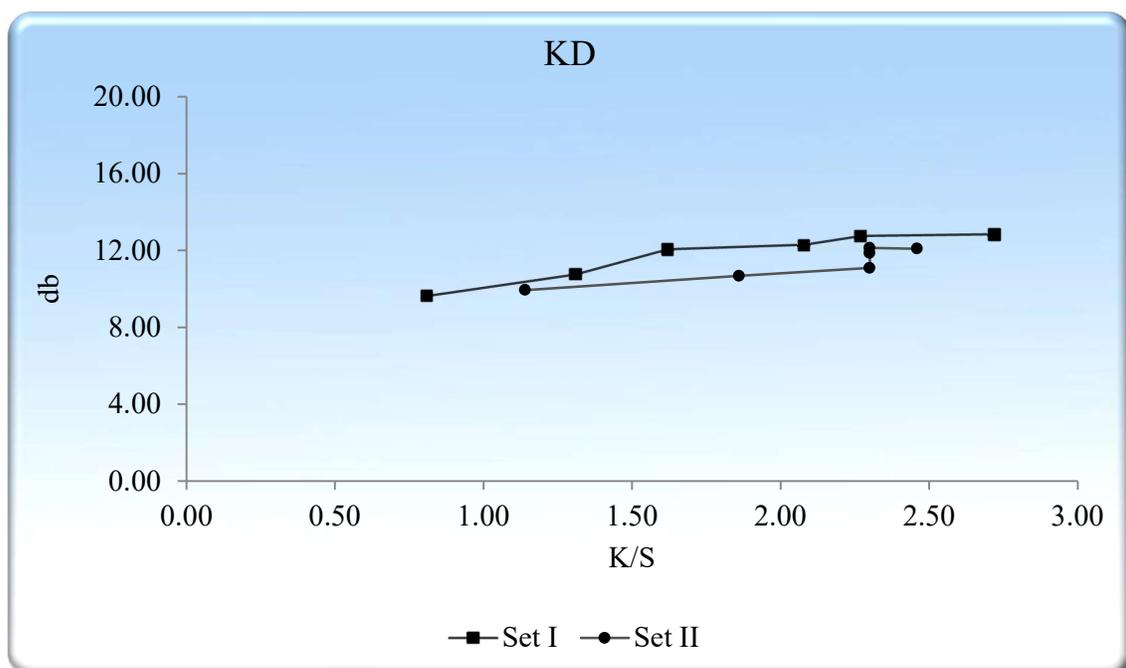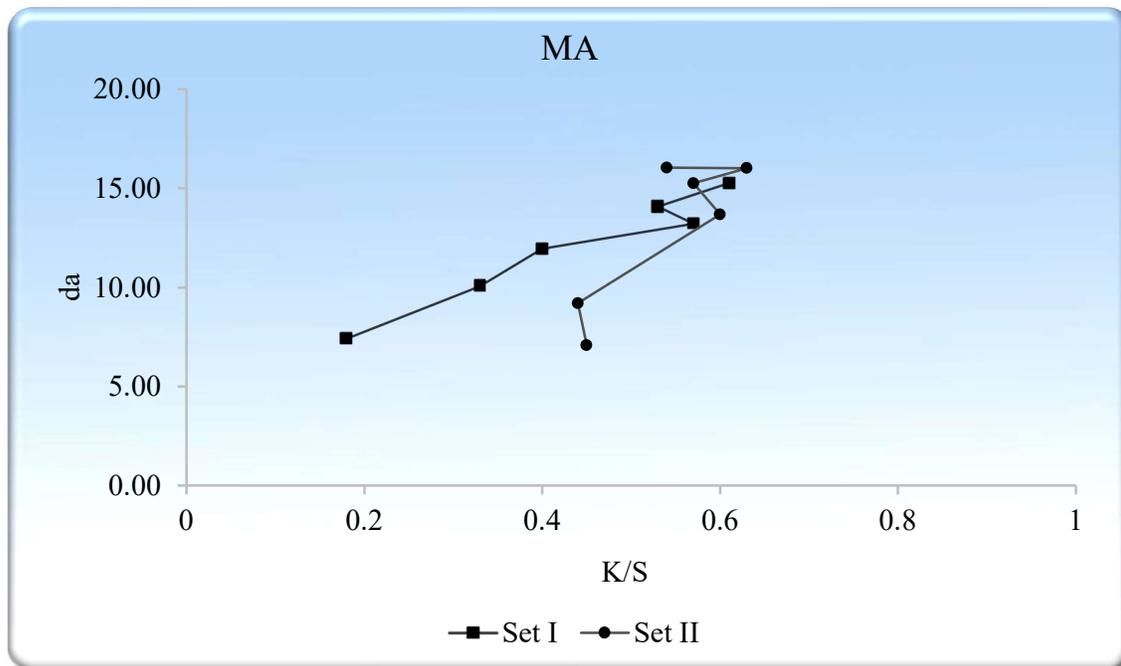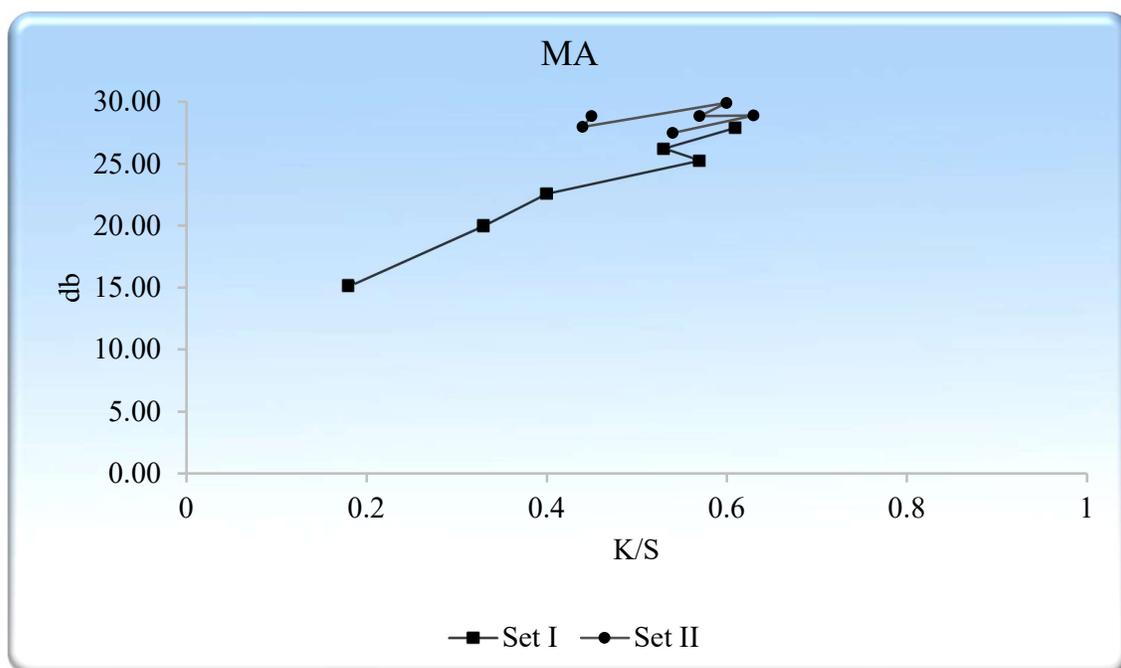
(a)

Figure 4.32: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Katha/Madder (KD) dye mixture
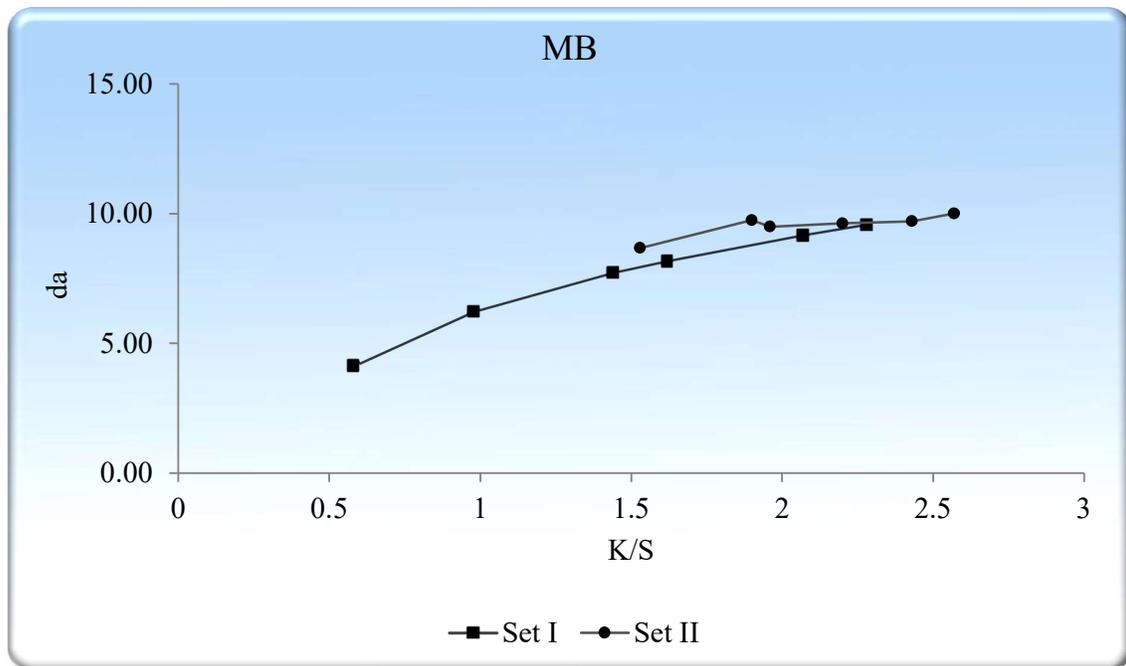
(a)

(b)

Figure 4.33: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Marigold/Annatto (MA) dye mixture

(a)

(b)

Figure 4.34: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Marigold/Babool (MB) dye mixture

(a)

(b)

Figure 4.35: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Marigold/Madder (MD) dye mixture
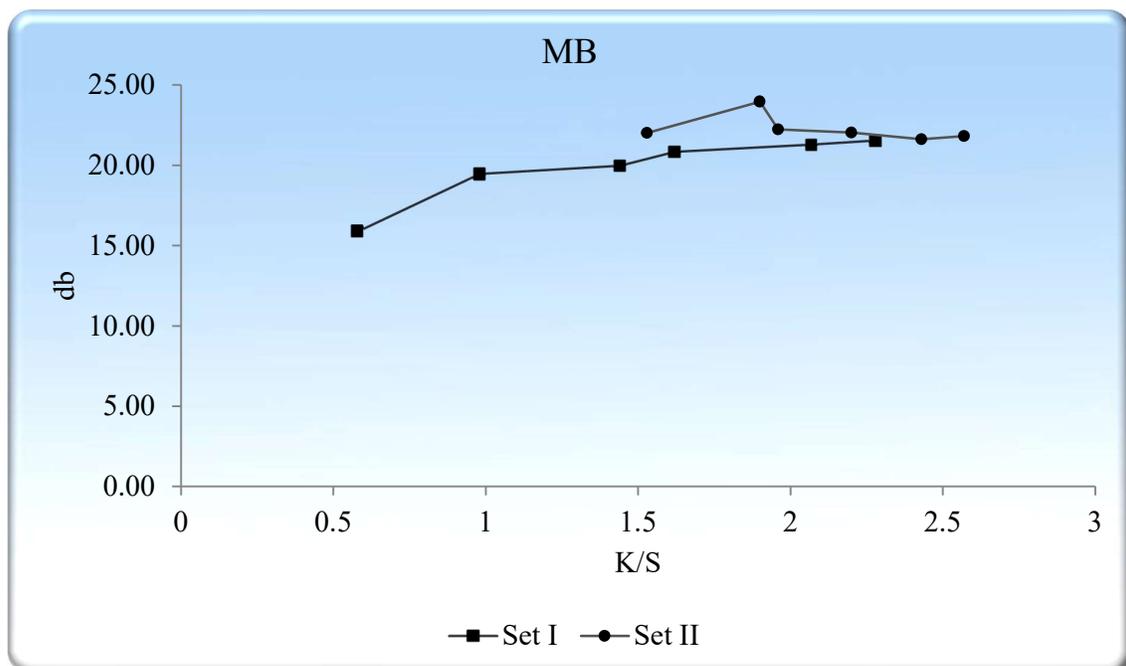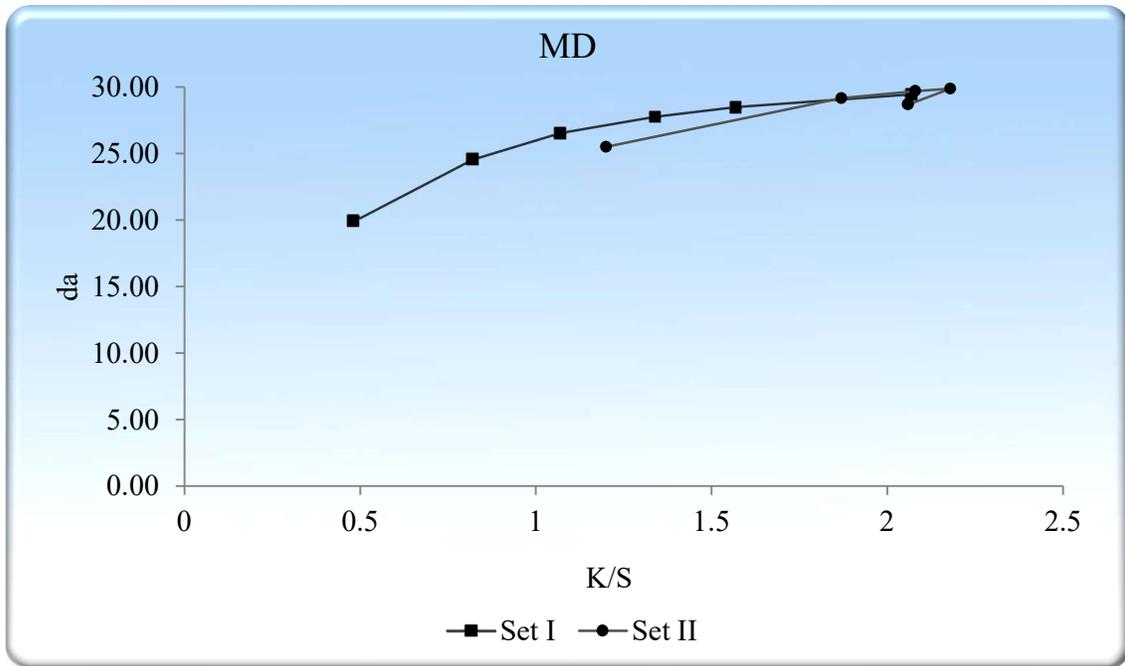
149

(a)

(b)

Figure 4.36: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Marigold/Katha (MK) dye mixture

(a)

(b)

Figure 4.37: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Pomegranate/Annatto (PA) dye mixture
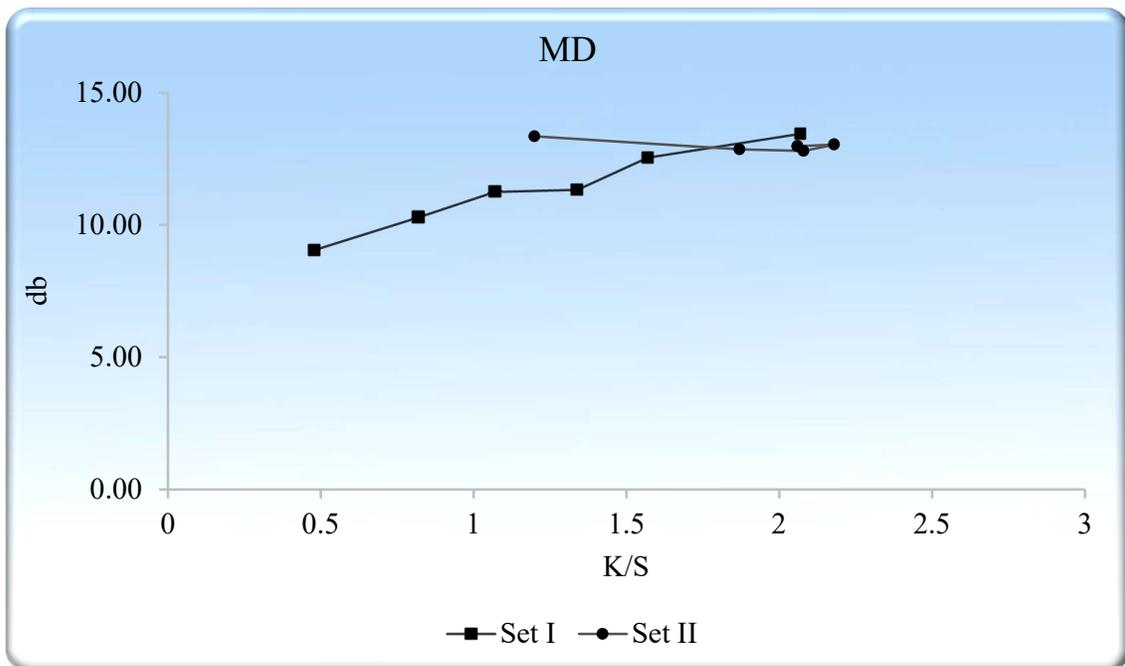
(a)

(b)

Figure 4.38: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Pomegranate/Babool (PB) dye mixture
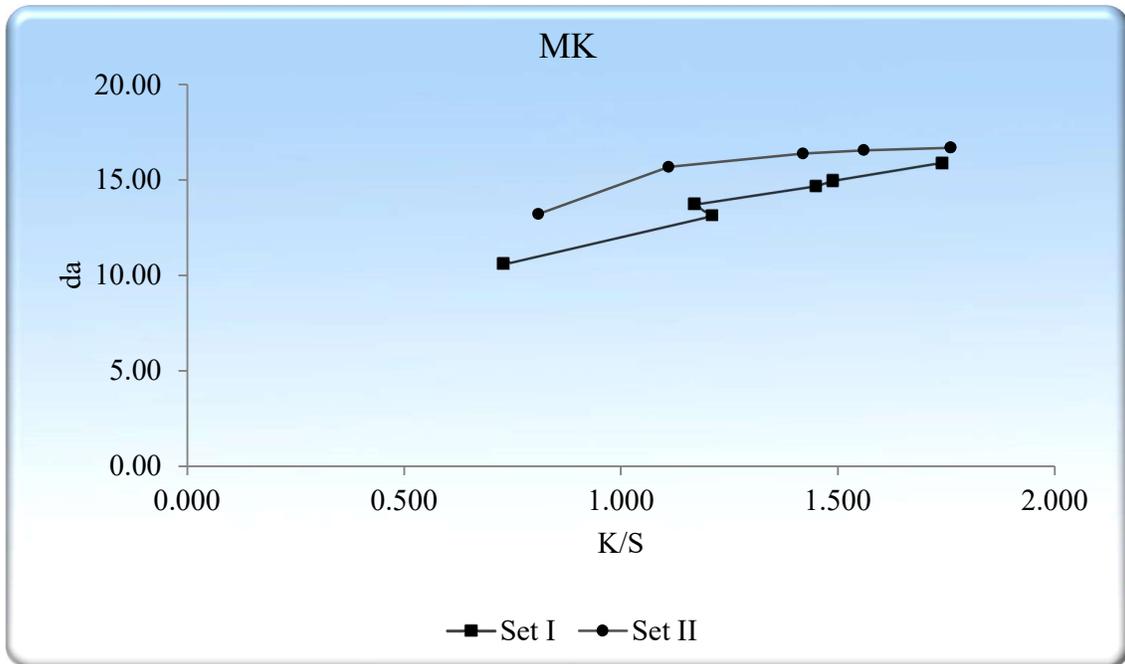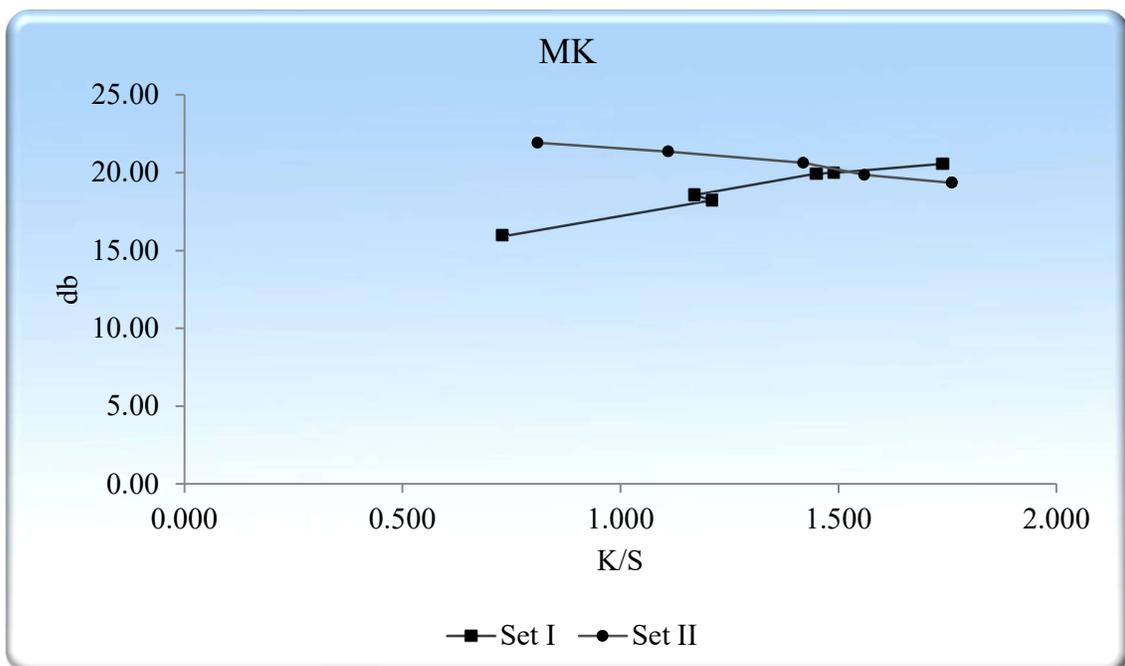
(a)

(b)

Figure 4.39: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Pomegranate/Madder (PD) dye mixture
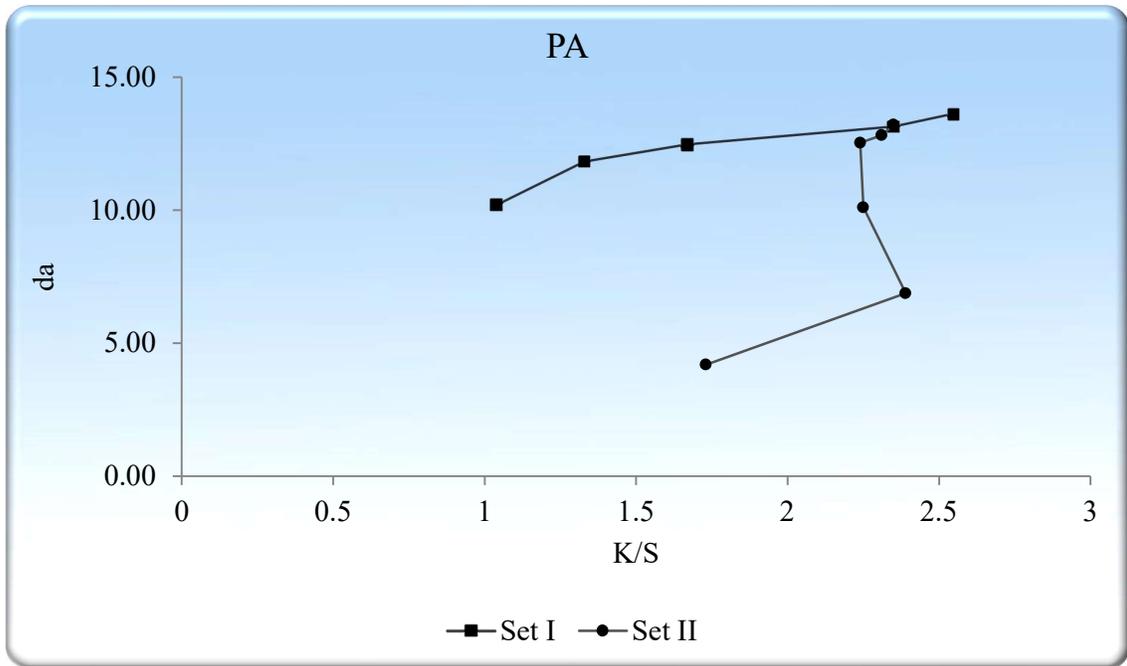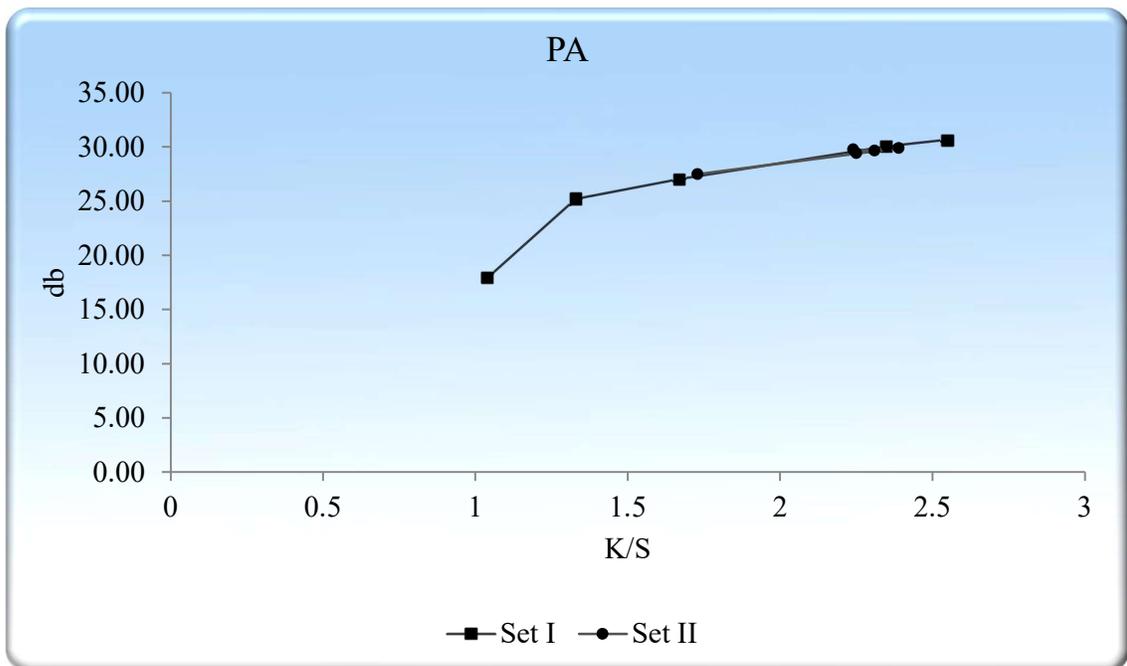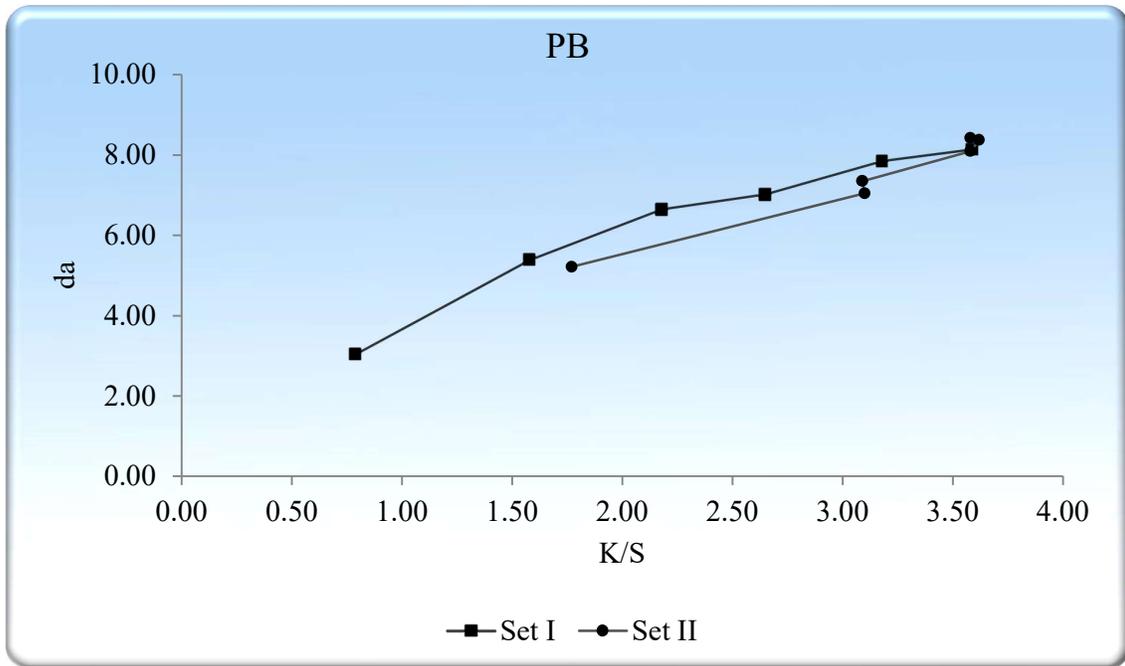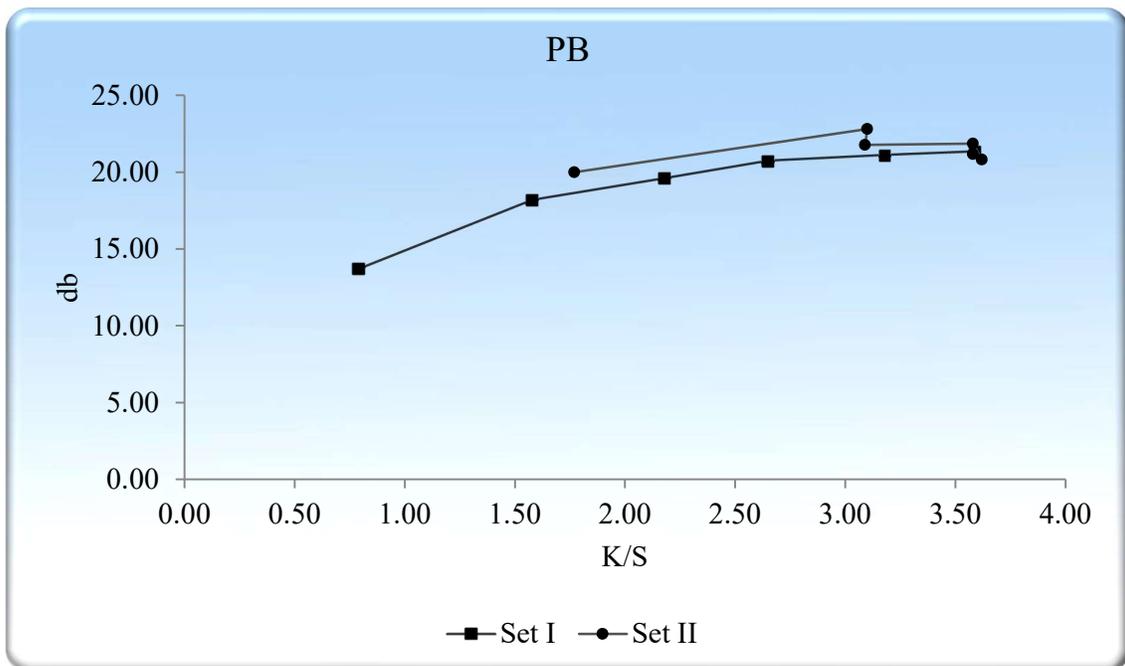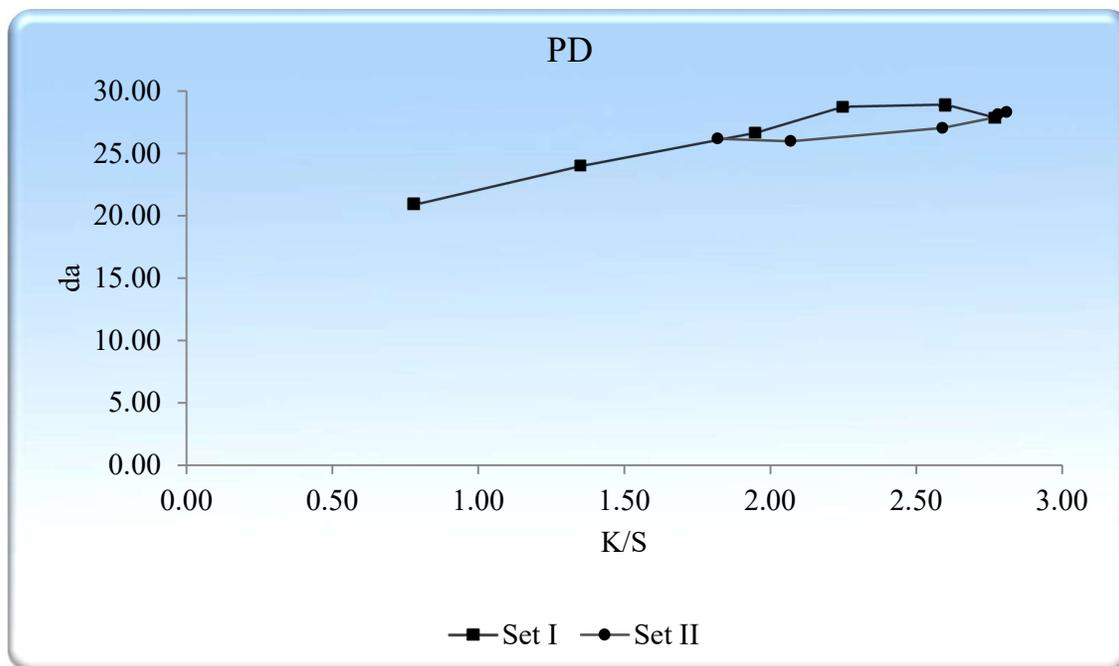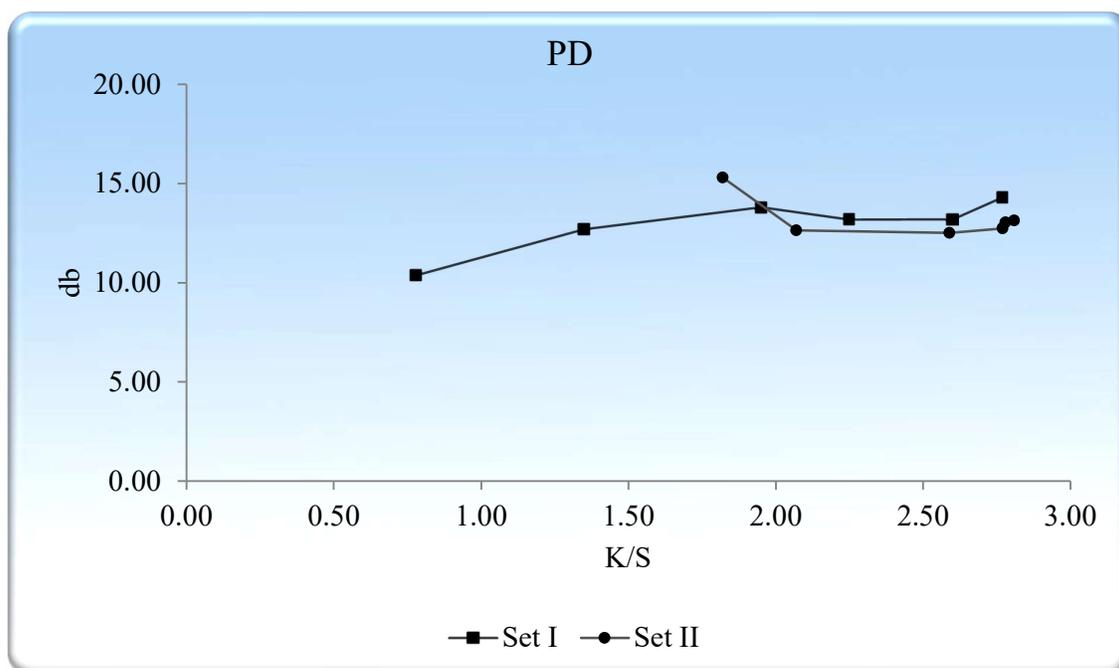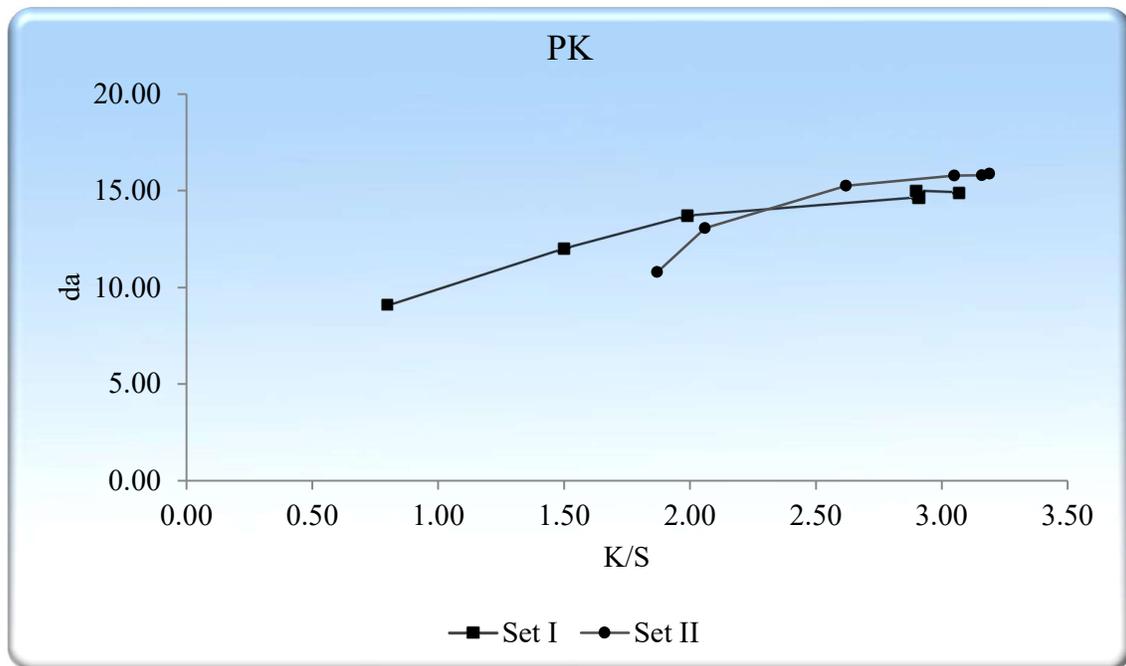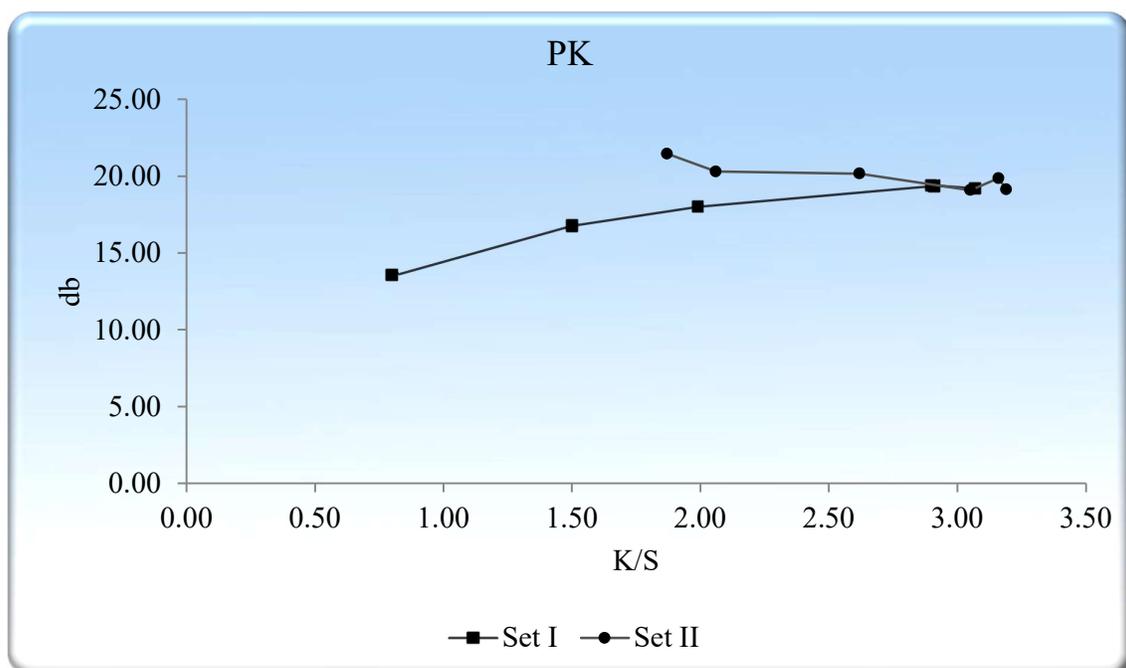
(a)

(b)

Figure 4.40: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Pomegranate/Katha (PK) dye mixture

(C) Based on change in Hue angle (h°)

(i) Using graphical analysis

The value of the hue angle provides information about the hue of the material. Ideally, the hue angle value should remain constant at all the dyeing conditions and concentration when dyed using a particular dye (either alone or in a mixture).

Hansford et al., (1982) state that when a dye recipe includes dyes with different dying rates, any unevenness resulting from temperature increase becomes apparent as variations in hue. The quantitative expression of any discrepancy between real and ideal behavior can be achieved by measuring the variation in hue between the extracted patterns at different intervals.

Mclaren, (1976) devised an objective method with a view to answer the doubts and disputes caused by the earlier methods of assessing compatibility because of its subjective nature. With the introduction of color measurement systems, a series of compatibility tests can be assessed by measuring, e.g., the hue angle.

Dye compatibility was assessed by finding the change in hue angle for all 12 samples in sets I & II. It was done by the hue angle vs. samples plot in both sets. The plots of all the 12 binary mixtures are shown in Figure 4.41 to Figure 4.44. It was observed that the samples in set I show less variation than set II samples. It means that the hue angle varied more by varying the time and temperature than by concentration change. It was also observed that in some cases, initial samples (No. 7 and 8) of set II samples are yellower than others. It seems that Pomegranate and Marigold had higher affinity than few other dyes.

Mixtures of Pomegranate/Madder (PD), Pomegranate/Babool (PB), Babool/ Madder (BD), Katha/Annatto (KA), and Marigold/Madder (MD) showed low variation in hue angle. They were considered to be satisfactory compatible mixtures using this method.

Mixtures of Marigold/Katha (MK), Katha/Madder (KD), Babool/Annatto (BA), and Marigold/Babool (MB) showed average variation in hue angle. These mixtures were considered partial compatible using this method.

High variation was shown by Pomegranate/Katha (PK), Marigold/Annatto (MA), and Pomegranate/Annatto (PA) mixtures, which were considered incompatible mixtures in this analysis.
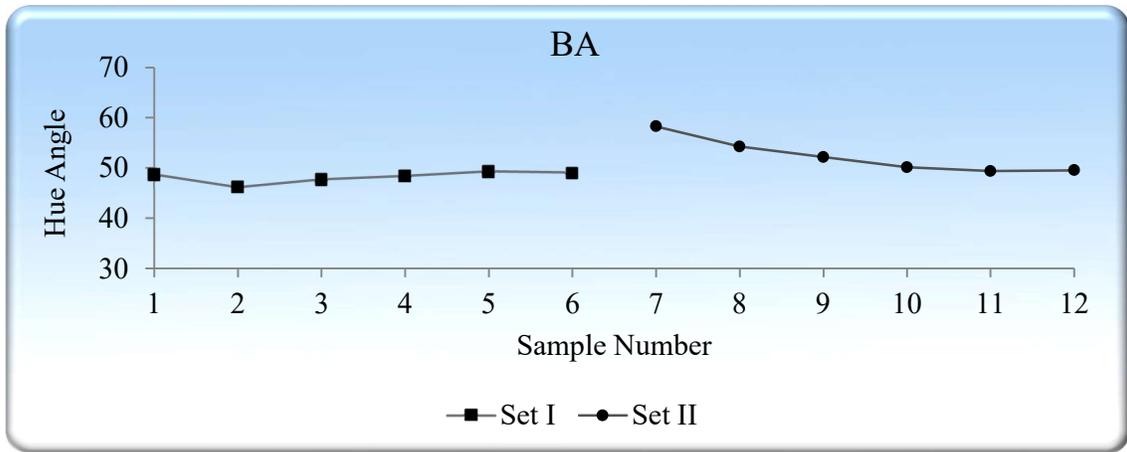
(a)
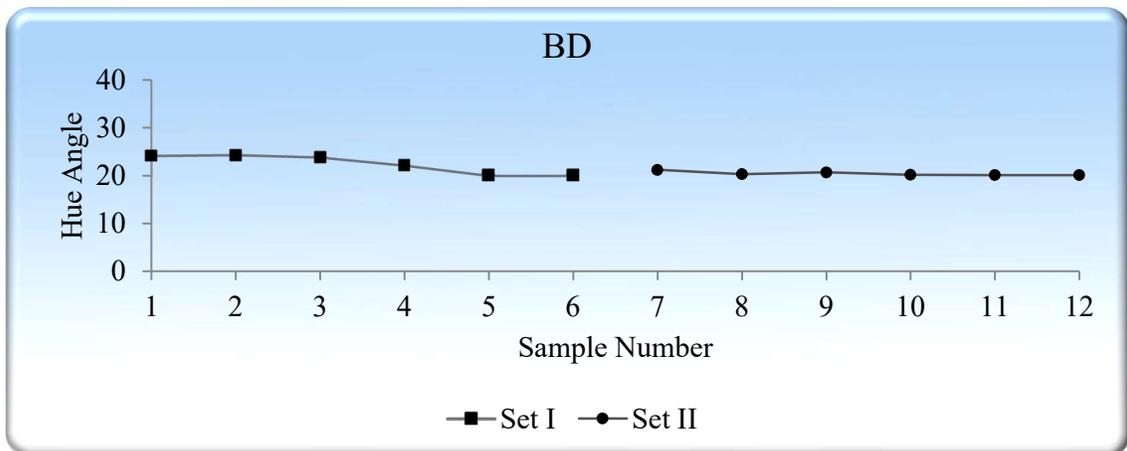
(b)
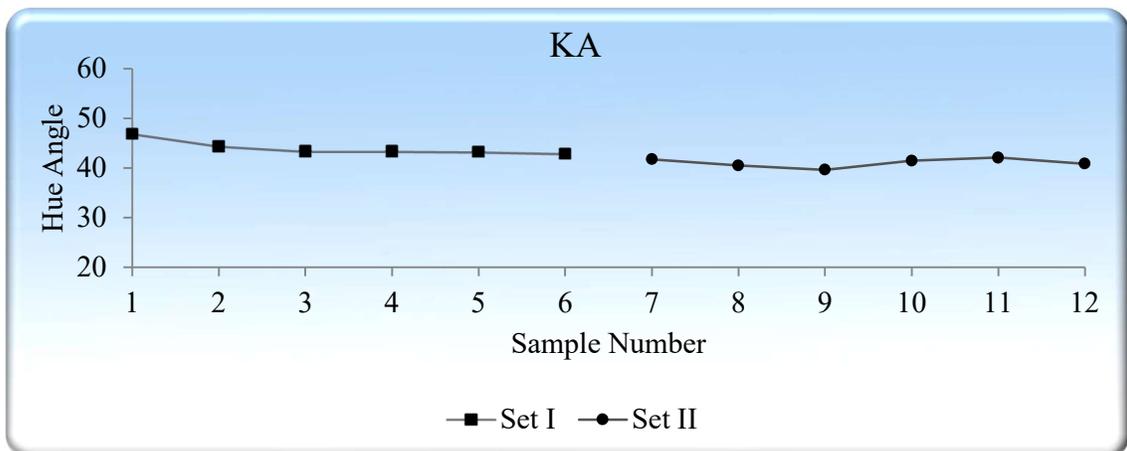
(c)

Figure 4.41: Hue vs. samples in sets I & II for a binary mixture of Babool/ Annatto (a), Babool/Madder (b), and Katha/Annatto (c)
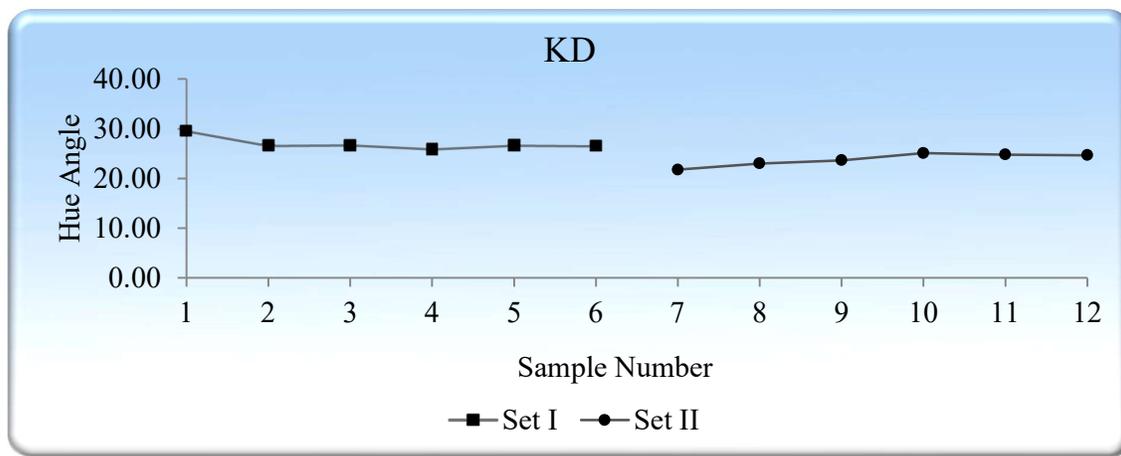
(a)
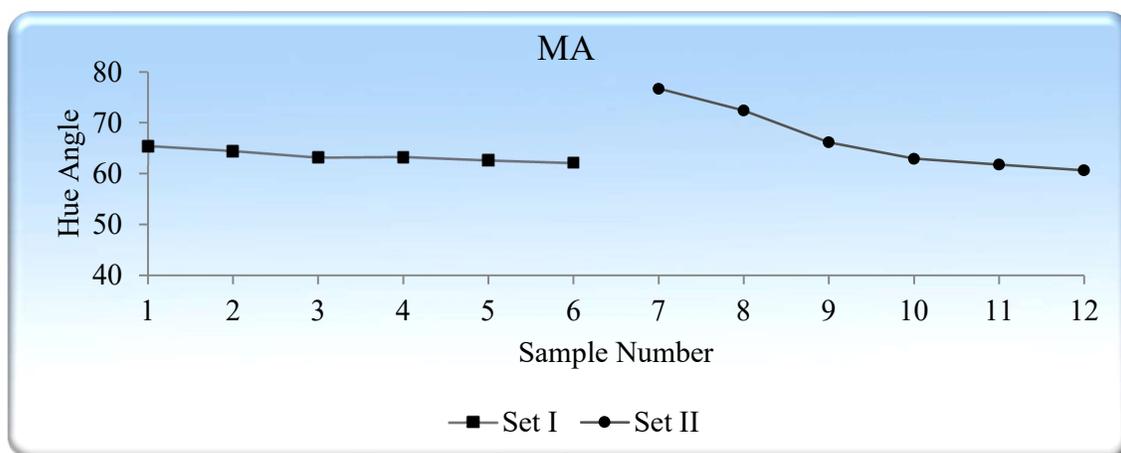
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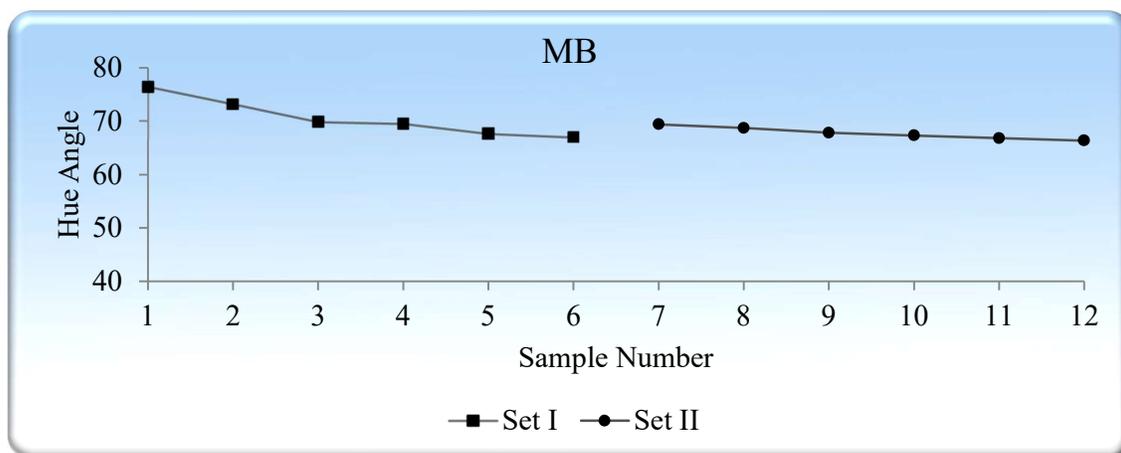
(c)

Figure 4.42: Hue vs. samples in sets I & II for a binary mixture of Katha/ Madder (a), Marigold/Annatto (b), and Marigold/Babool (c)
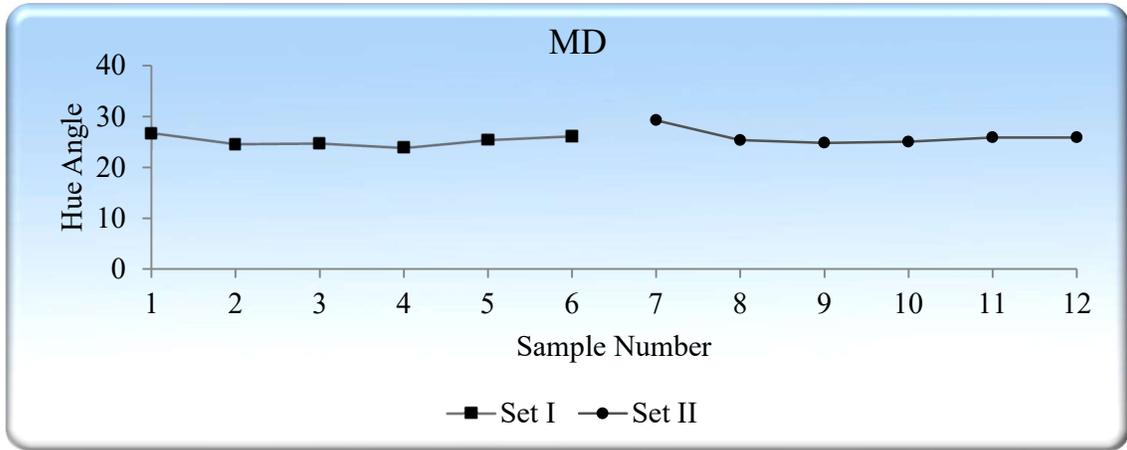
(a)
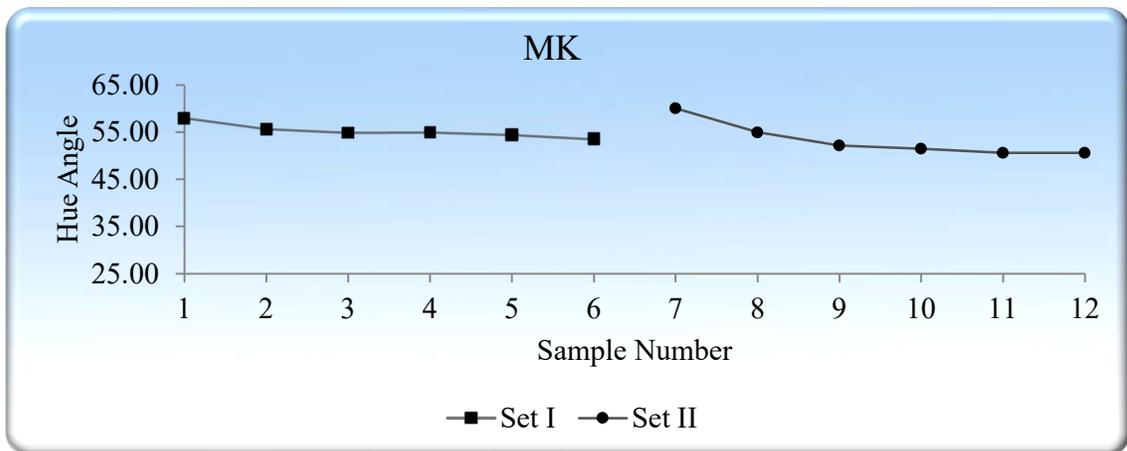
(b)
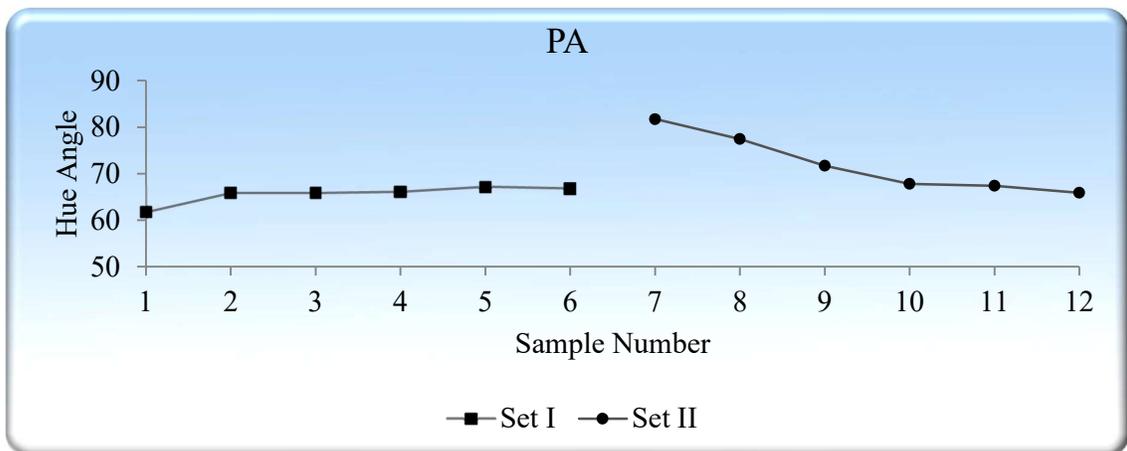
(c)

Figure 4.43: Hue vs. samples in sets I & II for a binary mixture of Marigold/Madder (a), Marigold/Katha (b), and Pomegranate/Annatto (c)
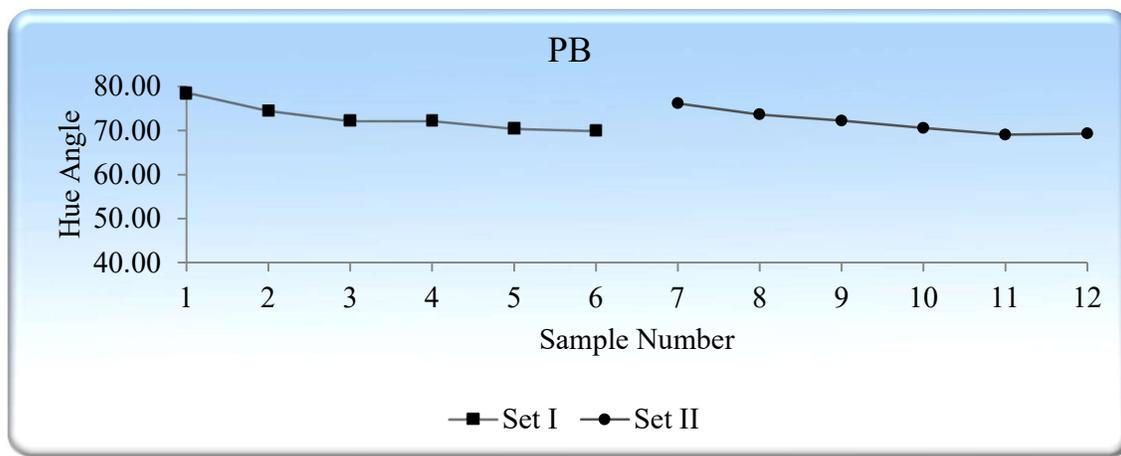
(a)
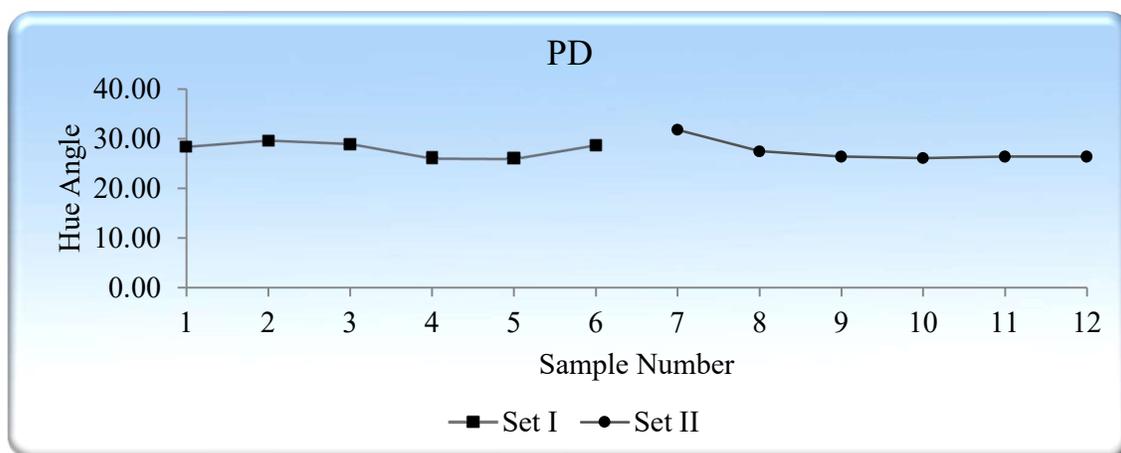
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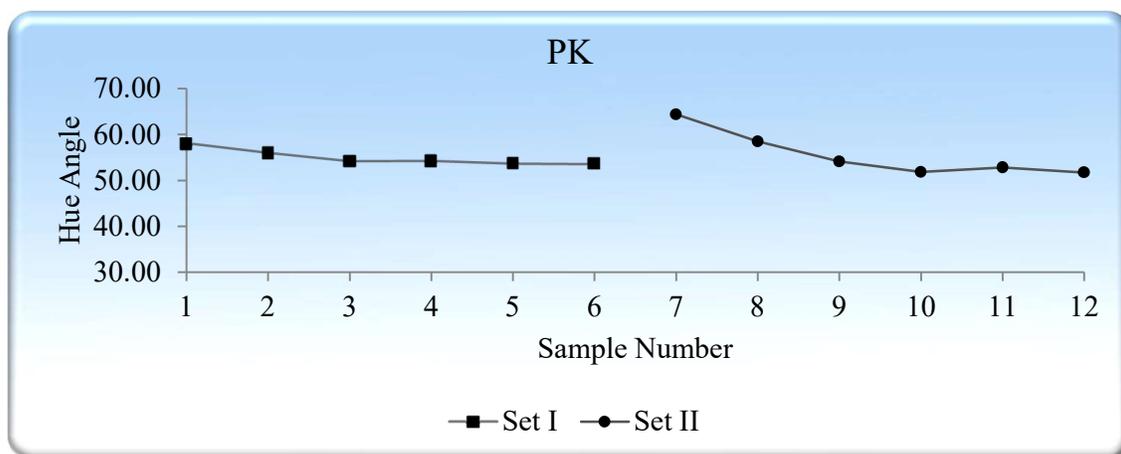
(c)

Figure 4.44: Hue vs. samples in sets I & II for a binary mixture of Pomegranate/ Babool (a), Pomegranate/Madder (b), and Pomegranate/Katha (c)

Using coefficient of variation (CV)

In continuation of the change in hue angle (h°), it was observed that the change in hue angle can be quantified by measuring the C.V.%. In this concern, the value of C.V. for set I and set II were measured for all the mixtures. It was also attempted to get a single value of C.V. for each mixture using the sum of C.V.'s of set I and set II. All the values are shown in Table 4.39 and shown graphically in Figure 4.45.

It was observed that the C.V. for set I and set II was different. The range of C.V. in set I was from 1.8 to 8.7, while in set II was 1.7 to 9.7. It was also observed that in the case of Marigold/Annatto (MA) and Pomegranate/Annatto (PA) mixtures, the C.V. in set I was low and high in set II. The opposite was true for Marigold/Babool (MB) and Babool/Madder (BD).

The compatibility was defined by using the sum of the coefficient of variation for set I and set II. It was concluded that the Pomegranate/Babool (PB), Babool/Annatto (BA), Katha/Annatto (KA), and Marigold/Babool (MB) showed low C.V. and can be considered as compatible mixtures. The mixtures *viz.* Marigold/Katha (MK), Katha/Madder (KD), Babool/Madder (BD), and Marigold/Madder (MD) were having mid-range C.V. and can be considered as partial compatible. The C.V. for Pomegranate/Madder (PD), Pomegranate/Katha (PK), Marigold/Annatto (MA), and Pomegranate/Annatto (PA) was high and were considered as incompatible mixtures.

Table 4.39: Coefficient of variation for set I, set II and sum of both sets

Mixture code	CV - Set I	CV -Set II	CV- Set I + CV-Set II
PD	5.3	8.0	13.3
MK	2.7	6.9	9.6
KD	4.7	5.4	10.1
PB	4.3	3.8	8.1
PK	3.1	9.0	12.1
BA	2.3	6.7	9.0
BD	8.7	2.2	10.9
KA	3.3	2.2	5.5
MA	1.8	9.7	11.5
MB	5.0	1.7	6.7
MD	4.1	6.3	10.4
PA	2.9	8.8	11.8
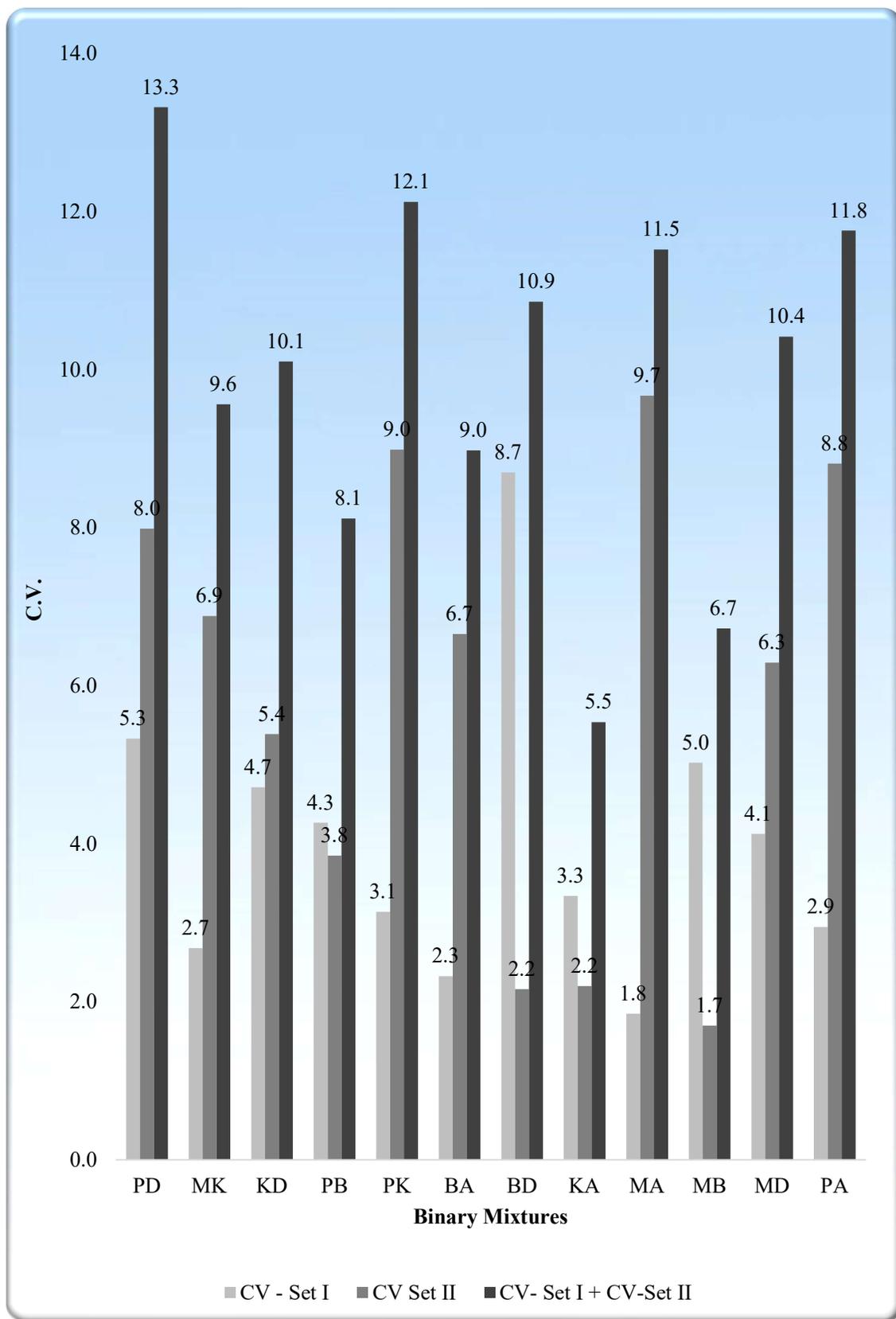
Figure 4.45: Coefficient of variation for set I, set II and sum of both sets

(D)   Compatibility Factor method

The K/S values are directly proportional to the colorant concentration on the fiber. To determine the K/S value of a mixture consisting of two or more colorants, you can add up the K/S values of the individual colorants that were dyed to the same depth as the mixture and measured at their respective λmax values. The ratio between the estimated and observed K/S values for the mixture at the respective λmax of component dyes should be as close as possible for compatibility.

The reported K/S ratio of the estimated mixture to the observed mixture is denoted as the compatibility factor (C.F.).

$$C.F. = \frac{(K/S) \text{ mix calculated}}{(K/S) \text{ mix observed}}$$

The compatibility factor (CF) should ideally be '1'. Such conditions are uncommon in real dye mixtures; hence, compatibility factor values always depart from "1" due to the fact that component dyes also contribute to the K/S values of the mixture at each λmax. Compatibility is assessed from the closeness of the C.F. values of both the component dyes calculated at their respective λmax.

The C.F. was obtained in the present study using the K/S data of mixture and component dyes. For binary mixtures, spectral data of sample number 5 from set I was used for all the mixtures. The dye concentration for sample 5 was 25% owf. The K/S data for component dyes was predicted at a dye concentration of 12.5% owf using design expert software. Primary dyes dyed samples were used for this purpose. The details of the K/S and C.F. are mentioned in Table 4.40.

It was observed that the Pomegranate/Babool (PB) and Pomegranate/Katha (PK) had the same C.F. at respective wavelengths of component dyes, indicating compatibility. Some mixtures showed less than 10% difference in the C.F. at the respective wavelength of component dyes and were considered compatible using this method. These mixtures were Marigold/Katha (MK), Katha/Annatto (KA), Marigold/Madder (MD) and Marigold/Babool (MB). Mixtures Babool/Madder (BD), Katha/Madder (KD), and Marigold/Annatto (MA) had 11-20% difference in the C.F. at a respective wavelength of component dyes and were considered partially compatible using this method. Babool/Annatto (BA), Pomegranate/Madder (PD), and Pomegranate/Annatto (PA) showed approximately 23%, 25%, and 70% differences in the C.F. at a respective wavelength of component dyes and were considered an incompatible mixture.

Table 4.40: Compatibility factor of binary mixtures

Mixture code	λmax of component A	K/S (Based on λmax of Component A)				Compatibility Factor	λmax of component B	K/S (Based on λmax of Component B)				Compatibility Factor
		Component A	Component B	Mixture (Calculated)	Mixture (Observed)			Component A	Component B	Mixture (Calculated)	Mixture (Observed)	
PD	360	0.47	0.76	1.23	2.85	0.43	510	0.08	1.52	1.60	2.78	0.58
MK	440	0.28	1.24	1.51	1.66	0.91	360	0.13	1.30	1.44	1.49	0.97
KD	360	1.30	0.76	2.06	2.27	0.91	510	1.04	1.52	2.57	3.25	0.79
PB	360	0.47	1.15	1.62	3.18	0.51	360	0.47	1.15	1.62	3.18	0.51
PK	360	0.47	1.30	1.77	2.90	0.61	360	0.47	1.30	1.77	2.90	0.61
BA	360	1.15	0.19	1.35	1.77	0.76	480	0.44	0.60	1.04	1.04	1.00
BD	360	1.15	0.76	1.91	3.13	0.61	510	0.39	1.52	1.91	3.75	0.51
KA	360	1.30	0.19	1.50	1.39	1.08	480	1.09	0.60	1.69	1.56	1.09
MA	440	0.28	0.37	0.65	0.68	0.95	480	0.19	0.60	0.79	0.68	1.17
MB	440	0.28	0.61	0.88	1.38	0.64	360	0.13	1.15	1.29	2.07	0.62
MD	440	0.28	0.91	1.18	1.73	0.69	510	0.07	1.52	1.59	2.24	0.71
PA	360	0.47	0.19	0.66	2.35	0.28	480	0.11	0.60	0.71	0.89	0.80

(E)   Visual Rating

All binary mixtures samples were visually assessed for the compatibility check. The visual check was done in a standard color-matching light box in a D-65 light source at a 45° angle. The compatibility was checked for sets I and II in terms of depth, hue, and chroma.

Two observers were asked to give the score to the 12 binary mixture samples for their compatibility. They were asked to rate the samples out of 30. The scores obtained are shown in Table 4.41. The rating was converted into ranks to calculate Spearman's rank correlation coefficient. A positive correlation of 0.86 was obtained, which indicates a strong positive correlation between the two observers. This means that there is substantial agreement between the two observers, indicating that their ranking is not occurring by chance.

<p align="center">**Table 4.41: Visual Score and Rating for Binary Mixture**</p>

Mixture	Visual Score		Average
	Observer I	**Observer II**	
KA	30	27	28.5
MD	28	24	26
PK	24.5	23	23.75
MK	23.5	19	21.25
BA	21.5	16	18.75
PB	20.5	17	18.75
MB	19.5	16.5	18
PA	19.5	15.5	17.5
MA	18	15	16.5
PD	17.5	14	15.75
KD	17	12.5	14.75
BD	17	12	14.5

The visual score was used to assess the compatibility of the mixtures. It was observed that mixture Katha/Annatto, Marigold/Madder, Pomegranate/Katha, and Marigold/Katha mixtures had a score of above 21 and were considered compatible mixtures. Babool/Annatto, Pomegranate/Babool, Marigold/Babool and Pomegranate/Annatto had average score and were considered as partially compatible mixtures. Other mixtures namely, Marigold/Annatto, Pomegranate/Madder, Katha/Madder and Babool/Madder had low score and considered as not compatible mixtures.

4.2.1.1.2 Summary of Different Method's results and overall rating

As per earlier sections, different methods were used to assess the compatibility. These methods showed different compatibility aspects for the particular mixture.

Table 4.42 shows the summary of different method's results and overall rating for binary mixtures under the dyeing conditions and processes followed in this study. It is visible that compatibility assessment varies for different methods for a particular mixture. This may be due to the different compatibility aspects covered in methods. The mixtures were given ratings based on the compatibility behavior shown for a particular method. These were highly

<p align="center">**165**</p>

compatible, compatible, partially compatible, and non-compatible mixtures. Thus, an overall rating was also given for each mixture based on the ratings obtained in all methods.

Marigold/Katha, Pomegranate/Babool, Katha/Annatto, Marigold/Babool and Marigold/ Madder mixtures were found as compatible mixtures. Pomegranate/ Madder, Katha/Madder, and Pomegranate/Katha were found as partially compatible mixtures. Other mixtures Babool/Annatto, Babool/Madder, Marigold/Annatto and Pomegranate/Annatto were found as non-compatible mixtures.

This will help in accomplishing the objective of the study to check the compatibility and obtain newer shades.

Table 4.42: Summary of different method's results and overall rating for binary mixtures

| Code | Plot -dL vs. dC | Plot -dL vs K/S | Plot da vs K/S | Plot db vs K/S | Based on change in Hue angle (h°) | | Compatibility factor method (CF) | Visual Rating | Overall Rating |
					Using graphical analysis	Using coefficient of variation (CV)			
PD	Not compatible	Highly Compatible	Compatible	Compatible	Compatible	Not compatible	Not compatible	Not compatible	Partially Compatible
MK	Not compatible	Highly Compatible	Compatible	Partially Compatible	Partially Compatible	Partially Compatible	Compatible	Compatible	Compatible
KD	Compatible	Compatible	Compatible	Compatible	Partially Compatible	Partially Compatible	Partially Compatible	Not compatible	Partially Compatible
PB	Not compatible	Highly Compatible	Highly Compatible	Compatible	Compatible	Compatible	Compatible	Partially Compatible	Compatible
PK	Not compatible	Compatible	Compatible	Partially Compatible	Not compatible	Not compatible	Compatible	Compatible	Partially Compatible
BA	Compatible	Not compatible	Not compatible	Compatible	Partially Compatible	Compatible	Not compatible	Partially Compatible	Not compatible
BD	Not compatible	Compatible	Partially Compatible	Compatible	Compatible	Partially Compatible	Partially Compatible	Not compatible	Not compatible
KA	Compatible	Compatible	Compatible	Compatible	Compatible	Compatible	Compatible	Compatible	Compatible

| Code | Plot -dL vs. dC | Plot -dL vs K/S | Plot da vs K/S | Plot db vs K/S | Based on change in Hue angle (h°) | | Compatibility factor method (CF) | Visual Rating | Overall Rating |
					Using graphical analysis	Using coefficient of variation (CV)			
MA	Not compatible	Compatible	Partially Compatible	Partially Compatible	Not compatible	Not compatible	Not compatible	Not compatible	Not compatible
MB	Not compatible	Highly Compatible	Highly Compatible	Compatible	Partially Compatible	Compatible	Partially Compatible	Partially Compatible	Compatible
MD	Highly Compatible	Highly Compatible	Highly Compatible	Compatible	Compatible	Partially Compatible	Compatible	Compatible	Compatible
PA	Compatible	Not compatible	Not compatible	Compatible	Not compatible	Not compatible	Not compatible	Partially Compatible	Not compatible

4.2.1.2 Dyeing results and Compatibility Assessment for Tertiary mixtures

The tertiary mixtures were used to dye the cotton material using equal proportions at various concentrations and time/temperature, denoted as sets I and II. The detailed dyeing conditions are mentioned in section 3.2.2.

As mentioned for binary mixtures, the K/S, CIE L*, a*, b*, C*,and h values were obtained for all Set I & II dyed samples. Both sets have six samples each for tertiary mixture. The undyed white fabric (RFD) was used as standard, and the color difference values dL*, da*, db*, and dC* were also determined. The CIE coordinates L*, a*, b*, C*, h, and K/S values of RFD fabric are given below:

L*	a*	b*	C*	h	K/S
92.48	-0.08	0.89	0.89	95.07	0.05

The colorimetric parameters L, A, B, C, H, K/S, -dL, da, db, and dC are mentioned in Table 4.43 to Table 4.50 for all eight tertiary mixtures. These parameters were used in the compatibility check methods. The dyeing outcome and color coordinates of the mixtures may be attributed to the interaction of dyes (with or without alum) and their respective complex formation. This may also be attributed to the comparative affinity of dyes, diffusion rate and effect of dyeing conditions in mixture.

Table 4.43: Colorimetric parameters for the fabric dyed with a tertiary mixture of Marigold, Babool, and Annatto dyes (MBA)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	85.89	6.52	12.84	14.4	63.06	0.21	6.59	6.60	11.95	13.51
	2	78.79	6.51	14.28	15.69	65.47	0.27	13.69	6.59	13.39	14.80
	3	78.98	11.54	19.95	23.05	59.93	0.56	13.50	11.62	19.06	22.16
	4	76.13	12.26	21.18	24.47	59.91	0.8	16.35	12.34	20.29	23.58
	5	73.87	12.27	22.53	25.65	61.41	1.1	18.61	12.35	21.64	24.76
	6	72.42	14.02	22.87	26.83	58.47	1.16	20.06	14.10	21.98	25.94
Set II **(Increasing Time Temperature samples)**	7	77.2	8.21	22.75	24.19	70.12	0.94	15.28	8.29	21.86	23.30
	8	75.85	9.64	23.54	25.44	67.7	0.93	16.63	9.72	22.65	24.55
	9	75.79	10.38	23.44	25.64	66.09	0.9	16.69	10.46	22.55	24.75
	10	75.34	11.88	23.16	26.03	62.82	0.88	17.14	11.96	22.27	25.14
	11	73.9	12.86	23.18	26.51	60.96	1.01	18.58	12.94	22.29	25.62
	12	72.89	13.4	23.22	26.81	59.99	1.17	19.59	13.48	22.33	25.92

Table 4.44: Colorimetric parameters for the fabric dyed with a tertiary mixture of Marigold, Babool, and Madder dyes (MBD)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	76.03	15.45	10.59	18.73	34.42	0.47	16.45	15.53	9.70	17.84
	2	69.44	20.64	12.54	24.15	31.26	0.82	23.04	20.72	11.65	23.26
	3	66.56	21.5	12.96	25.10	31.07	1.02	25.92	21.58	12.07	24.21
	4	63.07	23.12	13.38	26.71	30.04	1.32	29.41	23.20	12.49	25.82
	5	59.84	24.66	14.13	28.42	29.8	1.67	32.64	24.74	13.24	27.53
	6	56.67	25.88	13.99	29.42	28.38	2.04	35.81	25.96	13.10	28.53
Set II **(Increasing Time Temperature samples)**	7	62.36	24.47	13.71	28.05	29.26	1.2	30.12	24.55	12.82	27.16
	8	57.8	26.61	15.35	30.72	29.97	1.85	34.68	26.69	14.46	29.83
	9	56.9	26	14.29	29.67	28.78	1.86	35.58	26.08	13.40	28.78
	10	57.32	26.08	14.72	29.95	29.42	1.97	35.16	26.16	13.83	29.06
	11	56.37	26.54	13.8	29.91	27.45	2.03	36.11	26.62	12.91	29.02
	12	56.88	25.56	13.86	29.08	28.45	1.97	35.60	25.64	12.97	28.19

Table 4.45: Colorimetric parameters for the fabric dyed with a tertiary mixture of Marigold, Katha, and Annatto dyes (MKA)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	80.67	8.13	13.06	15.38	58.09	0.38	11.81	8.21	12.17	14.49
	2	74.63	12.48	18.18	22.05	55.51	0.7	17.85	12.56	17.29	21.16
	3	72.16	13.87	18.42	23.06	52.99	0.85	20.32	13.95	17.53	22.17
	4	69.32	15.63	19.87	25.28	51.78	1.06	23.16	15.71	18.98	24.39
	5	66.19	17.08	20.33	26.55	49.95	1.21	26.29	17.16	19.44	25.66
	6	65.2	17.69	21.15	27.57	50.07	1.39	27.28	17.77	20.26	26.68
Set II **(Increasing Time Temperature samples)**	7	74.21	13.85	19.05	23.55	53.97	0.68	18.27	13.93	18.16	22.66
	8	71.39	15.91	19.81	25.41	51.22	0.75	21.09	15.99	18.92	24.52
	9	68.96	17.5	20.51	26.96	49.51	0.91	23.52	17.58	19.62	26.07
	10	67.56	17.79	20.7	27.29	49.31	1.11	24.92	17.87	19.81	26.40
	11	66.99	17.85	20.49	27.17	48.92	1.15	25.49	17.93	19.60	26.28
	12	67.47	17.41	20.43	26.84	49.56	1.13	25.01	17.49	19.54	25.95

Table 4.46: Colorimetric parameters for the fabric dyed with a tertiary mixture of Marigold, Katha, and Madder dyes (MKD)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I (Increasing Concentration samples)	1	72.58	15.72	12.36	20.00	38.16	0.72	19.90	15.80	11.47	19.11
	2	68.3	18.44	14.04	23.18	37.27	0.93	24.18	18.52	13.15	22.29
	3	63.24	22.89	15.17	27.46	33.54	1.31	29.24	22.97	14.28	26.57
	4	60.05	23.15	15.3	27.75	33.45	1.58	32.43	23.23	14.41	26.86
	5	57.22	24.48	15.61	29.03	33.54	1.88	35.26	24.56	14.72	28.14
	6	53.88	25.97	16.28	30.65	32.07	2.39	38.60	26.05	15.39	29.76
Set II (Increasing Time Temperature samples)	7	61.16	25.76	14.32	29.47	29.07	1.16	31.32	25.84	13.43	28.58
	8	55.1	28.01	15.21	31.87	28.49	1.78	37.38	28.09	14.32	30.98
	9	54.64	27.45	15.23	31.39	29.01	1.93	37.84	27.53	14.34	30.50
	10	53.91	26.43	14.84	30.31	29.31	2.06	38.57	26.51	13.95	29.42
	11	55.03	26.36	14.76	30.21	29.23	1.91	37.45	26.44	13.87	29.32
	12	54.53	26.07	15.04	30.10	29.98	2.06	37.95	26.15	14.15	29.21

Table 4.47: Colorimetric parameters for the fabric dyed with a tertiary mixture of Pomegranate, Babool, and Annatto dyes (PBA)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I (Increasing Concentration samples)	1	85.17	6.63	11.81	13.54	60.68	0.31	7.31	6.71	10.92	12.65
	2	80.33	10.06	16.76	19.55	59	0.64	12.15	10.14	15.87	18.66
	3	77.75	11.19	19.15	22.18	59.68	0.9	14.73	11.27	18.26	21.29
	4	74.55	11.93	21.26	24.38	60.66	1.32	17.93	12.01	20.37	23.49
	5	69.45	12.21	22.87	25.93	61.88	2.23	23.03	12.29	21.98	25.04
	6	67.3	12.09	23.15	26.12	62.39	2.59	25.18	12.17	22.26	25.23
Set II (Increasing Time Temperature samples)	7	73.88	7.73	22.03	23.35	70.63	1.81	18.60	7.81	21.14	22.46
	8	71.43	9.06	22.83	24.56	68.33	2.2	21.05	9.14	21.94	23.67
	9	70.55	10.04	22.74	24.86	66.15	2.24	21.93	10.12	21.85	23.97
	10	69.35	11.65	23.05	25.83	63.17	2.25	23.13	11.73	22.16	24.94
	11	68.28	12.41	22.92	26.06	61.54	2.3	24.20	12.49	22.03	25.17
	12	67.95	12.17	23.18	26.18	62.27	2.49	24.53	12.25	22.29	25.29

Table 4.48: Colorimetric parameters for the fabric dyed with a tertiary mixture of Pomegranate, Babool, and Madder dyes (PBD)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	77.51	13.46	9.96	16.74	36.5	0.56	14.97	13.54	9.07	15.85
	2	70.80	19.67	11.34	22.70	29.95	0.82	21.68	19.75	10.45	21.81
	3	65.62	22.96	12.04	25.93	27.67	1.18	26.86	23.04	11.15	25.04
	4	59.28	25.22	13.81	28.75	28.68	2.01	33.20	25.30	12.92	27.86
	5	57.92	24.59	14.01	28.30	29.68	2.36	34.56	24.67	13.12	27.41
	6	53.47	26.05	14.50	29.81	29.08	3.14	39.01	26.13	13.61	28.92
Set II **(Increasing Time Temperature samples)**	7	61.09	24.90	14.10	28.62	29.50	1.74	31.39	24.98	13.21	27.73
	8	55.27	27.71	15.33	31.67	28.95	2.78	37.21	27.79	14.44	30.78
	9	55.83	24.91	13.64	28.40	28.69	2.49	36.65	24.99	12.75	27.51
	10	55.83	24.91	13.64	28.40	28.69	2.49	36.65	24.99	12.75	27.51
	11	54.30	25.82	14.91	29.82	29.99	3.04	38.18	25.90	14.02	28.93
	12	53.58	26.40	14.44	30.09	28.67	3.02	38.90	26.48	13.55	29.20

Table 4.49: Colorimetric parameters for the fabric dyed with a tertiary mixture of Pomegranate, Katha, and Annatto dyes (PKA)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I (Increasing Concentration samples)	1	81.93	8.02	11.51	14.03	55.11	0.37	10.55	8.10	10.62	13.14
	2	74.38	12.64	15.7	20.16	51.14	0.80	18.10	12.72	14.81	19.27
	3	70.78	14.47	17.7	22.86	50.70	1.10	21.70	14.55	16.81	21.97
	4	65.27	16.35	19.79	25.67	50.42	1.83	27.21	16.43	18.90	24.78
	5	63.94	16.88	20.26	26.37	50.18	2.02	28.54	16.96	19.37	25.48
	6	61.44	17.64	21.3	27.66	50.34	2.52	31.04	17.72	20.41	26.77
Set II (Increasing Time Temperature samples)	7	74.01	11.68	19.68	22.89	59.27	1.20	18.47	11.76	18.79	22.00
	8	67.46	15.29	21.53	26.41	54.60	1.86	25.02	15.37	20.64	25.52
	9	63.83	17.27	20.51	26.81	49.88	2.12	28.65	17.35	19.62	25.92
	10	63.33	17.81	20.61	27.24	49.15	2.09	29.15	17.89	19.72	26.35
	11	63.22	17.14	19.83	26.21	49.13	2.11	29.26	17.22	18.94	25.32
	12	62.5	17.06	19.95	26.25	49.45	2.23	29.98	17.14	19.06	25.36

Table 4.50: Colorimetric parameters for the fabric dyed with a tertiary mixture of Pomegranate, Katha, and Madder dyes (PKD)

Set	Sample Number	L*	a*	b*	C*	h	K/S	-dL*	da*	db*	dC*
	RFD	92.48	-0.08	0.89	0.89	95.07	0.05	--	--	--	--
Set I **(Increasing Concentration samples)**	1	77.27	14.4	11.41	17.67	38.37	0.55	15.21	14.48	10.52	16.78
	2	66.35	19.97	12.46	23.54	31.94	1.09	26.13	20.05	11.57	22.65
	3	60.35	23.22	13.80	27.01	30.71	1.68	32.13	23.30	12.91	26.12
	4	57.30	24.16	14.15	28.00	30.34	2.06	35.18	24.24	13.26	27.11
	5	53.68	25.32	14.68	29.27	30.09	2.60	38.80	25.40	13.79	28.38
	6	52.62	25.44	14.61	29.34	29.85	2.76	39.86	25.52	13.72	28.45
Set II **(Increasing Time Temperature samples)**	7	63.41	23.62	13.08	27.00	28.97	1.22	29.07	23.70	12.19	26.11
	8	54.24	25.50	14.21	29.19	29.11	2.27	38.24	25.58	13.32	28.30
	9	52.16	25.54	14.48	29.36	29.55	2.67	40.32	25.62	13.59	28.47
	10	52.04	25.80	14.52	29.61	29.37	2.75	40.44	25.88	13.63	28.72
	11	52.27	25.96	14.81	29.89	29.69	2.81	40.21	26.04	13.92	29.00
	12	52.14	25.63	15.39	29.90	30.96	2.96	40.34	25.71	14.50	29.01

**4.2.1.2.1 Compatibility Assessment Methods**

(A)   Method based on -dL vs. dC and -dL vs. K/S Plot

Plots for -dL vs. dC and -dL vs. K/S for each tertiary mixture are shown in Figure 4.46 to Figure 4.53. In -dL vs. dC plots for all tertiary mixtures, it was observed that the mixture of Marigold/Babool/Madder (MBD), Marigold/Katha/Annatto(MKA), Pomegranate/ Babool/Annatto (PBA), Pomegranate/Katha/Annatto (PKA) and, Pomegranate/ Katha/Madder (PKD) showed the good overlap of set I and set II curves. These mixtures were considered compatible mixtures.

The mixture Marigold/Katha/ Madder (MKD) showed some deviation in overlapping but can be viewed as a partially compatible mixture as per observation using this method. Certain mixtures had significant variations between both curves, which include Marigold/ Babool/Annatto (MBA) and Pomegranate/Babool/Madder (PBD). These mixtures were considered incompatible mixtures as per the study using this method.

For -dL vs. K/S plots, it was observed that the mixture of Marigold/ Babool/Madder (MBD), Pomegranate/Babool/Madder (PBD), and Pomegranate/Katha/Madder (PKD) showed very good overlap and found to be highly compatible mixtures.

Marigold/Katha/Annatto(MKA), Pomegranate/ Babool/ Annatto (PBA), and Pomegranate/Katha/ Annatto (PKA), showed good overlap of set I and set II curves. These mixtures were considered compatible mixtures. The mixture Marigold/Katha/Madder (MKD) showed some deviation in overlapping but can be considered a partially compatible mixture as per observation using this method. The mixture Marigold/Babool/Annatto (MBA) showed significant deviation and was considered an incompatible mixture.
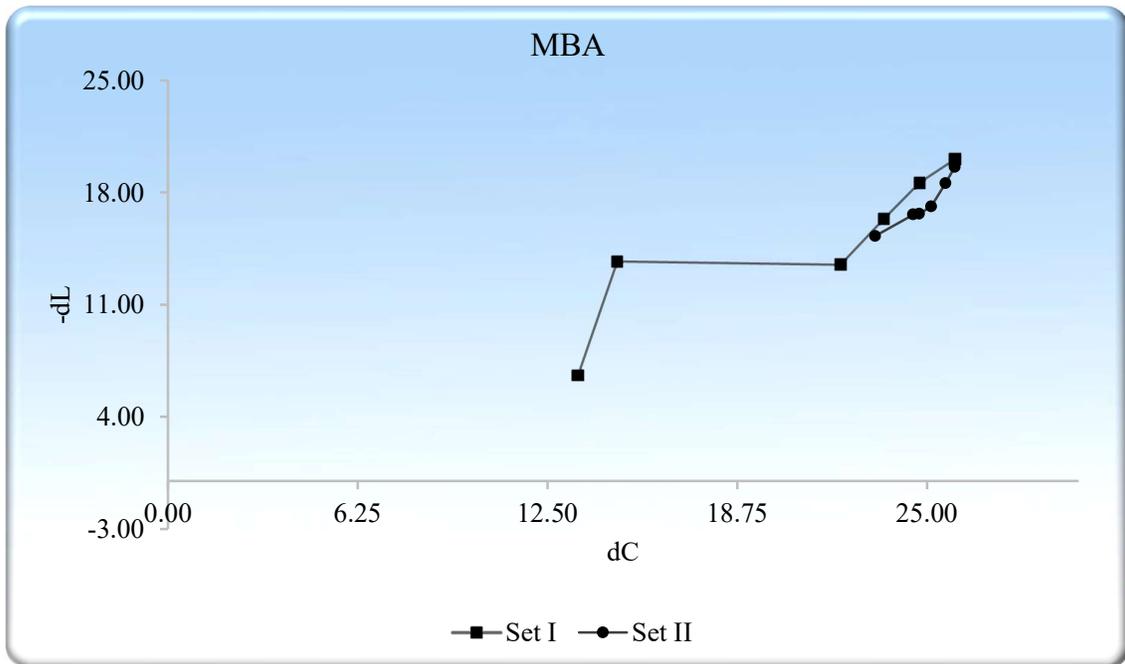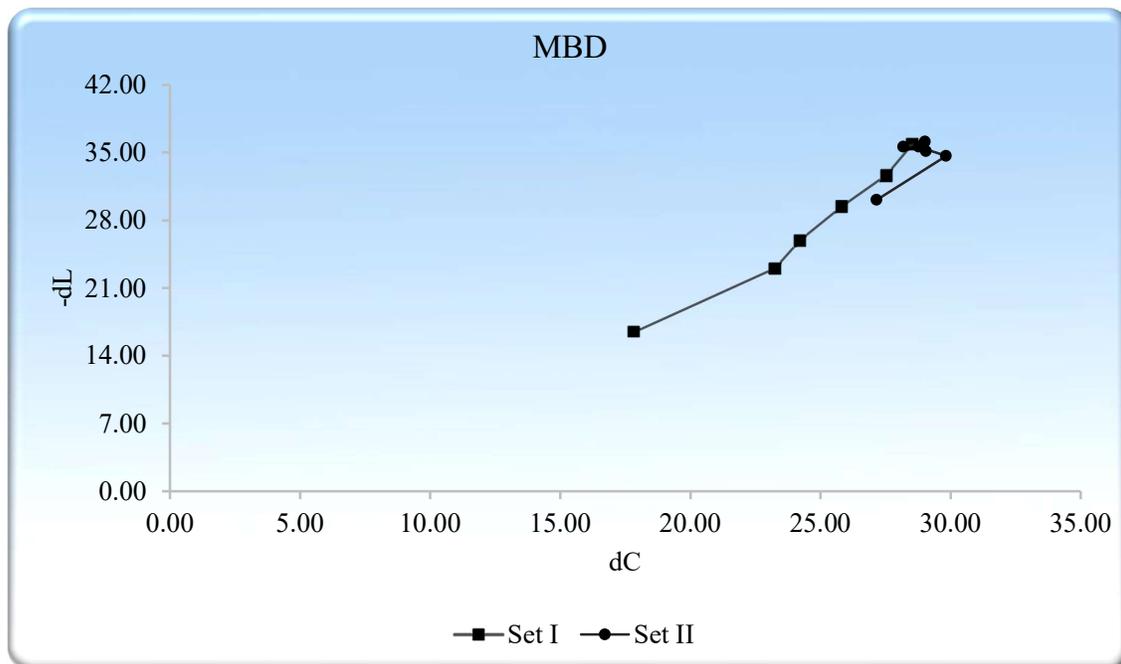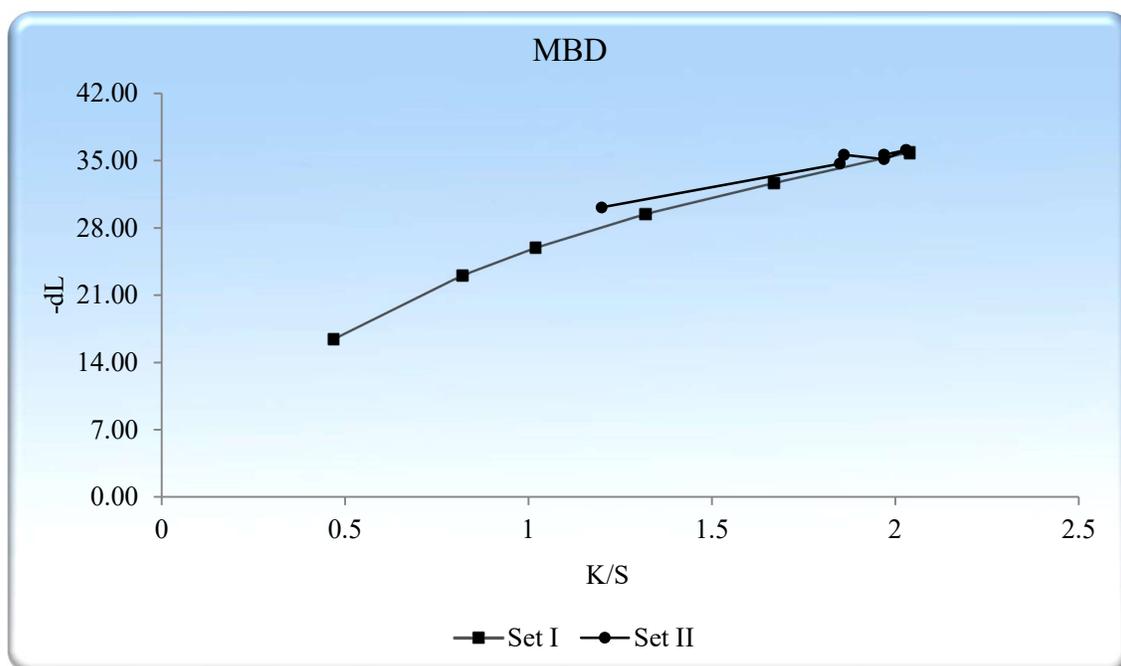
(a)
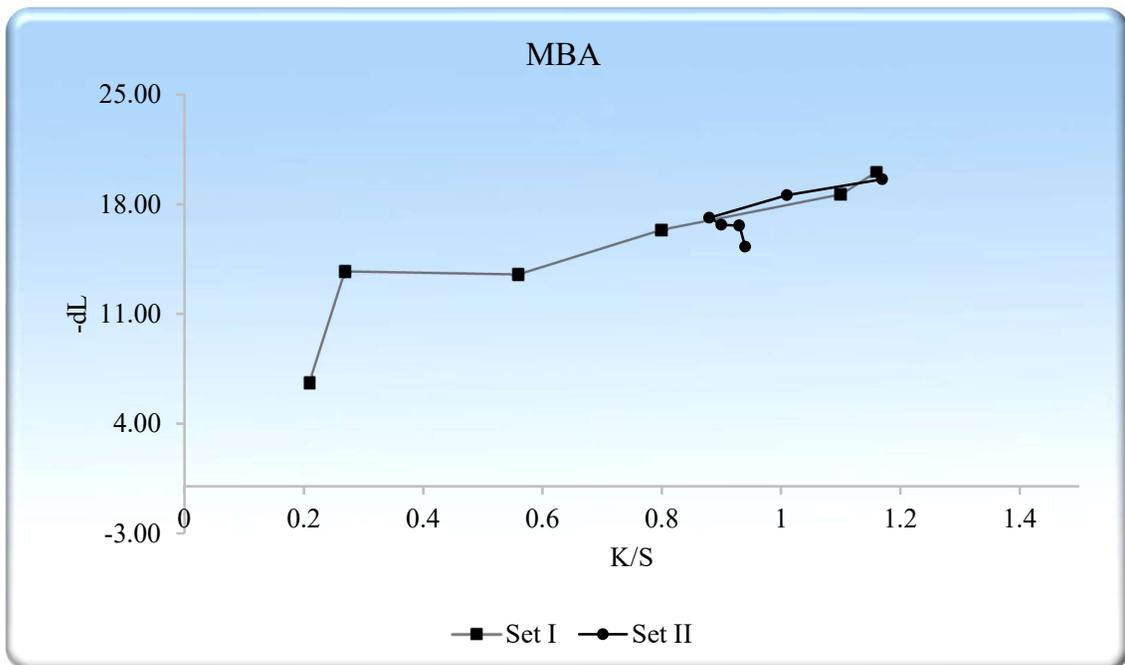
(b)

Figure 4.46: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Marigold, Babool, and Annatto (MBA) dye mixture
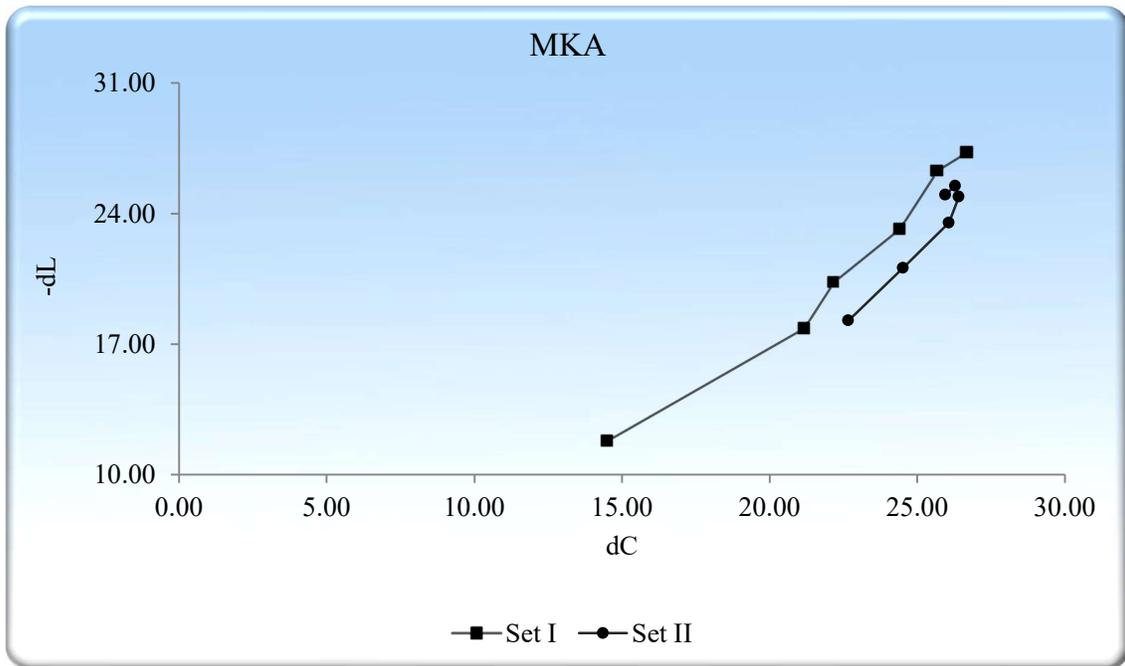
179

(a)

(b)

Figure 4.47: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Marigold, Babool, and Madder (MBD) dye mixture

(a)

(b)

Figure 4.48: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Marigold, Katha, and Annatto (MKA) dye mixture
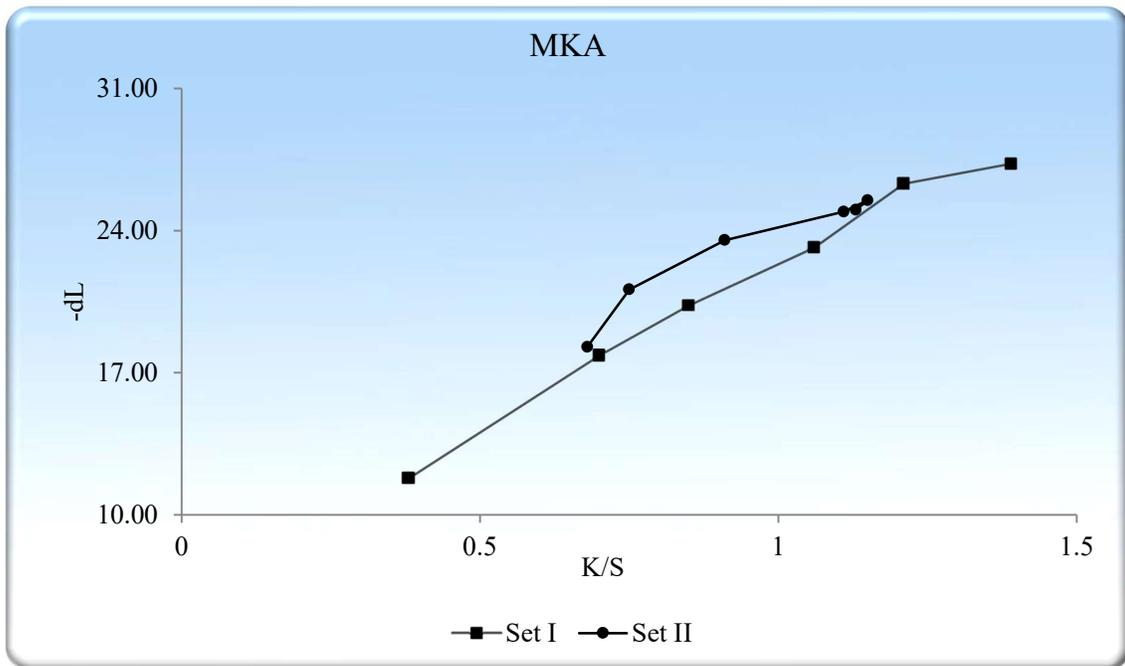
(a)

(b)

Figure 4.49: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Marigold, Katha, and Madder (MKD) dye mixture
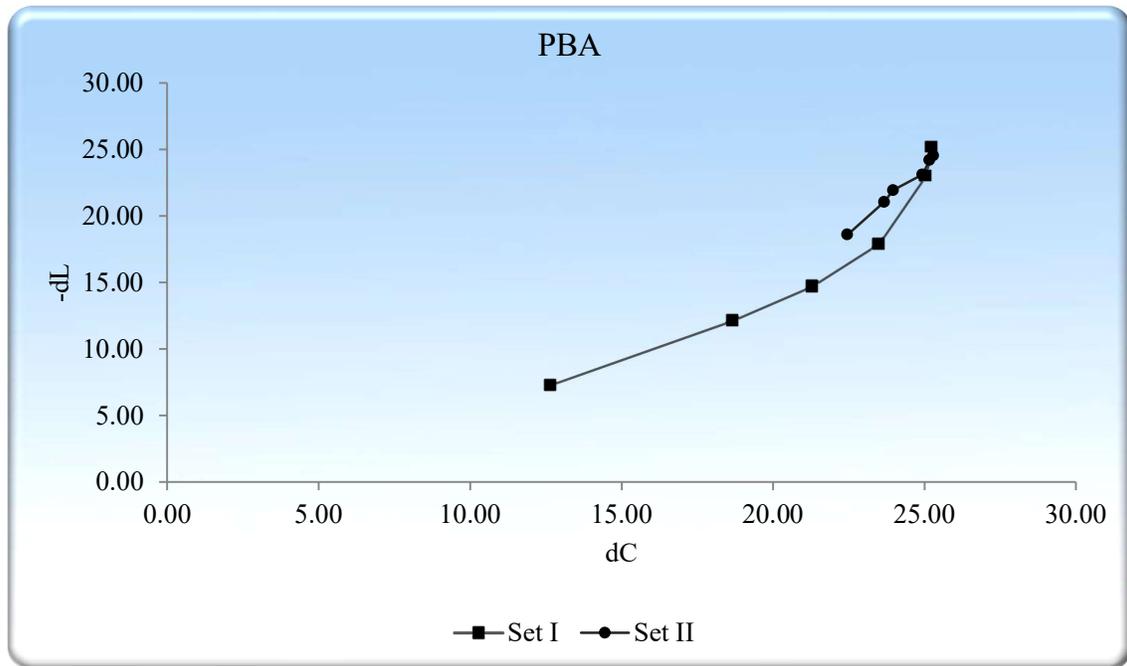
(a)
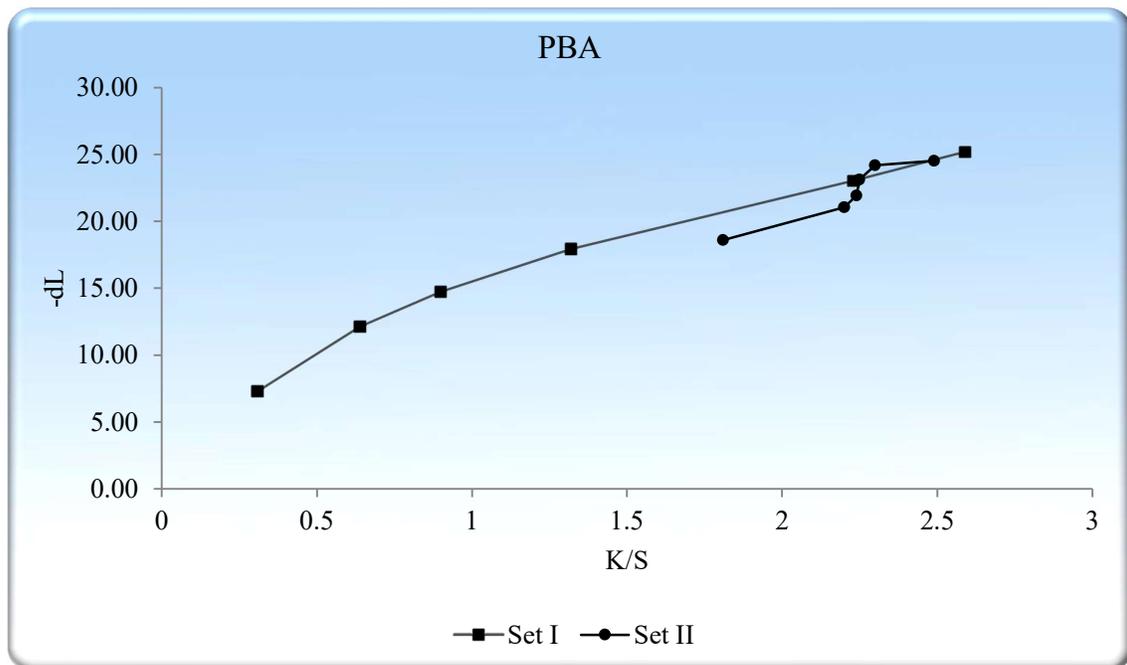
(b)

Figure 4.50: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Pomegranate, Babool, and Annatto (PBA) dye mixture
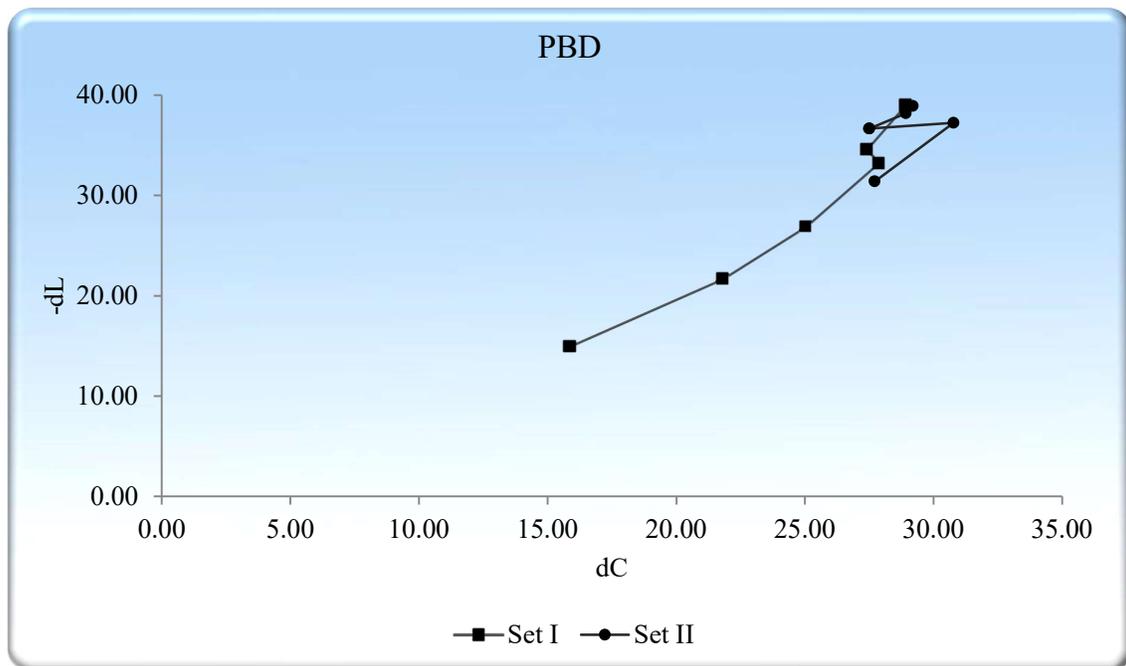
(a)
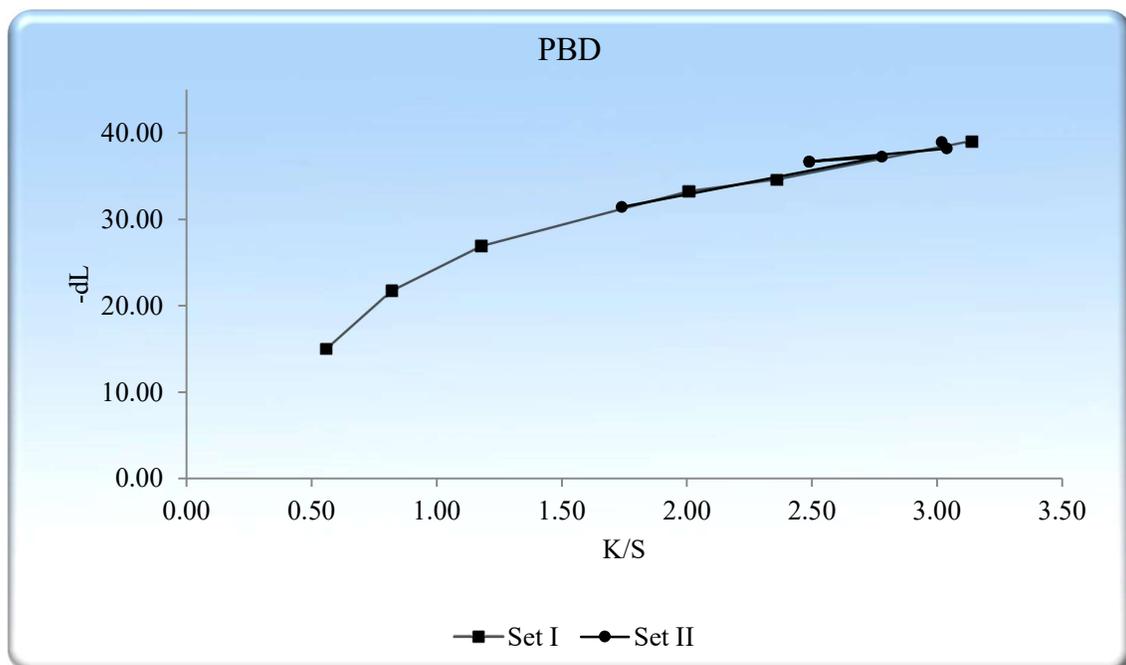
(b)

Figure 4.51: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Pomegranate, Babool, and Madder (PBD) dye mixture
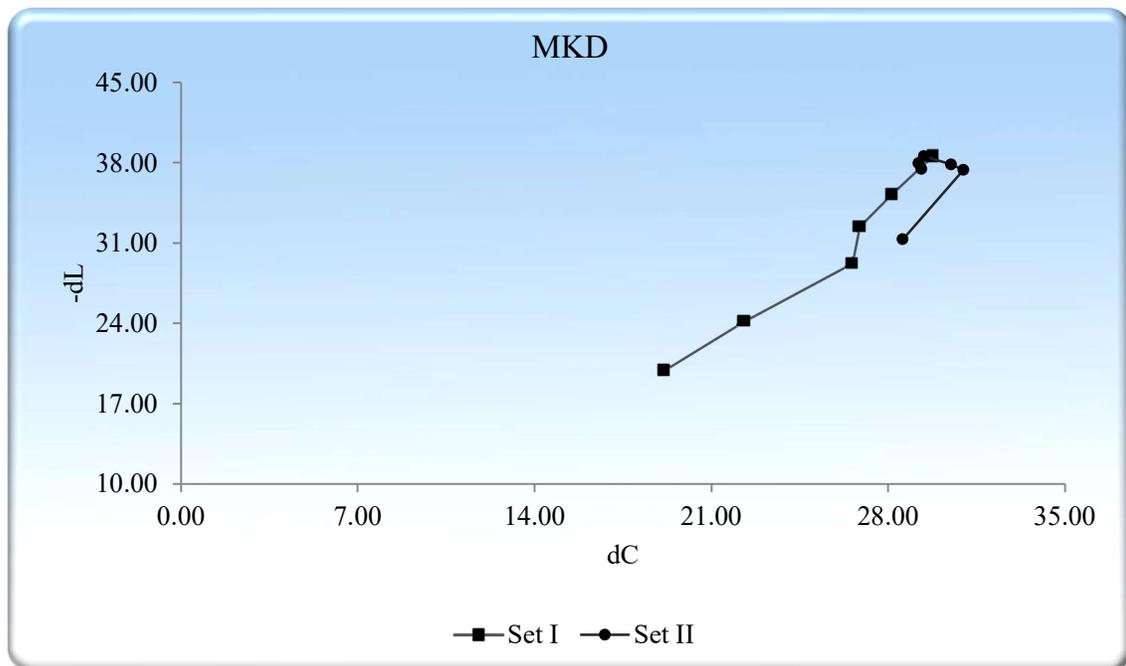
184
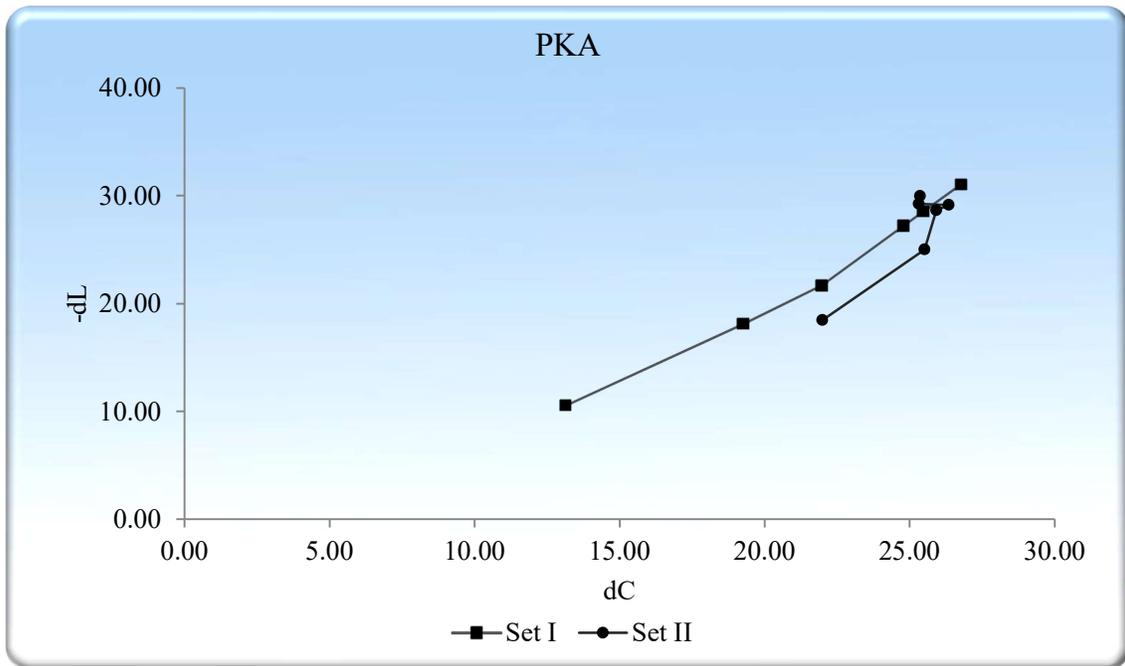
(a)
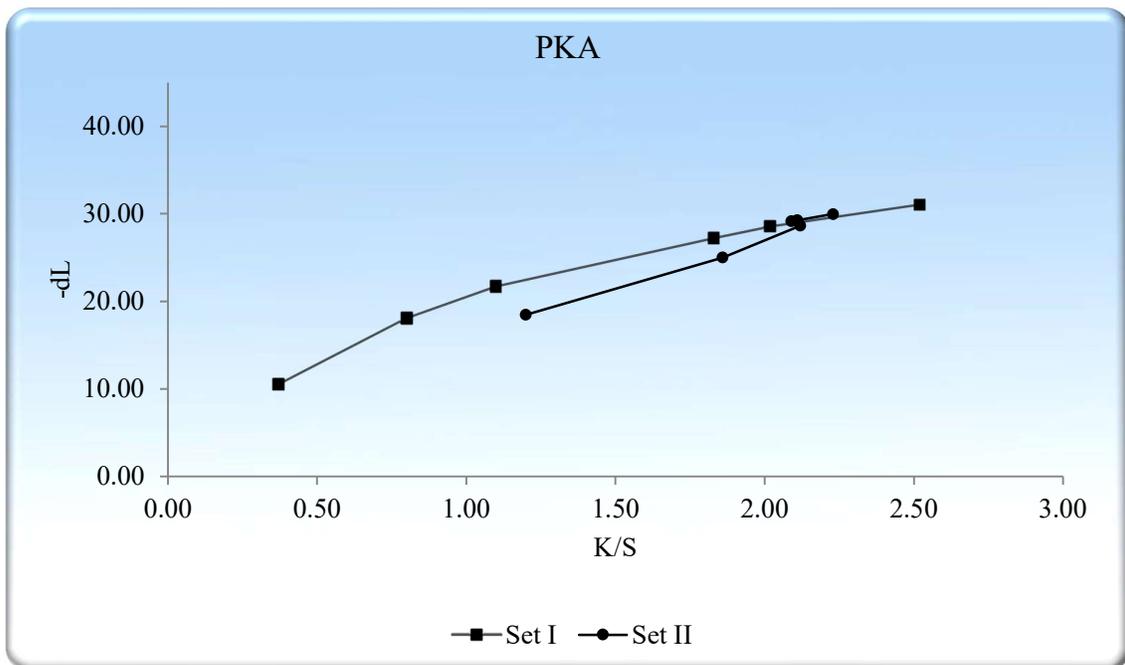
(b)

Figure 4.52: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Pomegranate, Katha, and Annatto (PKA) dye mixture
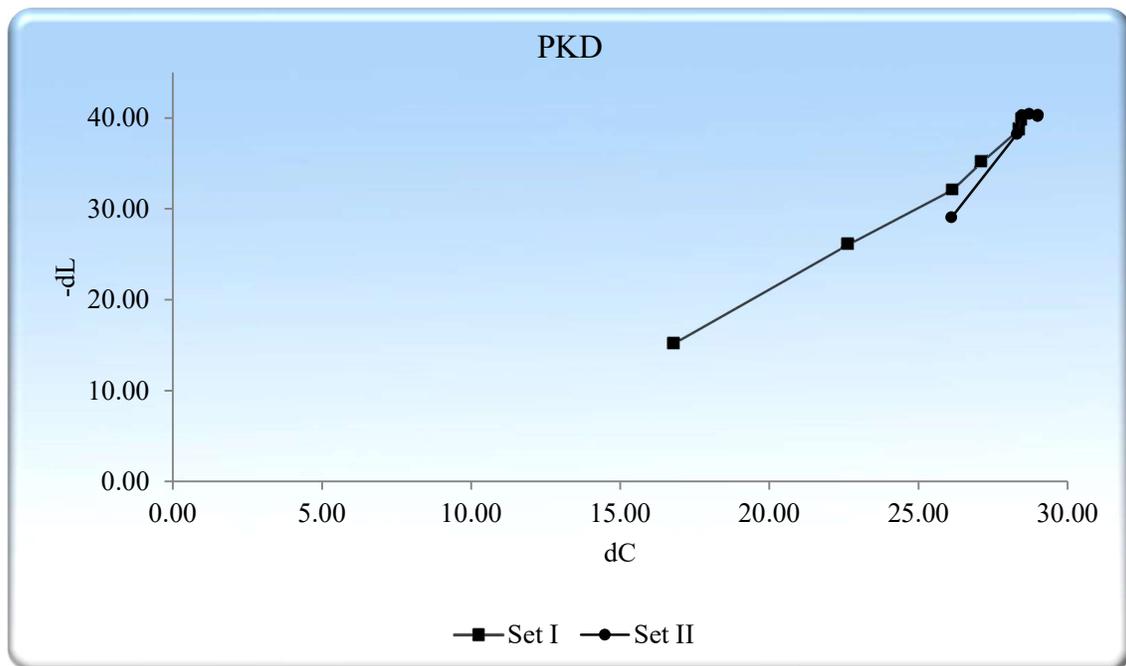
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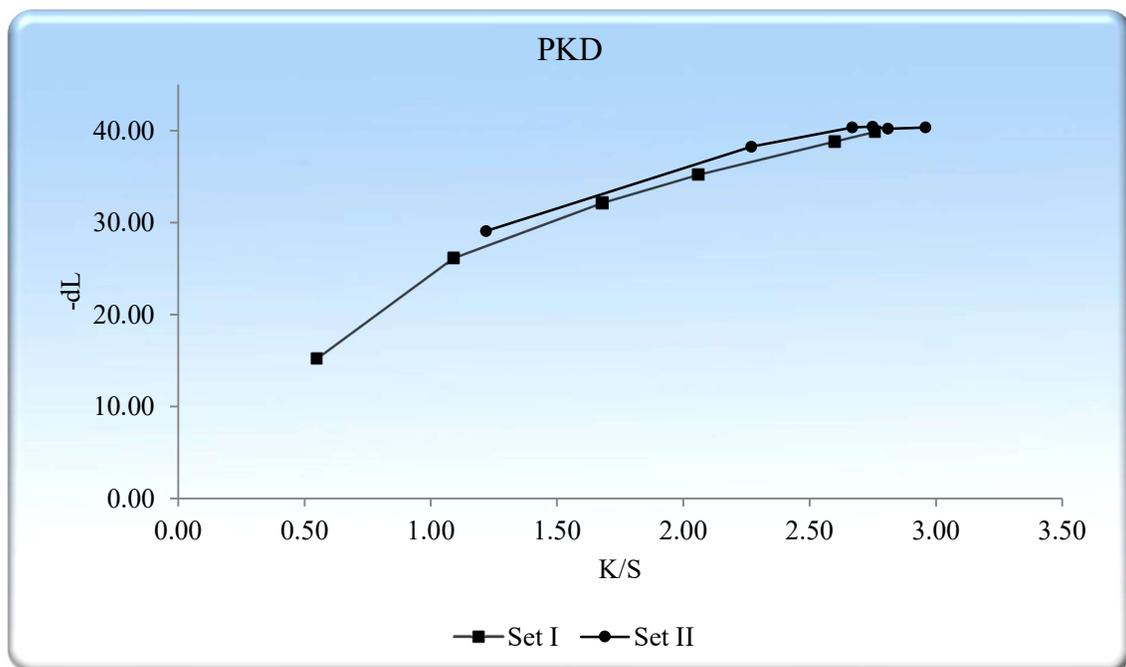
(b)

Figure 4.53: Plot of -dL vs. dC (a) and -dL vs. K/S (b) for samples in sets I & II for Pomegranate, Katha, and Madder (PKD) dye mixture

(B)   **Method based on da vs. K/S and db vs. K/S Plot**

Plots for da vs. K/S and db vs. K/S for each mixture are shown in Figure 4.54 to Figure 4.61. It is visible from the plots that both the curves of set I and set II are not represented by a single curve. Generally, both curves are distinct, and the set II curve joins the set I curve. Both curves take the common path toward the end of the curves. The observation method used here is the same as done in the case of binary mixtures.

In da vs. K/S plot for all mixtures, it was observed that the mixture of Marigold/Babool/Madder (MBD), Pomegranate/Babool/Madder (PBD), Pomegranate/ Katha/Annatto (PKA), and Pomegranate/Katha/Madder (PKD) showed good overlap of set I and set II curves. This mixture was considered a compatible mixture.

Some mixtures showed some deviation in overlapping but can be considered partial compatible mixtures as per observation using this method, which includes Marigold/Katha/ Annatto (MKA) and Marigold/Katha/Madder (MKD) mixtures. Mixtures Marigold/ Babool/Annatto (MBA) and Pomegranate/Babool/Annatto (PBA) showed significant deviations and were considered incompatible mixtures.

As per plots of db vs. K/S, it was observed that the mixtures Marigold/Babool/Madder (MBD), and Pomegranate/Katha/Madder (PKD) showed very good overlap and were considered as highly compatible mixtures. All the other mixtures showed good overlap of set I and set II curves and were considered compatible mixtures.
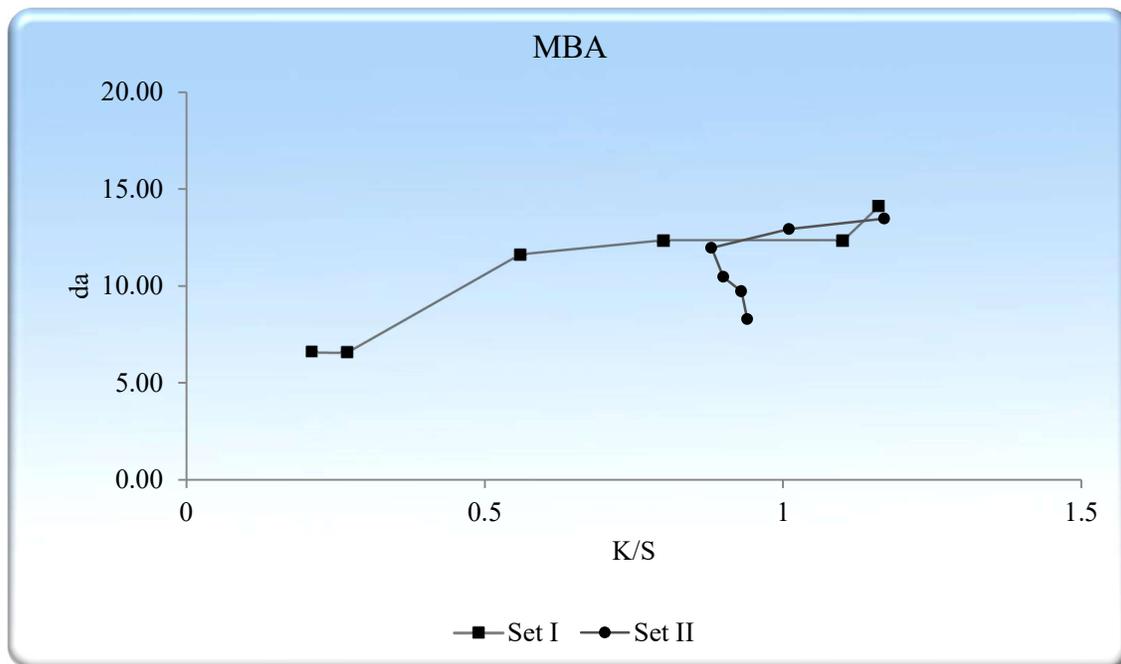
(a)
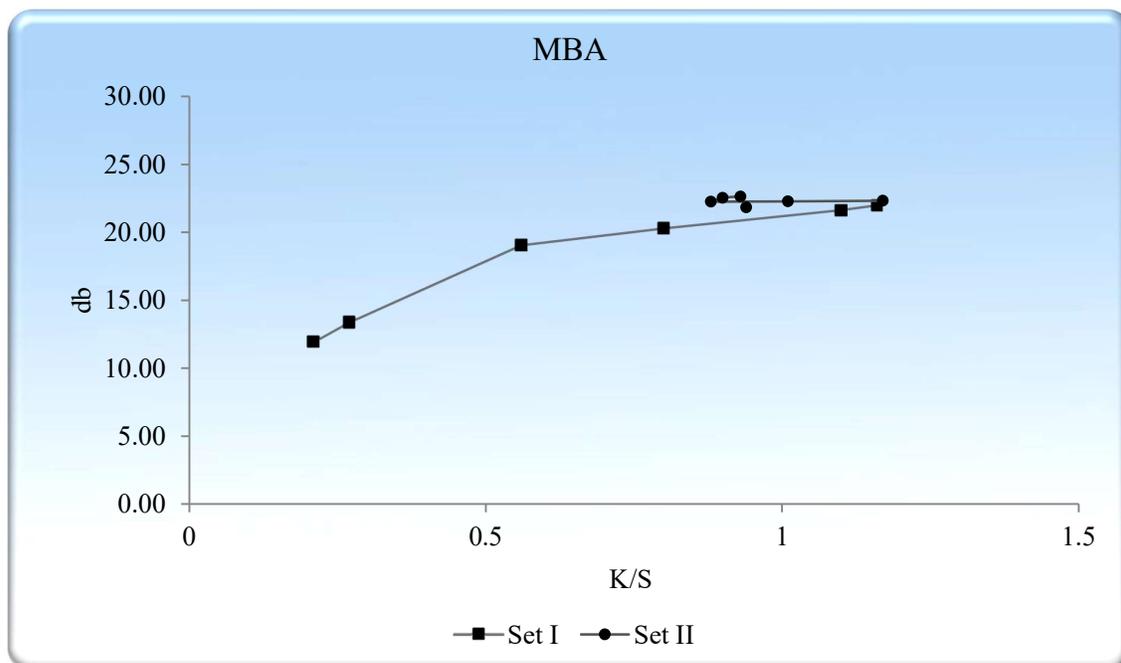
(b)

Figure 4.54: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Marigold, Babool, and Annatto (MBA) dye mixture
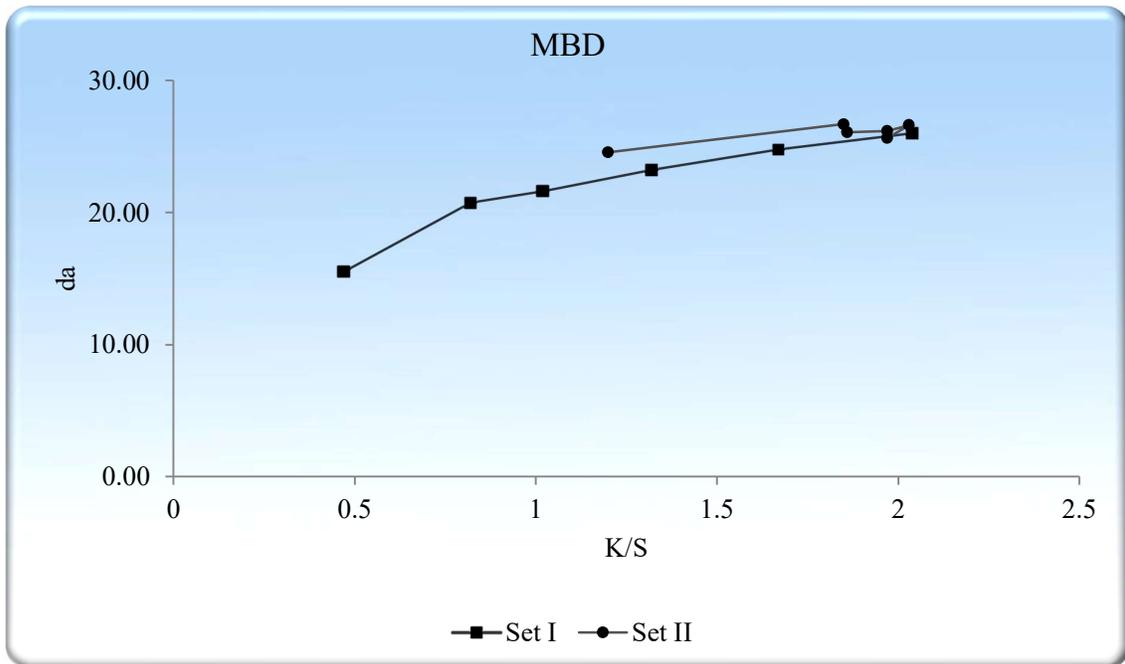
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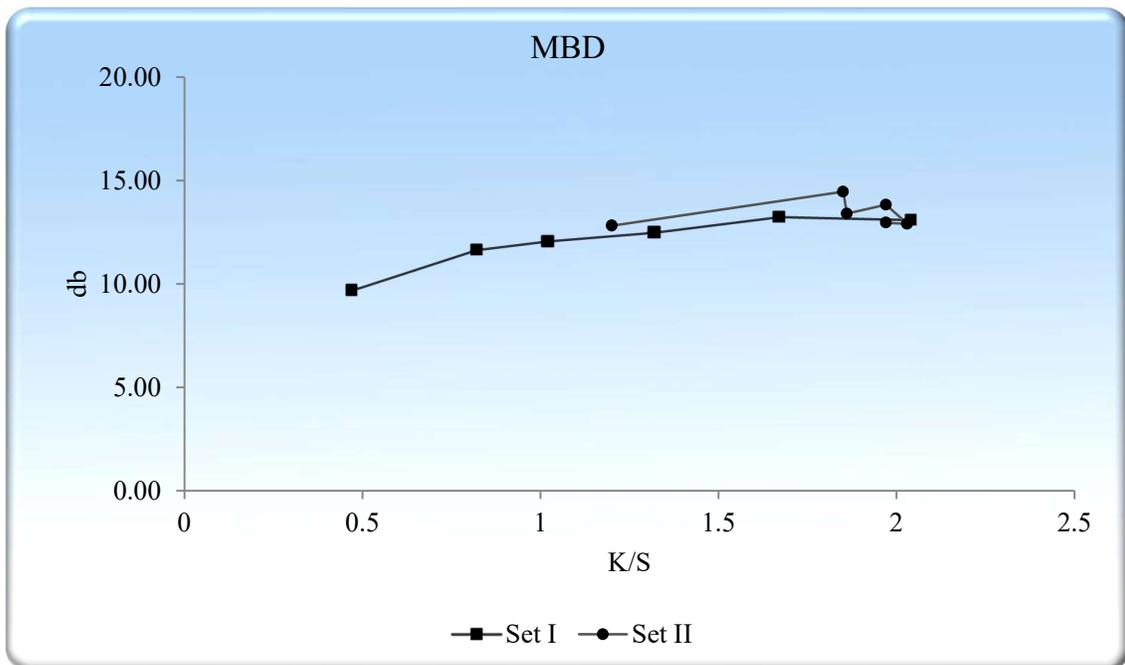
(b)

Figure 4.55: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Marigold, Babool, and Madder (MBD) dye mixture
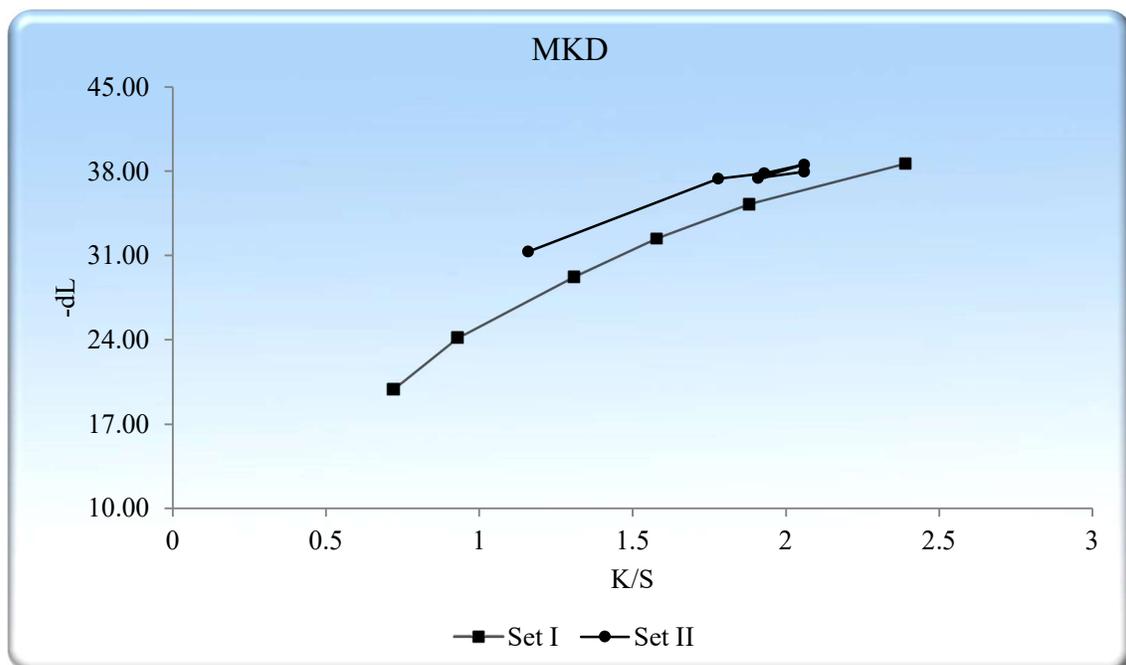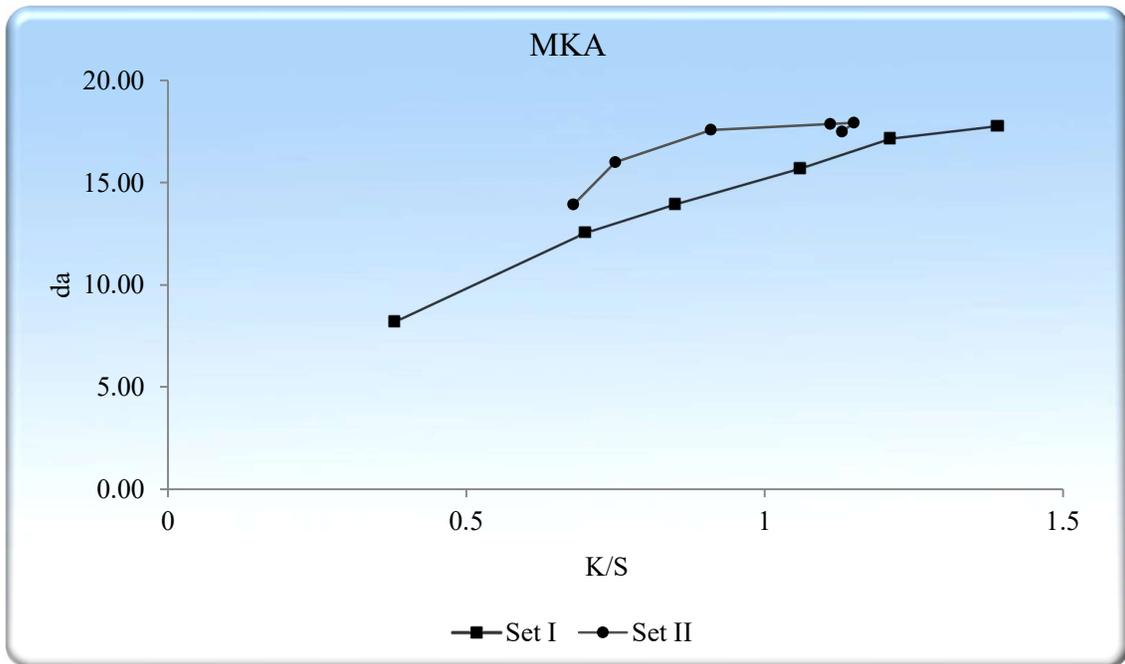
(a)
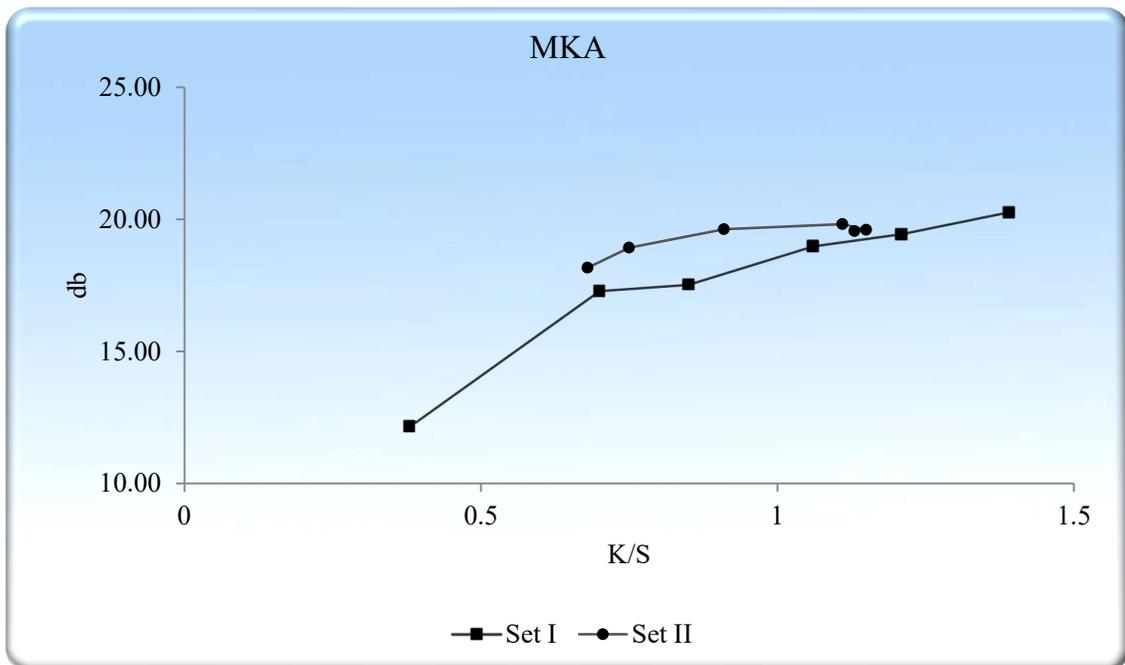
(b)

Figure 4.56: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Marigold, Katha, and Annatto (MKA) dye mixture
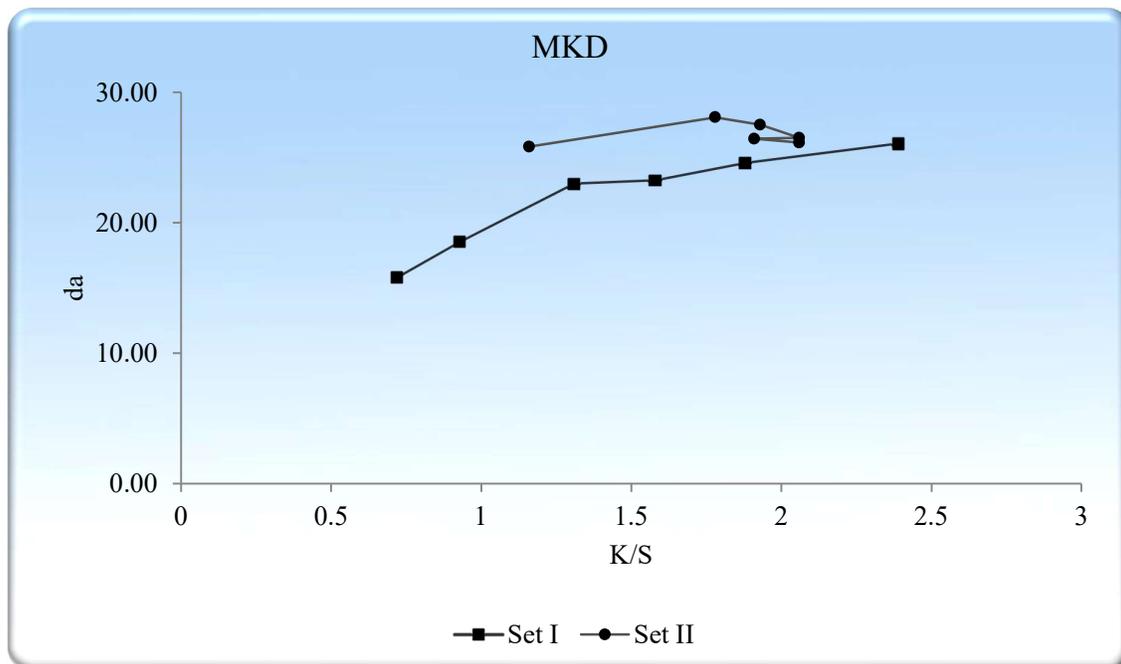
(a)
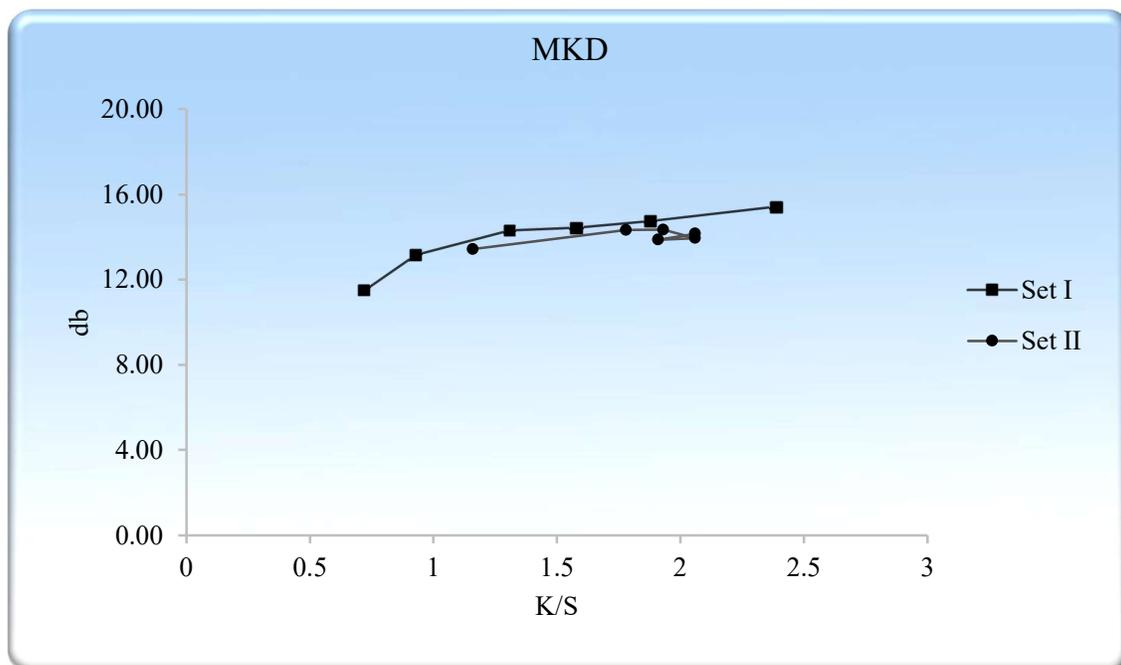
(b)

Figure 4.57: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Marigold, Katha, and Madder (MKD) dye mixture
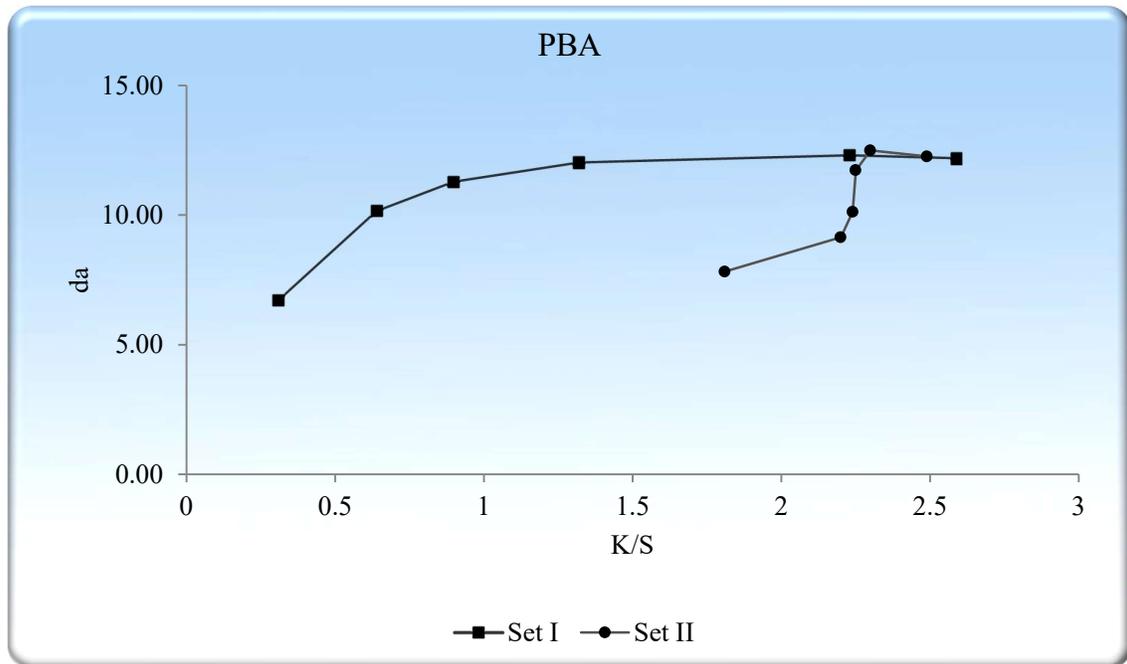
(a)
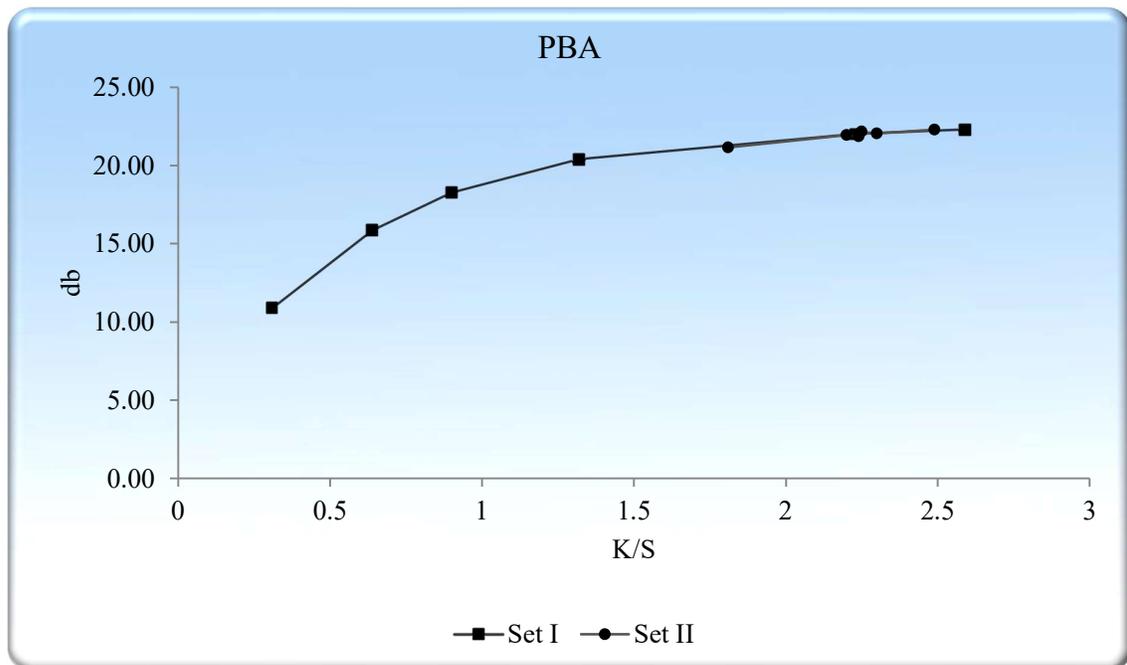
(b)

Figure 4.58: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Pomegranate, Babool, and Annatto (PBA) dye mixture
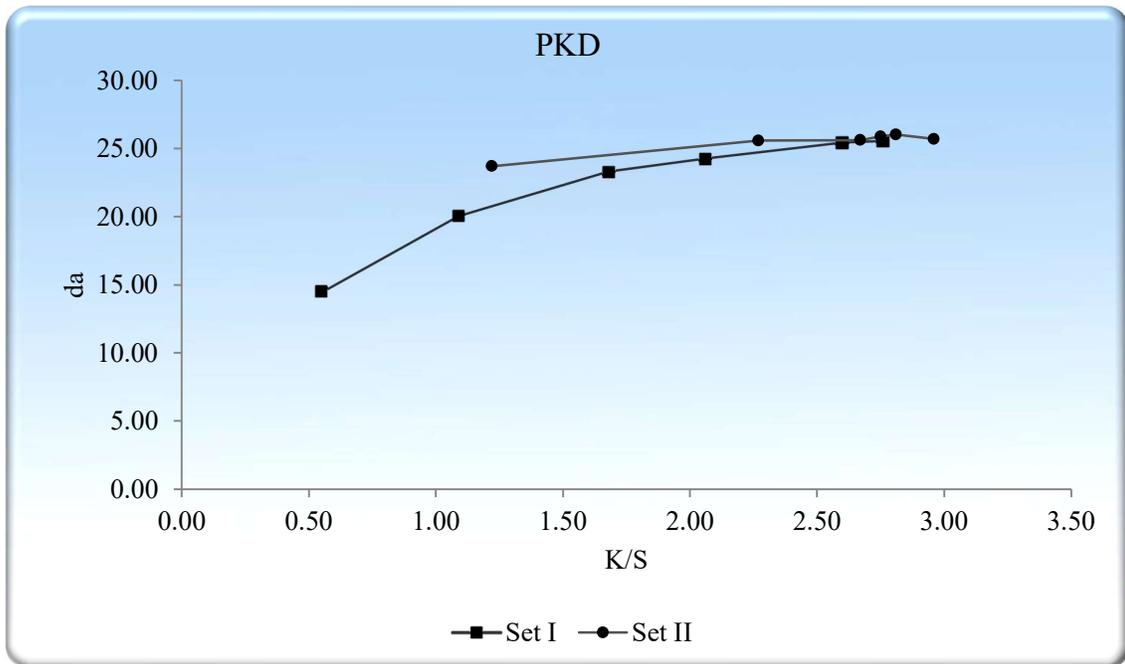
(a)
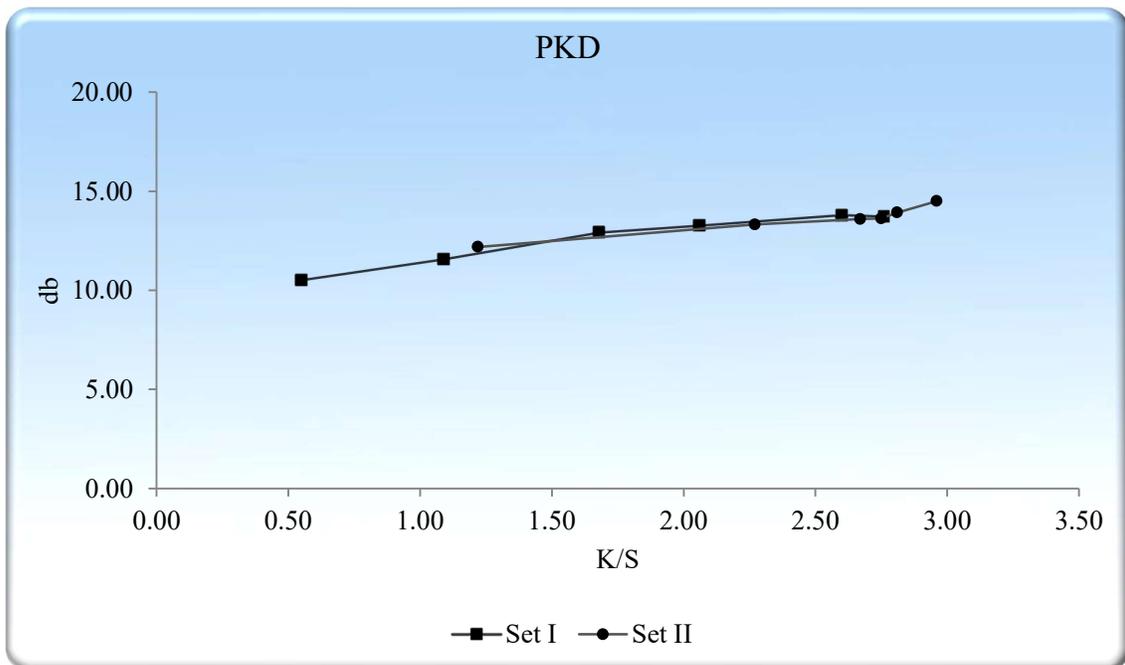
(b)

Figure 4.59: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Pomegranate, Katha, and Madder (PKD) dye mixture
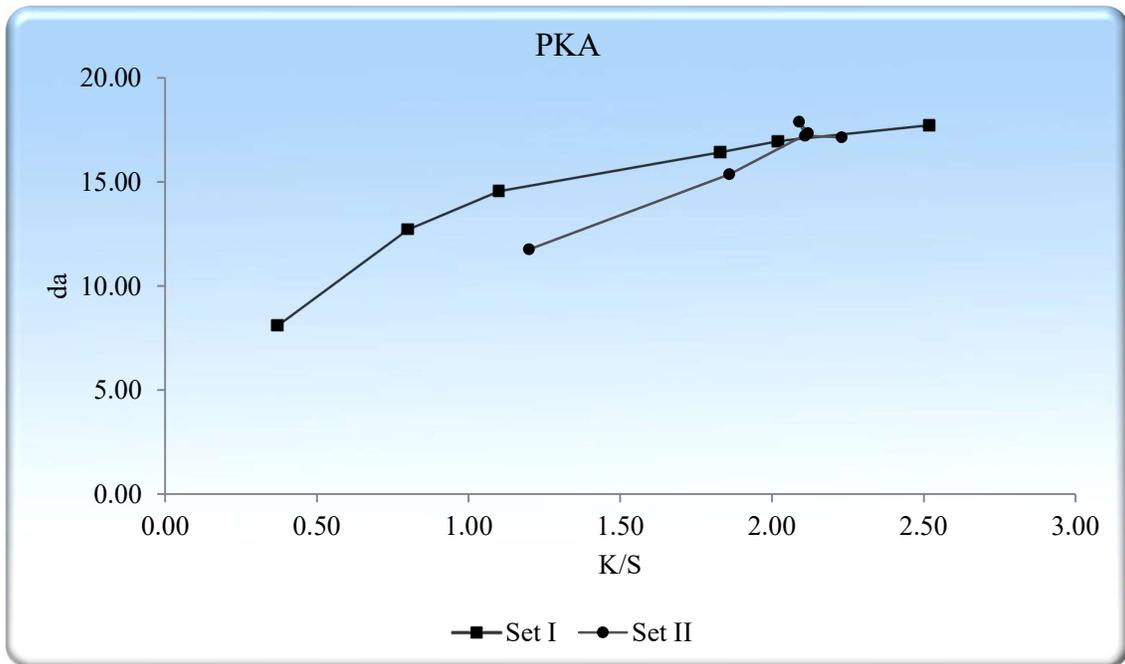
(a)
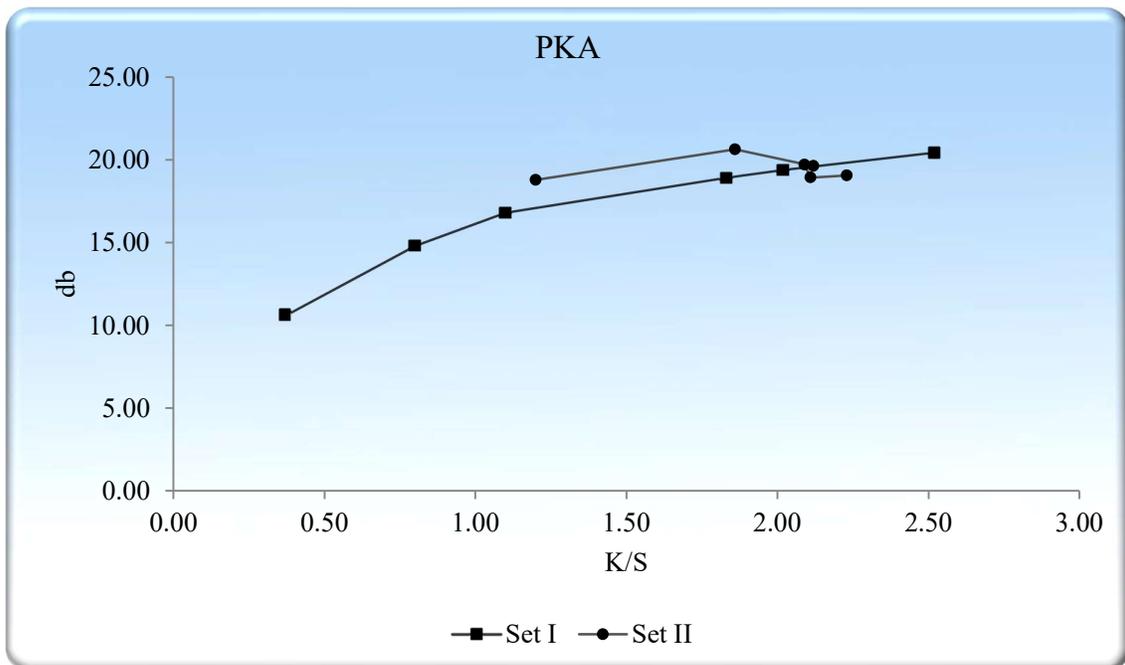
(b)

Figure 4.60: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Pomegranate, Katha, and Annatto (PKA) dye mixture
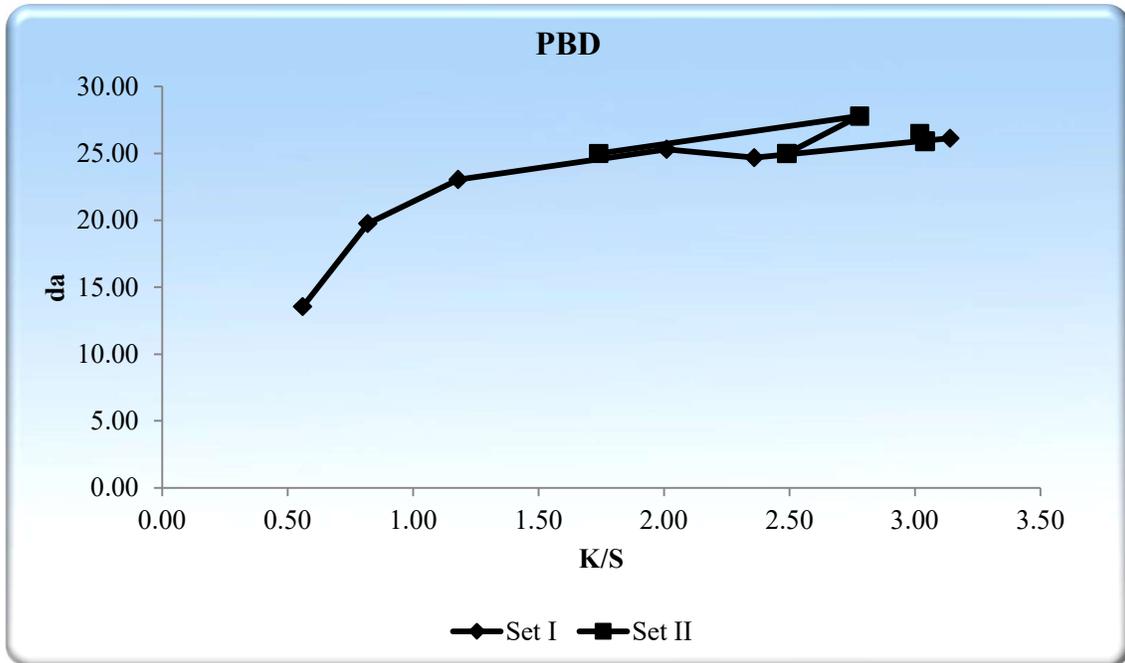
(a)
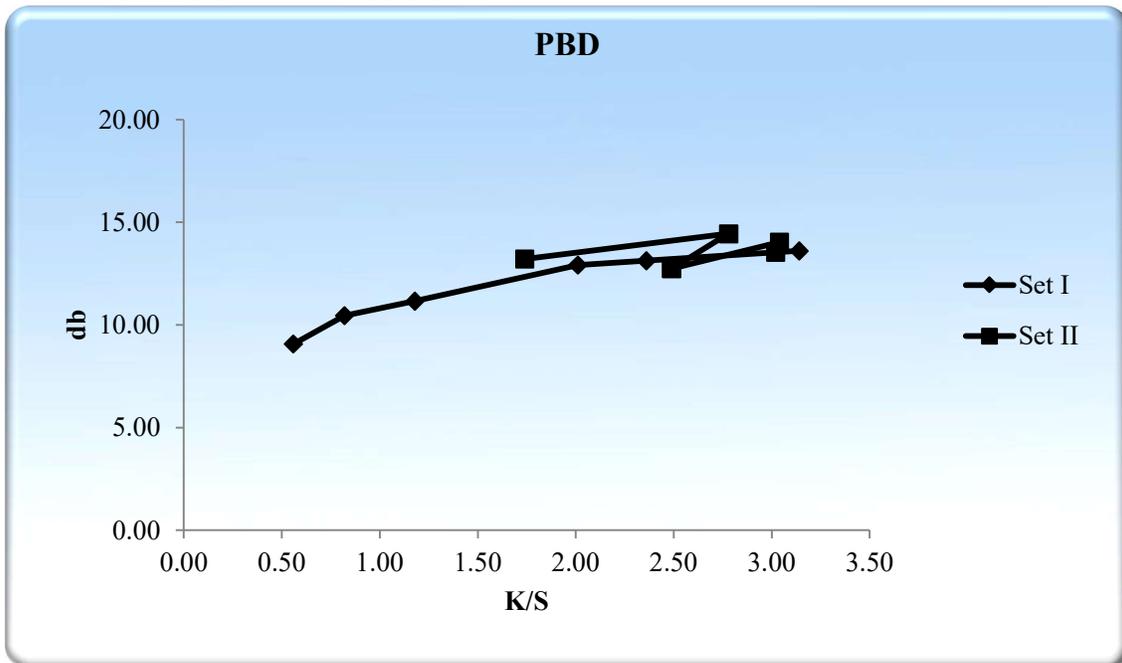
(b)

Figure 4.61: Plot of da vs. K/S (a) and db vs. K/S (b) for samples in sets I & II for Pomegranate, Babool, and Madder (PBD) dye mixture

(A) Based on change in Hue angle (h°)

(i) Using graphical analysis

As done in the case of binary mixtures, dye compatibility for the tertiary mixture was assessed by finding the change in hue angle for all 12 samples in sets I & II. It was done by the hue angle vs. samples plot in both sets. The plots of all eight tertiary mixtures are shown from Figure 4.62 to Figure 4.64.

It was observed that the mixtures of Pomegranate/Katha/Madder (PKD) and Marigold/Babool/Madder (MBD) showed low variation in hue angle. They were considered to be satisfactory compatible mixtures using this method.

Mixtures of Marigold/Katha/Annatto (MKA), Marigold/Katha/Madder (MKD), Pomegranate/Babool/Annatto (PBA), Pomegranate/Babool/Madder (PBD) and Pomegranate/Katha/Annatto (PKA) showed average variation in hue angle. These mixtures were considered partially compatible using this method.

This analysis showed high variation in the Marigold/Babool/Annatto (MBA) mixture, which was considered incompatible.
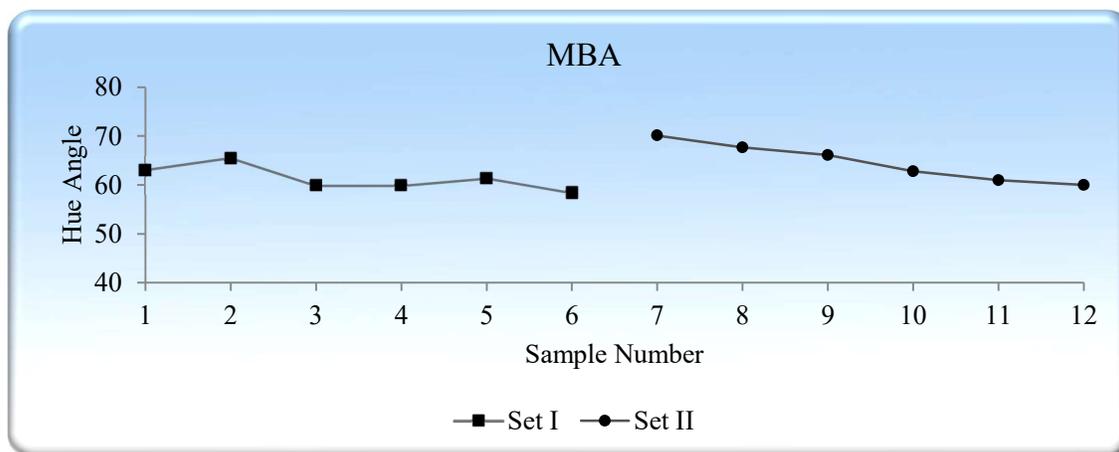
(a)
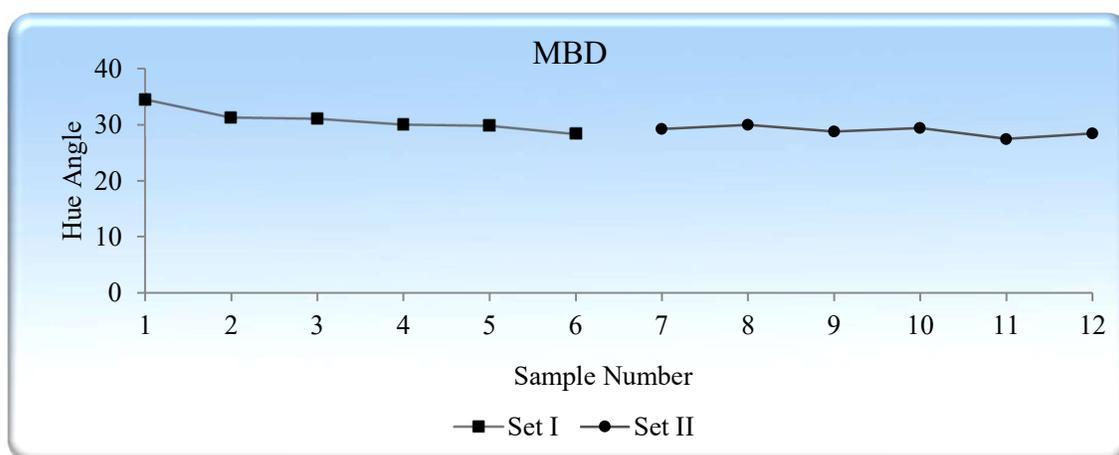
(b)
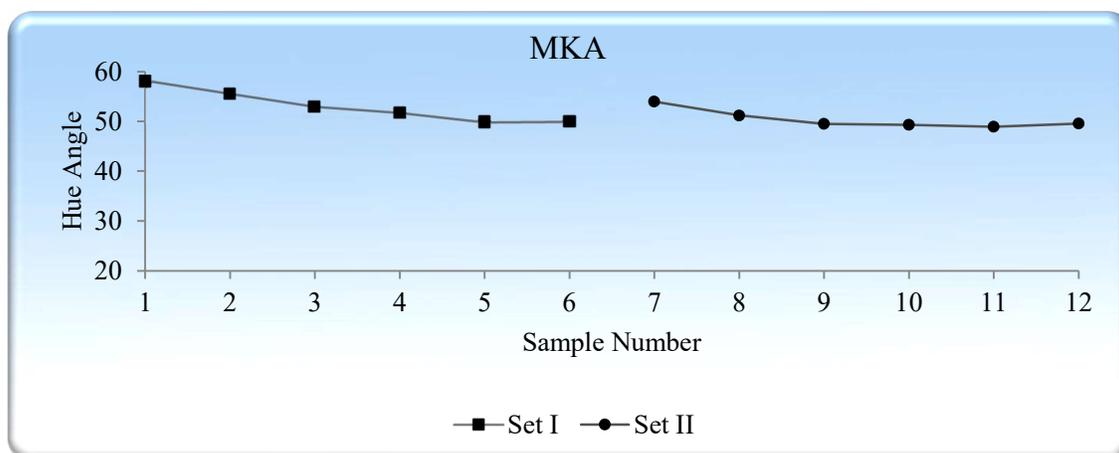
(c)

Figure 4.62: Hue vs. samples in sets I & II for a tertiary mixture of Marigold/ Babool/Annatto (a), Marigold/Babool/Madder (b), and Marigold/Katha/Annatto (c)
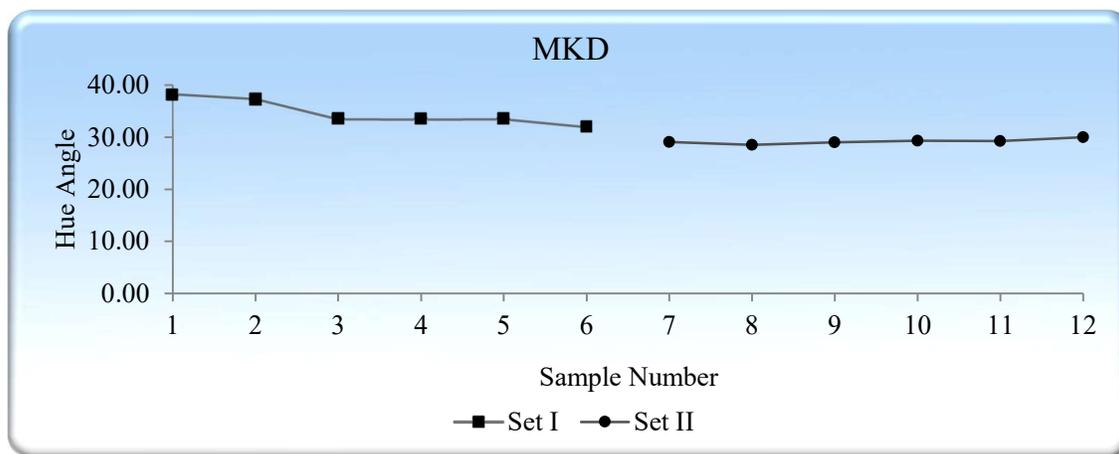
(a)
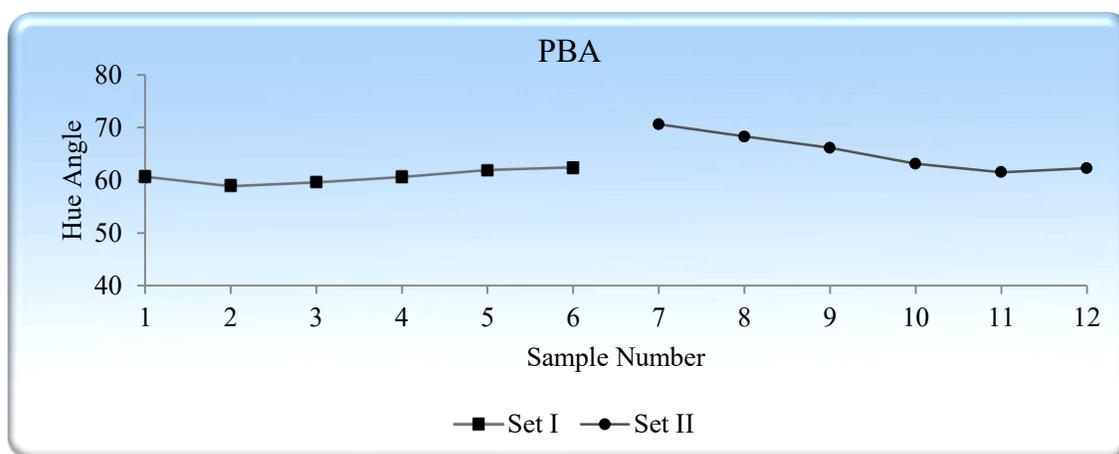
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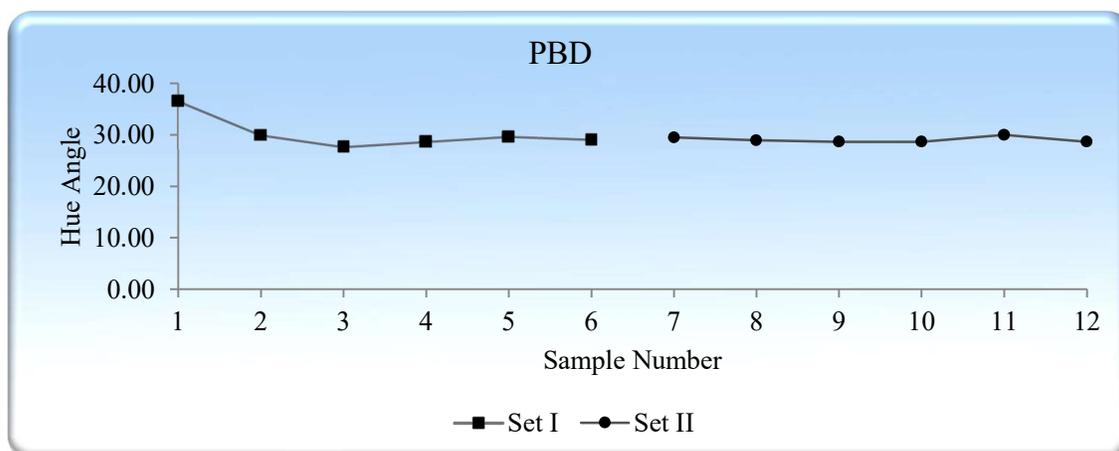
Figure 4.63: Hue vs. samples in sets I & II for a tertiary mixture of Marigold/Katha/ Madder (a), Pomegranate/Babool/Annatto (b), and Pomegranate/Babool/Madder (c)
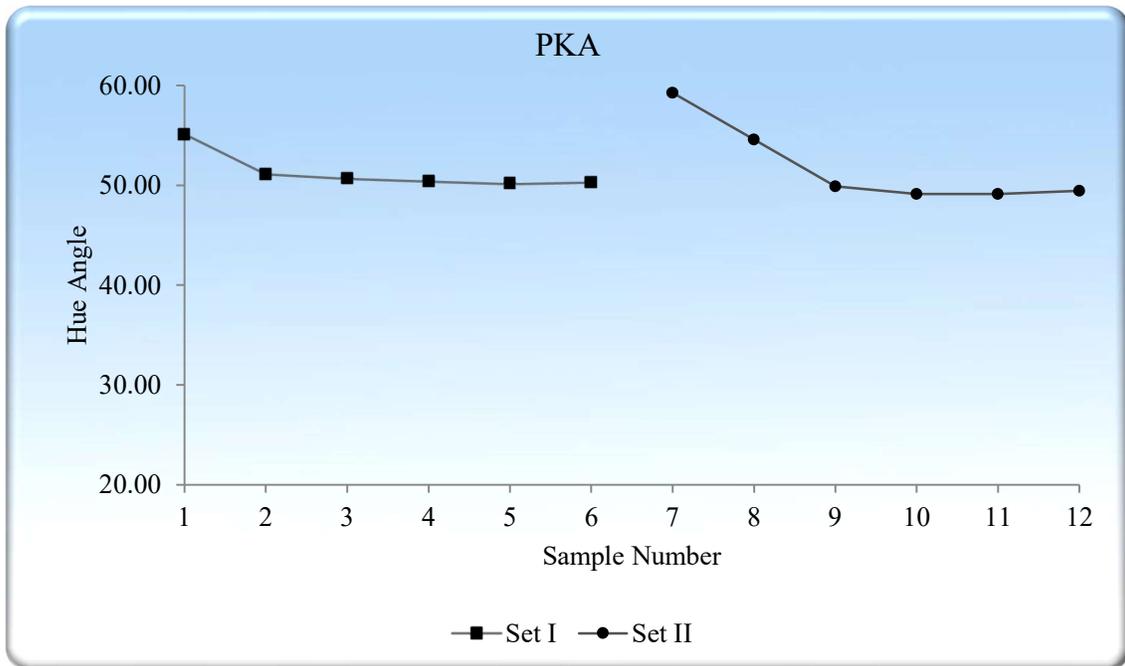
(a)
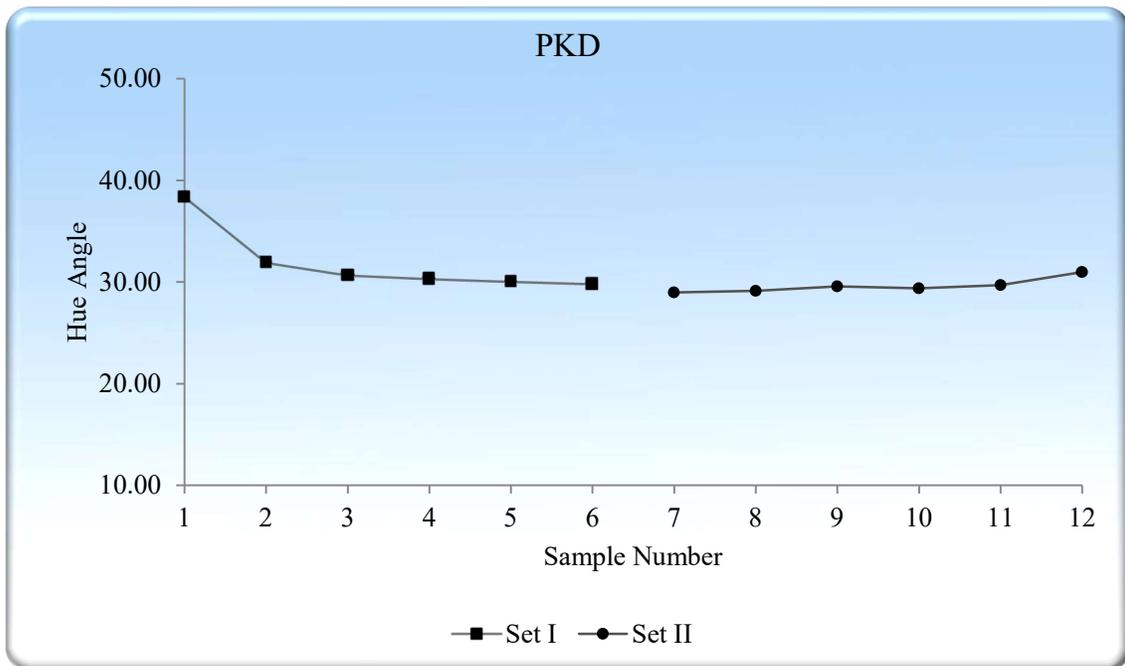
(b)

Figure 4.64: Hue vs. samples in sets I & II for a tertiary mixture of Pomegranate/Katha/Annatto (a) and Pomegranate/Katha/Madder (b)

(ii) Using coefficient of variation (CV)

As mentioned in the case of binary mixtures, the C.V. values for sets I and II were measured for all the tertiary mixtures. It was also attempted to get a single value of C.V. for each mixture using the sum of C.V.'s of sets I and II. All the values are shown in Table 4.51 and shown graphically in Figure 4.65.

It was observed that the C.V. for sets I and II were different and generally higher for sets I with exceptions. It was concluded that the Marigold/Babool/Annatto (MBA), Marigold/Katha/Madder (MKD), and Pomegranate/Babool/Annatto (PBA) showed low C.V. and can be considered as compatible mixtures. The mixtures *viz.* Marigold/Babool/Madder (MBD), Marigold/Katha/Annatto (MKA), and Pomegranate/Katha/Annatto (PKA) were having mid-range C.V. and can be considered as partially compatible. The C.V. for Pomegranate/Babool/Madder (PBD) and Pomegranate/Katha/Madder (PKD) was high and were considered incompatible mixtures.

Table 4.51: Coefficient of variation for set I, set II, and the sum of both sets

Mixture code	CV - Set I	CV -Set II	CV- Set I + CV-Set II
MBA	2.6	6.2	8.8
MBD	6.6	3.0	9.6
MKA	6.1	3.8	9.9
MKD	7.0	1.7	8.7
PBA	2.1	5.6	7.7
PBD	10.4	1.9	12.3
PKA	3.7	8.0	11.7
PKD	10.2	2.4	12.6
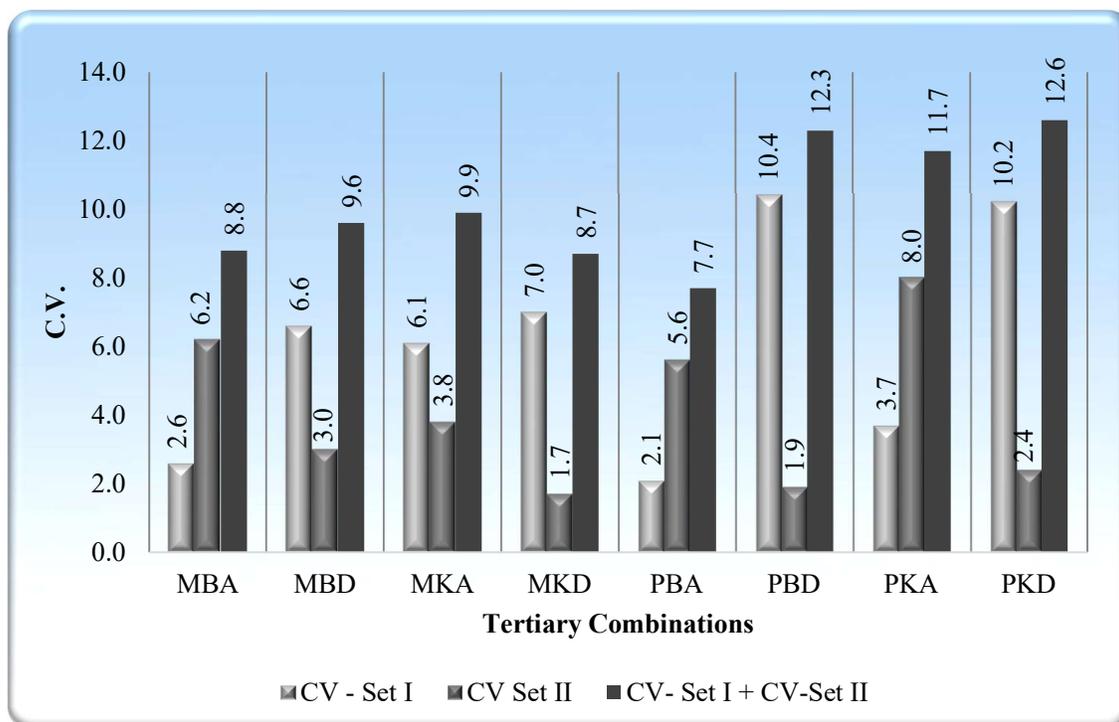
Figure 4.65: Coefficient of variation for set I, set II, and the sum of both sets

(D)   Compatibility Factor method

As per the concept mentioned for binary mixtures, the study was carried out similarly for tertiary mixtures. The C.F. was obtained in the present analysis using the K/S data of mixture and component dyes—spectral data of sample number 5 from set I was used for all the mixtures. The dye concentration for sample 5 was 25% owf. The K/S data for component dyes was predicted at a dye concentration of 8.33 % owf using design expert software. Primary dyes dyed samples were used for this purpose. The details of the K/S and C.F. are mentioned in Table 4.52 (A, B & C) based on the λmax of components A, B & C. The coefficient of variation (C.V.) was calculated to check the deviation between the three values of C.F. which is shown in Table 4.53. The higher C.V. value leads to higher incompatibility.

It was observed that the Marigold/Babool/Madder (MBD), Marigold/Katha/ Annatto (MKA) Marigold/Katha/Madder (MKD), Pomegranate/Babool/Madder (PBD), and Pomegranate/Katha/Madder (PKD) showed less than 10% C.V. in compatibility factor values

at the respective wavelength of component dyes and may be considered as compatible mixtures. In the case of Marigold/Babool/Annatto (MBA) and Pomegranate/Katha/Annatto (PKA) mixtures, the C.V. was found in the range of 10-16% and considered as partially compatible using this method. The C.V. for Pomegranate/Babool/Annatto (PBA) was 29.74% and was considered an incompatible mixture.

Table 4.52(A): Compatibility factor for tertiary mixtures based on λmax of Component A

Mixture code (ABC)	λ max of component A	K/S (Based on λmax of Component A)			K/S Mixture (Calculated)	K/S Mixture (Observed)	Compatibility Factor (based on component A)
		Component A	Component B	Component C			
MBA	440	0.21	0.35	0.27	0.83	0.91	0.91
MBD	440	0.21	0.35	0.53	1.09	1.53	0.71
MKA	440	0.21	0.85	0.27	1.32	1.40	0.94
MKD	440	0.21	0.85	0.53	1.58	1.98	0.80
PBA	360	0.24	0.67	0.14	1.05	2.23	0.47
PBD	360	0.24	0.67	0.47	1.37	2.36	0.58
PKA	360	0.24	0.96	0.14	1.34	2.02	0.66
PKD	360	0.24	0.96	0.47	1.66	2.60	0.64

(B)   Compatibility factor for tertiary mixtures based on λmax of Component B

Mixture code (ABC)	λ max of component B	K/S (Based on λmax of Component B)			K/S Mixture (Calculated)	K/S Mixture (Observed)	Compatibility Factor (based on component B)
		Component A	Component B	Component C			
MBA	360	0.10	0.67	0.14	0.92	1.10	0.83
MBD	360	0.10	0.67	0.47	1.24	1.67	0.74
MKA	360	0.10	0.96	0.14	1.20	1.31	0.92
MKD	360	0.10	0.96	0.47	1.53	1.88	0.81
PBA	360	0.24	0.67	0.14	1.05	2.23	0.47
PBD	360	0.24	0.67	0.47	1.37	2.36	0.58
PKA	360	0.24	0.96	0.14	1.34	2.02	0.66
PKD	360	0.24	0.96	0.47	1.66	2.60	0.64

(C)   Compatibility factor for tertiary mixtures based on λmax of Component C

Mixture code (ABC)	λmax of component C	K/S (Based on λmax of Component C)			K/S Mixture (Calculated)	K/S Mixture (Observed)	Compatibility Factor (based on component C)
		Component A	Component B	Component C			
MBA	480	0.14	0.26	0.44	0.84	0.82	1.02
MBD	510	0.05	0.23	0.84	1.12	1.78	0.63
MKA	480	0.14	0.73	0.44	1.31	1.30	1.01
MKD	510	0.05	0.69	0.84	1.59	2.15	0.74
PBA	480	0.06	0.26	0.44	0.75	0.99	0.76
PBD	510	0.05	0.23	0.84	1.12	2.03	0.55
PKA	480	0.06	0.73	0.44	1.23	1.43	0.86
PKD	510	0.05	0.69	0.84	1.58	2.75	0.58

Table 4.53: C.V. for compatibility factors

Mixture code (ABC)	Compatibility Factor (based on component A)	Compatibility Factor (based on component B)	Compatibility Factor (based on component C)	C.V.
MBA	0.91	0.83	1.02	10.22
MBD	0.71	0.74	0.63	8.17
MKA	0.94	0.92	1.01	4.92
MKD	0.80	0.81	0.74	5.14
PBA	0.47	0.47	0.76	29.74
PBD	0.58	0.58	0.55	3.28
PKA	0.66	0.66	0.86	15.61
PKD	0.64	0.64	0.58	6.00

(E) **Visual Rating**

As worked for binary mixtures, the visual assessment was done for tertiary mixtures. Two observers were asked to give the score to the 8 tertiary mixture samples for their compatibility. They were asked to rate the samples out of 20. The scores obtained are shown in Table 4.54 The rating was converted into ranks to calculate Spearman's rank correlation coefficient. A positive correlation of 0.67 was obtained, which indicates a strong positive correlation between the two observers. This means that there is substantial agreement between the two observers, indicating that their ranking is not occurring by chance.

Table 4.54: Visual Score and Rating for Tertiary Mixture

Mixture	Visual Score		Average
	Observer I	Observer II	
PKA	18.5	15	16.75
MKD	18	14	16
PKD	18	13.5	15.75
MKA	17	12	14.5
MBD	15.5	11	13.25
PBD	15	10.5	12.75
MBA	14	10	12
PBA	14	9	11.5

The visual score was used to assess the compatibility of the mixtures. It was observed that the mixtures Pomegranate/Katha/Annatto (PKA), Marigold/Katha/ Madder (MKD), Pomegranate/Katha/Madder (PKD), and Marigold/Katha/ Annatto(MKA) had a score of above 14 and were considered compatible mixtures. Marigold/Babool/Madder (MBD), Pomegranate/Babool/Madder (PBD), Marigold/ Babool/Annatto (MBA), and Pomegranate/Babool/Annatto (PBA) had average scores and were considered as partially compatible mixtures.

4.2.1.2.2 Summary of Different Method's results and Overall rating

As per earlier sections, different methods were used to assess the compatibility. These methods showed different compatibility aspects for the particular mixture.

Table 4.55 shows the summary of the results of different methods and the overall rating for tertiary mixtures under the dyeing conditions and processes followed in this study. As mentioned for binary mixtures, the mixtures were given ratings based on the compatibility behavior shown for a particular method. These were highly compatible, compatible, partially compatible, and non-compatible mixtures. Thus, an overall rating was also given for each mixture based on the ratings obtained in all methods.

Marigold/Babool/Madder (MBD), Marigold/Katha/Annatto (MKA), Marigold/ Katha/Madder (MKD), and Pomegranate/Katha/Madder (PKD) mixtures were found to be compatible mixtures. Pomegranate/Babool/Madder (PBD) and Pomegranate/ Katha/Annatto (PKA) were seen as partially compatible mixtures. Other mixtures of Marigold/Babool/Annatto (MBA) and Pomegranate/Babool/Annatto (PBA) were found to be non-compatible.

This will help in accomplishing the objective of the study to check the compatibility and obtain newer shades.

The compatible mixtures found in tertiary mixture assessment were analysed with binary combinations.

The first tertiary mixture Marigold/Katha/Madder (MKD) was found compatible. The compatibility was checked for its possible binary combinations Marigold/Katha (MK), Katha/Madder (KD) and Marigold/Madder (MD) from previous results. Marigold/Katha (MK), and Marigold/Madder (MD) were compatible mixtures while Katha/Madder (KD) was found to be partially compatible mixture. It may be concluded from this that the three dyes Marigold, Katha, and Madder are compatible amongst themselves in all types of combinations.

The second tertiary mixture Marigold/Babool/Madder (MBD) was found compatible. The compatibility was checked for its possible binary combinations Marigold/Babool (MB), Babool/Madder (BD) and Marigold/Madder (MD) from previous results. Marigold/Babool (MB), and Marigold/Madder (MD) were compatible mixtures while Babool/Madder (BD) was found to be non-compatible mixture. It may be concluded from this that the three dyes

Marigold, Babool, and Madder are compatible amongst themselves in all types of combinations except binary combination of Babool/Madder (BD).

The third tertiary Marigold/Katha/Annatto (MKA) was found compatible. The compatibility was checked for its possible binary combinations Marigold/Katha (MK), Katha/Annatto (KA) and Marigold/Annatto (MA) from previous results. Marigold/Katha (MK), and Katha/Annatto (KA) were compatible mixtures while Marigold/Annatto (MA) was found to be non-compatible mixture. It may be concluded from this that the three dyes Marigold, Katha, and Annatto are compatible amongst themselves in all types of combinations except binary combination of Marigold/Annatto (MA).

Another tertiary Pomegranate/Katha/Madder (PKD) was found compatible. The compatibility was checked for its possible binary combinations Pomegranate/Katha (PK), Katha/Madder (KD), and Pomegranate/Madder (PD) from previous results. All the binary combinations were found to be partially compatible mixtures. It may be concluded from this that the three dyes Pomegranate, Katha, and Madder are compatible amongst themselves in all types of combinations keeping in mind about the partial compatibility in binary mixtures.

Table 4.55: Summary of different method's results and overall rating for tertiary mixtures

| Code | Plot -dL vs. dC | Plot -dL Vs K/S | Plot da vs K/S | Plot db vs K/S | Based on change in Hue angle (h°) | | Compatibility factor method (CF) | Visual Rating | Overall Rating |
					Using graphical analysis	Using coefficient of variation (CV)			
MBA	Not compatible	Not compatible	Not compatible	Compatible	Not compatible	Compatible	Partially Compatible	Partially Compatible	Not compatible
MBD	Compatible	Highly Compatible	Compatible	Highly Compatible	Compatible	Partially Compatible	Compatible	Partially Compatible	Compatible
MKA	Compatible	Compatible	Partially Compatible	Compatible	Partially Compatible	Partially Compatible	Compatible	Compatible	Compatible
MKD	Partially Compatible	Partially Compatible	Partially Compatible	Compatible	Partially Compatible	Compatible	Compatible	Compatible	Compatible
PBA	Compatible	Compatible	Not compatible	Compatible	Partially Compatible	Compatible	Not compatible	Partially Compatible	Not compatible
PBD	Not compatible	Highly Compatible	Compatible	Compatible	Partially Compatible	Not compatible	Compatible	Partially Compatible	Partially Compatible
PKA	Compatible	Compatible	Compatible	Compatible	Partially Compatible	Partially Compatible	Partially Compatible	Compatible	Partially Compatible
PKD	Compatible	Highly Compatible	Compatible	Highly Compatible	Compatible	Not compatible	Compatible	Compatible	Compatible

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4.2.2 Dyeing Results of Primary Dyes

Dyeing of each of the six selected dyes was done at varied percentages to prepare the spectral data on the spectrophotometer for recipe prediction. Ten samples were made for each dye, starting from the minimum to maximum possible concentrations. The dye material concentrations (% owf) used were 1%, 2%, 4%, 8%, 12%, 20%, 24%, 32%, 40%, and 44%.

Ten samples were dyed for each dye. A total of 60 samples were dyed for six dyes. These samples were scanned using a spectrophotometer and served as spectral data to predict the recipe. Colorimetric parameters at concentrations mentioned above are mentioned in Table 4.56 (from A to F) for Annatto, Madder, Marigold, Pomegranate, Katha, and Babool dyes.

Table 4.56: Colorimetric parameters of various concentrations for Annatto, Madder, Marigold, Pomegranate, Katha, and Babool dyes (from A to F)

(A)

Sample Number	Annatto Dye Concentration (%)	L*	a*	b*	C*	h	K/S
1	1	89.54	5.4	4.53	7.05	39.99	0.088
2	2	87.81	8.97	7.44	11.65	39.65	0.154
3	4	86.24	11.74	10.04	15.45	40.51	0.233
4	8	82.47	16.54	14.7	22.13	41.62	0.441
5	12	81.44	18.25	17.05	24.97	43.03	0.528
6	20	78.9	21.04	20.31	29.25	43.97	0.75
7	24	78.53	22.01	20.98	30.41	43.61	0.793
8	32	77.46	23.12	22.85	32.5	44.65	0.928
9	40	76.81	23.62	23.86	33.57	45.28	0.998
10	44	76.69	23.54	24.11	33.7	45.66	1.011

(B)

Sample Number	Madder Dye Concentration (%)	L*	a*	b*	C*	h	K/S
1	1	84.7	8.84	2.12	9.09	13.49	0.14
2	2	79.45	13.65	2.68	13.91	11.09	0.286
3	4	75.16	17.4	3.36	17.72	10.91	0.461
4	8	70.17	21.4	4.97	21.96	13.07	0.748
5	12	61.8	26.8	5.98	27.46	12.58	1.517
6	20	54.15	30.12	6.78	30.88	12.68	2.695
7	24	50.14	30.73	7.27	31.58	13.3	3.576
8	32	45.71	27.77	5.83	28.37	11.85	4.417
9	40	44.51	27.25	5.74	27.84	11.89	4.765
10	44	47.37	24.65	4.59	25.07	10.55	3.663

(C)

Sample Number	Marigold Dye Concentration (%)	L*	a*	b*	C*	h	K/S
1	1	90.81	0.64	7.03	7.05	84.77	0.073
2	2	90.8	-0.97	12.31	12.35	94.52	0.122
3	4	89.91	-1.05	15.07	15.1	94.02	0.17
4	8	89.63	-1.24	17.5	17.55	94.08	0.208
5	12	88.81	-1.19	22.43	22.46	93.08	0.306
6	20	88.53	-1.14	27.24	27.26	92.43	0.409
7	24	87.89	-1.17	28.43	28.45	92.4	0.462
8	32	87	-0.44	32.11	32.11	90.81	0.591
9	40	86.33	0.15	34.05	34.05	89.71	0.689
10	44	86.05	0.25	34.45	34.45	89.55	0.72

(D)

Sample Number	Pomegranate Dye Concentration (%)	L*	a*	b*	C*	h	K/S
1	1	91.77	0.05	2.3	2.3	88.8	0.049
2	2	91.39	-0.01	2.68	2.68	90.26	0.056
3	4	91.17	-0.11	3.59	3.59	91.71	0.072
4	8	89.6	-0.97	8.55	8.61	96.53	0.213
5	12	88.16	-1.01	12.86	12.9	94.52	0.383
6	20	82.24	-1.13	25.79	25.81	92.54	1.438
7	24	79.86	-0.47	28.95	28.95	90.97	2.003
8	32	76.29	0.69	31.96	31.97	88.72	2.854
9	40	73.52	1.45	33.62	33.65	87.5	3.887
10	44	71.62	2.27	32.71	32.78	85.99	3.915

(E)

Sample Number	Katha Dye Concentration (%)	L*	a*	b*	C*	h	K/S
1	1	84.79	4.21	7.19	8.33	59.61	0.195
2	2	81.44	6.26	9.77	11.61	57.34	0.322
3	4	77.62	9.36	11.82	15.07	51.6	0.473
4	8	69.1	13.8	14.3	19.87	45.99	0.945
5	12	68.24	14.3	14.51	20.38	45.41	1.002
6	20	60.83	16.92	15.77	23.13	42.97	1.704
7	24	58.4	17.72	15.97	23.85	42.01	2.003
8	32	55.34	18.77	16.96	25.3	42.08	2.542
9	40	53.96	19.33	17.61	26.15	42.32	2.834
10	44	54.26	18.12	15.9	24.11	41.25	2.582

(F)

Sample Number	Babool Dye Concentration (%)	L*	a*	b*	C*	h	K/S
1	1	89.11	1.32	5.12	5.29	75.45	0.107
2	2	87.23	2.03	7.04	7.32	73.87	0.168
3	4	86.11	2.52	8.46	8.83	73.37	0.217
4	8	81.56	5.06	11.82	12.85	66.81	0.422
5	12	74.69	7.93	14.73	16.73	61.66	0.85
6	20	66.41	10.63	16.67	19.77	57.45	1.628
7	24	63.6	11.22	16.87	20.25	56.36	1.953
8	32	58.34	11.92	15.72	19.73	52.81	2.475
9	40	57.1	12.23	16.96	20.91	54.18	2.897
10	44	58.77	11.39	15.6	19.32	53.84	2.361

Dye concentrations vs. K/S for Annatto, Madder, Marigold, Pomegranate, Katha, and Babool dyes are shown in Figure 4.66 (from A to F). It is visible from the plots that the K/S increased with an increase in concentration for all the dyes. In most cases, with the increases in concentration, the K/S increased to a certain extent and then became constant or decreased. It was also observed that the plot of dye concentrations vs. K/S was almost linear for most cases. In the case of Pomegranate dye, the plot was not linear, and K/S increased at a lower rate for the first five samples and then increased at a faster rate. The data was stored successfully in a spectrophotometer for recipe prediction.
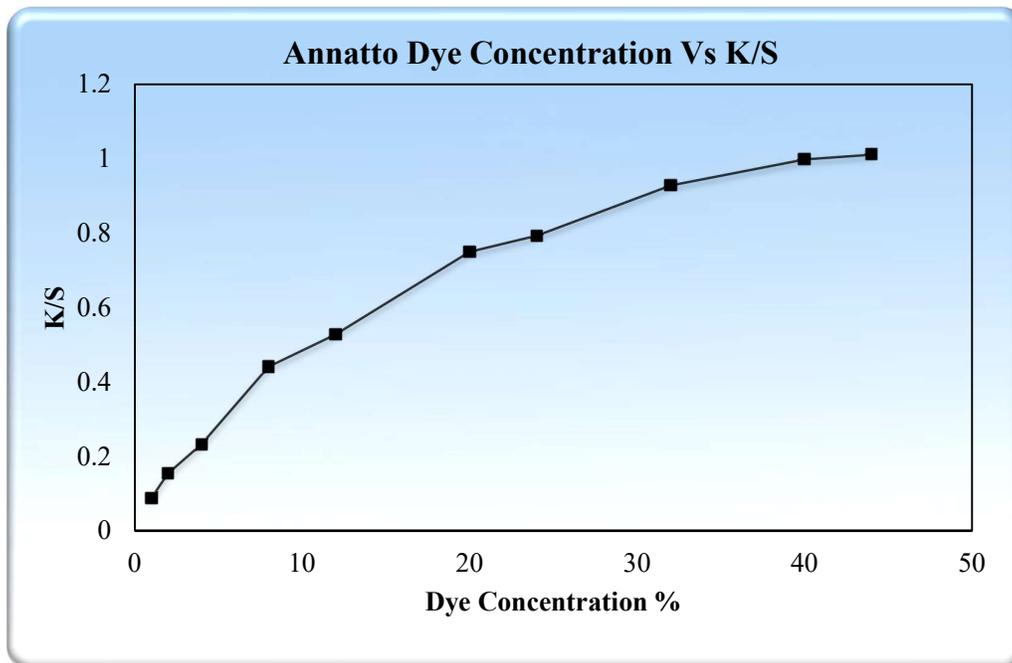
(A)
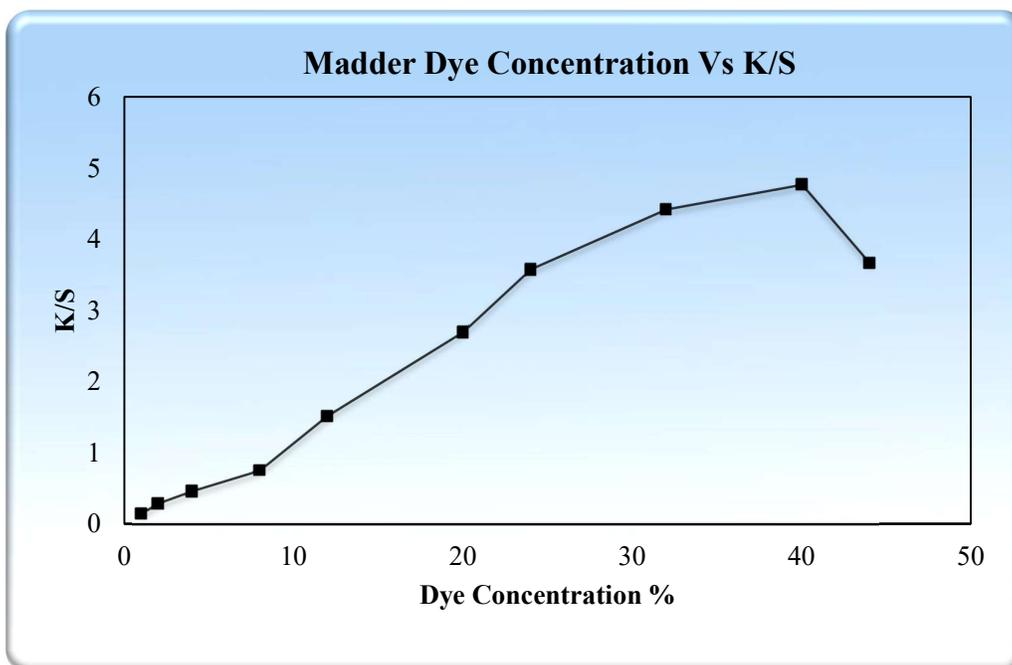
(B)
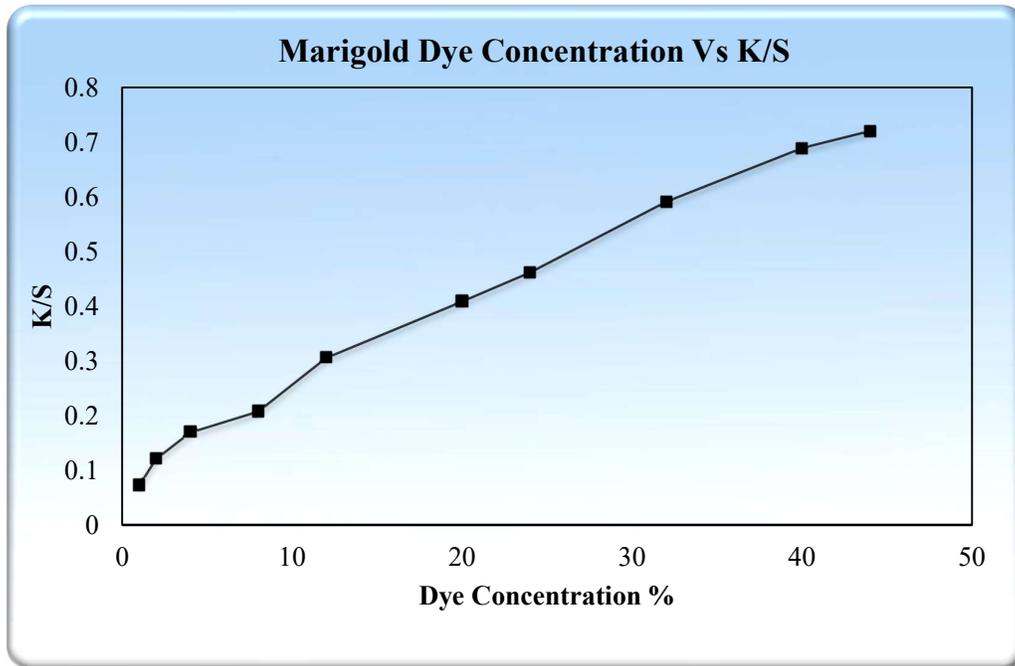
(C)
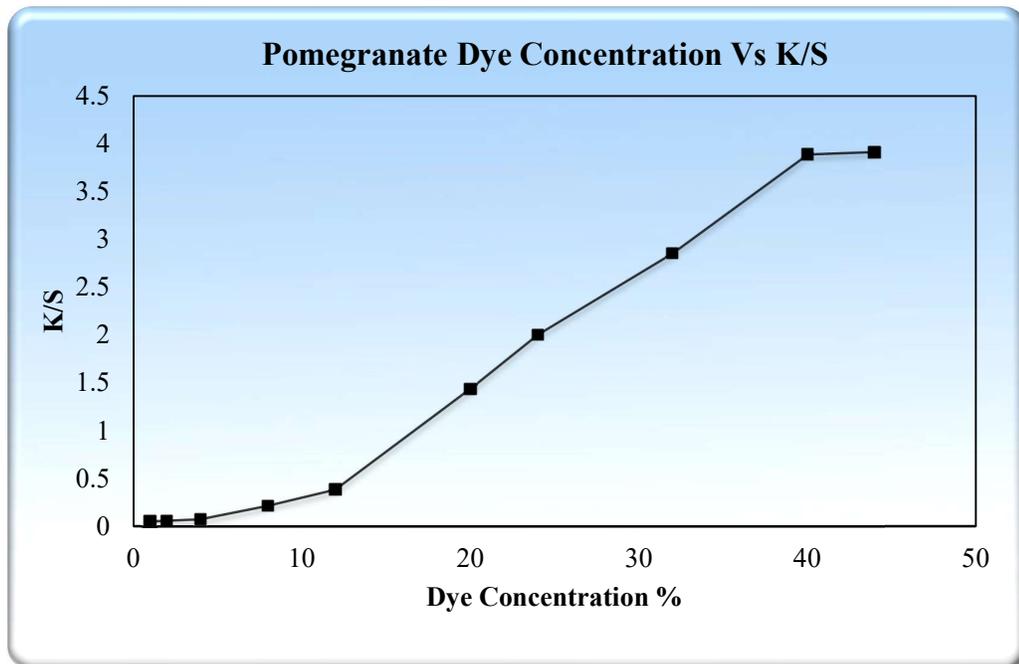
(D)
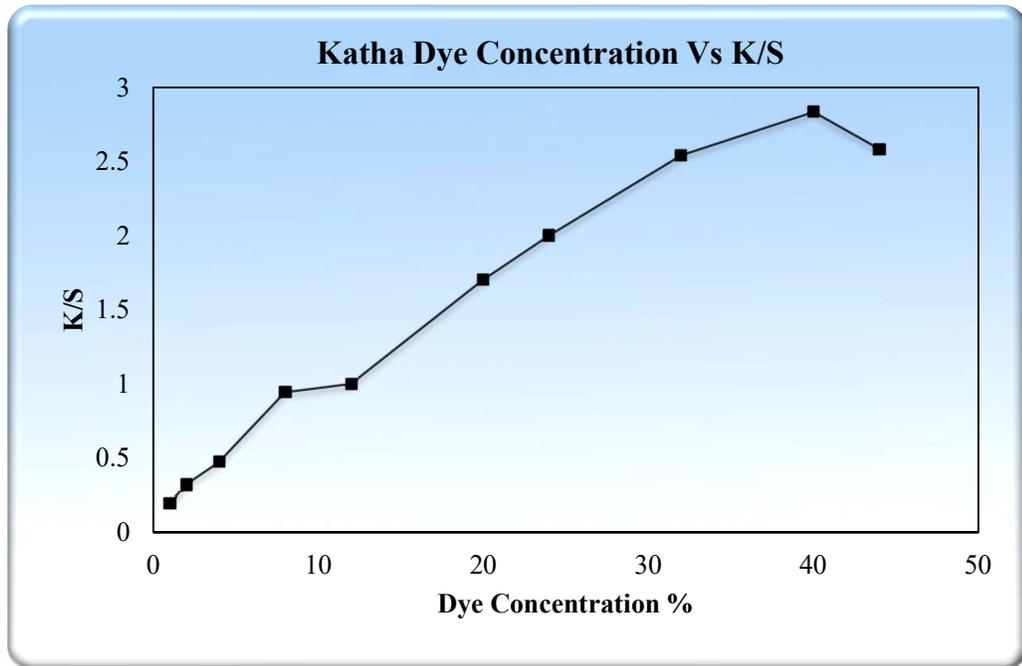
(E)
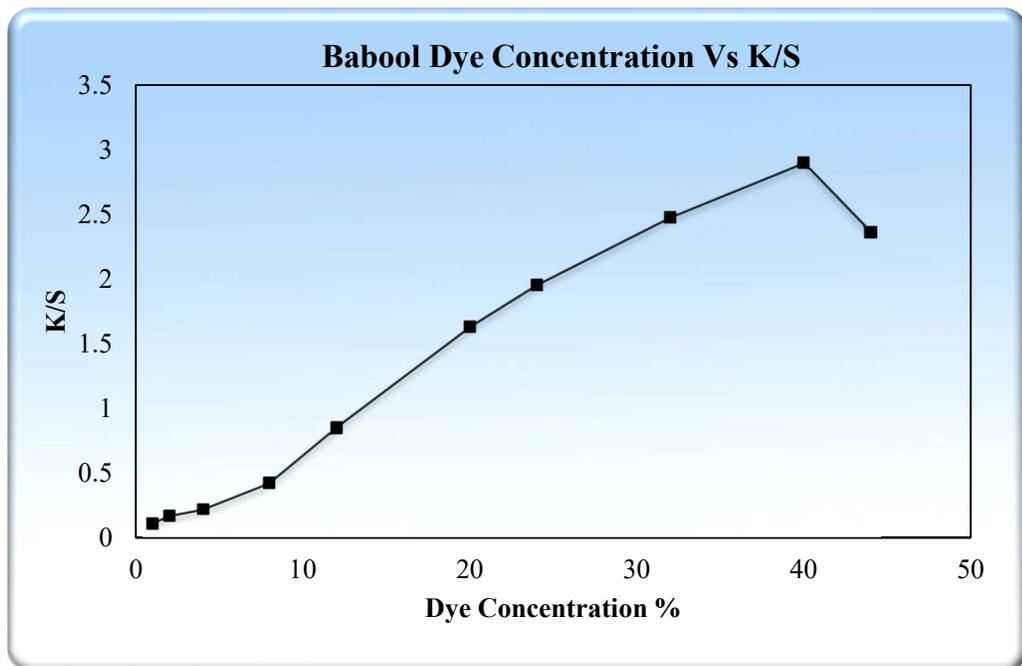
(F)

Figure 4.66: Dye concentrations vs. K/S for Annatto, Madder, Marigold, Pomegranate, Katha, and Babool dyes (from A to F)

4.2.3 Prediction of Recipe and Dyeing of Samples as per standard

As per the study's objective, the recipe was predicted for several chosen standards using computer color-matching equipment. The predicted recipe for each standard was used to dye the samples. The suitable standards from the PANTONE – Cotton planner were selected as per Table 4.57.

Table 4.57: List of Pantone standards for recipe prediction

S. No.	PANTONE-TCX number
1	TCX 15-1327
2	TCX 16-1317
3	TCX 15-1317
4	TCX 14-1122
5	TCX 16-1220
6	TCX 15-1213
7	TCX 15-1415
8	TCX 14-1316

The recipe was predicted using a spectrophotometer, and some recipe options were obtained. A compatible, suitable recipe option was selected from the obtained options. It has been observed in practical work with CCM that the sample dyed using the predicted recipe does not match entirely with the standard, and hence, the recipe was optimized to match visually. Colorimetric and color difference parameters were recorded for the standard and dyed samples using two CIE standard illuminants, D65 and A. The L*, a*, b*, C*, and h values were obtained for standard and sample in both light sources. The color difference parameters dE, dL*, dC*, dh, and metamerism index were also calculated. Recipe prediction and matching details of the standards are mentioned in Table 4.58 to Table 4.65.

1.   Color Matching for TCX 15-1327

For this matching, there was some adjustment in the predicted recipe to match the standard. The observed dE value in the primary light source was 1.15, and the metamerism

value was 0.9. The results obtained are satisfactory, and the recipe may be used for dyeing. The sample of shade matching done is shown in Figure 4.67.

Table 4.58: Recipe prediction and matching details for TCX 15-1327 (A, B, C & D)

(A)   Pantone number and sample code

PANTONE Number	TCX 15-1327
Sample Dyed Code	MDS1

(B)   Recipe by spectrophotometer and optimized recipe

Recipe by CCM		Optimized Sample Recipe (MDS1)	
Dye	**Concentration (%)**	**Dye**	**Concentration (%)**
Marigold	25.45	Marigold	21.5
Madder	7.15	Madder	3

(C)   Colorimetric parameters for standard and dyed sample

Colorimetric Parameters	Standard		Sample	
	Light Source			
	D65	**A**	**D65**	**A**
L*	68.83	72.52	68.81	72.4
a*	19.78	24.12	18.79	22.19
b*	24.25	30.01	24.47	30.26
C*	31.29	38.5	30.86	37.52
h	50.78	51.2	52.46	53.72

(D)   Color difference parameters

Color Difference Parameters in different light sources	Light Source	dE	dL*	dC*	dh	Metamerism Index (MI)	Verbal Comments for dyed sample
	D65	1.15	0.01	0.21	1.13	0	Darker, Greener (Less Red),Yellow (Less blue), Duller
	A	1.96	0.05	0.43	1.91	0.9	Darker, Greener (Less Red),Yellow (Less blue), Duller

2.   Color Matching for TCX 16-1317

For this matching, there was some adjustment in the predicted recipe to match the standard. The required concentration of Marigold was adjusted significantly. The observed dE value in the primary light source was 4.99, and the metamerism value was 0.66. The recipe may be further adjusted to match the standard and reduce the dE value, and the recipe can be used for dyeing. The sample of shade matching done is shown in Figure 4.67.

Table 4.59: Recipe prediction and matching details for TCX 16-1317 (A, B, C & D)

(A)   Pantone number and sample code

PANTONE Number	TCX 16-1317
Sample Dyed Code	MBS2

(B)   Recipe by spectrophotometer and optimized recipe

Recipe by CCM		Optimized Sample Recipe (MBS2)	
Dye	Concentration (%)	Dye	Concentration (%)
Marigold	10.75	Marigold	4
Babool	15.7	Babool	13.5

(C)   Colorimetric parameters for standard and dyed sample

Colorimetric Parameters	Standard		Sample	
	Light Source			
	D65	A	D65	A
L*	68.16	70.55	66.49	68.76
a*	11.96	15.43	9.8	13.32
b*	16.12	19.86	18.41	21.47
C*	20.07	25.15	20.85	25.27
h	53.41	52.12	61.95	58.17

(D)   Color difference parameters

	Light Source	dE	dL*	dC*	dh	Metamerism Index (MI)	Verbal Comments for dyed sample
Color Difference Parameters in different light sources	D65	4.99	0.66	0.47	4.92	0	Darker, Greener (Less Red), Yellow (Less blue), Brighter
	A	3.85	0.7	0.06	3.78	0.66	Darker, Greener (Less Red), Yellow (Less blue), Brighter

3.   Color Matching for TCX 15-1317

For this matching, there was some adjustment in the predicted recipe to match the standard. The observed dE value in the primary light source was 2.54, and the metamerism value was 1.13. The results obtained are satisfactory, and the recipe may be used for dyeing. The sample of shade matching done is shown in Figure 4.67.

Table 4.60: Recipe prediction and matching details for TCX 15-1317 (A, B, C & D)

(A)   Pantone number and sample code

PANTONE Number	TCX 15-1317
Sample Dyed Code	BAS2

(B)   Recipe by spectrophotometer and optimized recipe

Recipe by CCM		Optimized Sample Recipe (BAS2)	
Dye	**Concentration (%)**	**Dye**	**Concentration (%)**
Babool	15	Babool	19
Annatto	9	Annatto	9

(C)   Colorimetric parameters for standard and dyed sample

Colorimetric Parameters	Standard		Sample	
	Light Source			
	D65	**A**	**D65**	**A**
L*	68.03	70.42	62.78	65.42
a*	11.91	15.37	13.52	16.08
b*	16.08	19.81	17.35	21.44
C*	20.01	25.07	21.99	26.81
h	53.45	52.17	52.04	53.11

(D)   Color difference parameters

	Light Source	dE	dL*	dC*	dh	Metamerism Index (MI)	Verbal Comments for dyed sample
Color Difference Parameters in different light sources	D65	2.54	-2.07	1.2	-0.84	0	Darker, Redder (Less Green), Yellow (Less blue), Brighter
	A	2.24	-1.94	0.94	0.6	1.13	Darker, Redder (Less Green), Yellow (Less blue), Brighter

4.   Color Matching for TCX 14-1122

For this matching, there was high adjustment in the predicted recipe to match the standard. The observed dE value in the primary light source was 2.15, and the metamerism value was 0.9. The results obtained are satisfactory, and the recipe may be used for dyeing. The sample of shade matching done is shown in Figure 4.67.

Table 4.61: Recipe prediction and matching details for TCX 14-1122 (A, B, C & D)

(A)   Pantone number and sample code

PANTONE Number	TCX 14-1122
Sample Dyed Code	MBDS1

(B)   Recipe by spectrophotometer and optimized recipe

Recipe by CCM		Optimized Sample Recipe (PBS1)	
Dye	Concentration (%)	Dye	Concentration (%)
Marigold	10	Marigold	25
Babool	12.5	Babool	4
Madder	6.5	Madder	1.5

(C)   Colorimetric parameters for standard and dyed sample

Colorimetric Parameters	Standard		Sample	
	Light Source			
	D65	A	D65	A
L*	75.72	78.49	71.9	74.95
a*	10.49	14.48	12.26	16.36
b*	26.92	30.54	28.82	33.06
C*	28.89	33.8	31.32	36.89
h	68.68	64.61	66.93	63.65

(D)   Color difference parameters

	Light Source	dE	dL*	dC*	dh	Metamerism Index (MI)	Verbal Comments for dyed sample
Color Difference Parameters in different light sources	D65	2.15	-1.44	1.23	-1.02	0	Darker, Redder (Less Green),Yellow (Less blue), Brighter
	A	2.06	-1.31	1.45	-0.65	0.9	Darker, Redder (Less Green), Yellow (Less blue), Brighter

5.   Color Matching for TCX 16-1220

For this matching, there was some adjustment in the predicted recipe to match the standard. The observed dE value in the primary light source was 2.25, and the metamerism value was 1.9. The value of metamerism was high in this case and the recipe may be avoided for this standard. The sample of shade matching done is shown in Figure 4.67.

Table 4.62: Recipe prediction and matching details for TCX 16-1220 (A, B, C & D)

(A)   Pantone number and sample code

PANTONE Number	TCX 16-1220
Sample Dyed Code	MKDS2

(B)   Recipe by spectrophotometer and optimized recipe

Recipe by CCM		Optimized Sample Recipe (MKDS2)	
Dye	**Concentration (%)**	**Dye**	**Concentration (%)**
Marigold	3.9	Marigold	4
Katha	9.1	Katha	7
Madder	2.1	Madder	1.5

(C)   Colorimetric parameters for standard and dyed sample

Colorimetric Parameters	Standard		Sample	
	Light Source			
	D65	**A**	**D65**	**A**
L*	65.8	68.83	63.66	66.82
a*	16.91	20.91	18.19	20.59
b*	17.87	22.35	16.91	22.2
C*	24.6	30.61	24.84	30.28
h	46.58	46.89	42.89	47.14

(D)   Color difference parameters

	Light Source	dE	dL*	dC*	dh	Metamerism Index (MI)	Verbal Comments for dyed sample
Color Difference Parameters in different light sources	D65	2.25	-0.86	0.13	-2.08	0	Darker, Redder (Less Green), Blue (Less Yellow), Brighter
	A	0.82	-0.79	-0.16	0.16	1.9	Darker, Greener (Less Red), Blue (Less Yellow), Duller

6.   Color Matching for TCX 15-1213

For this matching, there was some adjustment in the predicted recipe to match the standard. The required concentration of Pomegranate was adjusted significantly. The observed dE value in the primary light source was 2.96, and the metamerism value was 3.43. The value of metamerism was high in this case and the recipe may be avoided for this standard. The sample of shade matching done is shown in Figure 4.67.

Table 4.63: Recipe prediction and matching details for TCX 15-1213 (A, B, C & D)

(A)   Pantone number and sample code

PANTONE Number	TCX 15-1213
Sample Dyed Code	PBS1

(B)   Recipe by spectrophotometer and optimized recipe

Recipe by CCM		Optimized Sample Recipe (PBS1)	
Dye	**Concentration (%)**	**Dye**	**Concentration (%)**
Pomegranate	14.95	Pomegranate	6
Babool	11.45	Babool	14.5

(C)   Colorimetric parameters for standard and dyed sample

Colorimetric Parameters	**Standard**		**Sample**	
	Light Source			
	D65	**A**	**D65**	**A**
L*	68.93	70.8	66.67	68.79
a*	5.9	13.18	8.18	12.29
b*	19.64	20.68	19.19	21.5
C*	20.51	24.52	20.86	24.77
h	73.25	57.47	66.89	60.23

(D)   Color difference parameters

	Light Source	**dE**	**dL***	**dC***	**dh**	**Metamerism Index (MI)**	**Verbal Comments for dyed sample**
Color Difference Parameters in different light sources	D65	2.96	0.89	0.21	2.82	0	Darker, Redder (Less Green), Blue (Less Yellow), Brighter
	A	1.89	0.78	0.13	1.72	3.43	Darker, Greener (Less Red), Yellow (Less blue), Brighter

7.   **Color Matching for TCX 15-1415**

For this matching, there was some adjustment in the predicted recipe to match the standard. The required concentration of Annatto was adjusted significantly. The observed dE value in the primary light source was 4.39, and the metamerism value was 0.69. The recipe may be further adjusted to match the standard and reduce the dE value, and the recipe can be used for dyeing. The dyed sample code was KAS1. The sample of shade matching done is shown in Figure 4.67.

Table 4.64: Recipe prediction and matching details for TCX 15-1415 (A, B, C & D)

(A)   Pantone number and sample code

PANTONE Number	TCX 15-1415
Sample Dyed Code	KAS1

(B)   Recipe by spectrophotometer and optimized recipe

Recipe by CCM		Optimized Sample Recipe (KAS1)	
Dye	**Concentration (%)**	**Dye**	**Concentration (%)**
Katha	4.4	Katha	3
Annatto	3.4	Annatto	14

(C)   Colorimetric parameters for standard and dyed sample

Colorimetric Parameters	Standard		Sample	
	Light Source			
	D65	**A**	**D65**	**A**
L*	73.88	76.94	72.79	75.71
a*	19.44	20.87	16.83	17.51
b*	12.35	17.63	15.36	20.74
C*	23.04	27.32	22.79	27.15
h	32.42	40.18	42.37	49.82

(D)   Color difference parameters

	Light Source	dE	dL*	dC*	dh	Metamerism Index (MI)	Verbal Comments for dyed sample
Color Difference Parameters in different light sources	D65	4.39	-0.42	-0.14	4.37	0	Darker, Greener (Less Red), Yellow (Less blue), Duller
	A	5.16	-0.46	-0.09	5.14	0.69	Darker, Greener (Less Red), Yellow (Less blue), Duller

8.   Color Matching for TCX 14-1316

For this matching, there was some adjustment in the predicted recipe to match the standard. The required concentration of Annatto was adjusted significantly. The observed dE value in the primary light source was 0.93, and the metamerism value was 3.04. The value of metamerism was high in this case, and the recipe may be avoided for this standard.

It may be noted that PANTONE TCX 14-1316 and PANTONE TCX 15-1415 (previous number 7) tones are closer to each other, and dyed sample KAS1 was the same for both of them. It was observed that the color match for PANTONE TCX 14-1316 was more suitable. The sample of shade matching done is shown in Figure 4.67.

Table 4.65: Recipe prediction and matching details for TCX 14-1316 (A, B, C & D)

(A)   Pantone number and sample code

PANTONE Number	TCX 14-1316
Sample Dyed Code	KAS1

(B)   Recipe by spectrophotometer and optimized recipe

Recipe by CCM		Optimized Sample Recipe (KAS1)	
Dye	Concentration (%)	Dye	Concentration (%)
Katha	4.6	Katha	3
Annatto	2.4	Annatto	14

(C)   Colorimetric parameters for standard and dyed sample

Colorimetric Parameters	Standard		Sample	
	Light Source			
	D65	A	D65	A
L*	73.72	76.46	72.79	75.71
a*	15.88	19.39	16.83	17.51
b*	14.3	18.74	15.36	20.74
C*	21.37	26.97	22.79	27.15
h	41.98	44	42.37	49.82

(D)   Color difference parameters

	Light Source	dE	dL*	dC*	dh	Metamerism Index (MI)	Verbal Comments for dyed sample
Color Difference Parameters in different light sources	D65	0.93	-0.36	0.83	0.19	0	Darker, Redder (Less Green), Yellow (Less blue), Brighter
	A	3.3	-0.28	0.09	3.29	3.04	Darker, Greener (Less Red), Yellow (Less blue), Brighter

As per the color match and its analysis, it was established that the color matching could be done successfully. However, in some cases, the selected recipe may not be suitable and have to be revised. This will help the dyer to select the appropriate combination and recipe.

This also accomplishes the objective of the study to obtain newer shades. However, the dyes chosen in this study are limited, and hence, the color matching can be done for that gamut only.
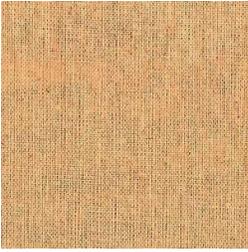
TCX 15-1327		MDS1
TCX 16-1317		MBS2
TCX 15-1317		BAS2
TCX 14-1122		MBDS1
TCX 16-1220		MKDS2
TCX 15-1213		PBS1
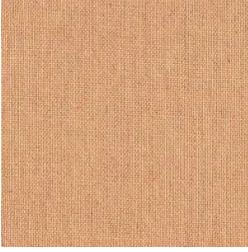
TCX 15-1415   KAS1
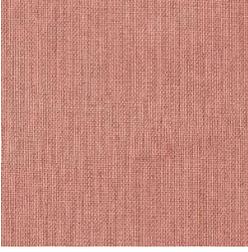
TCX 14-1316   KAS1
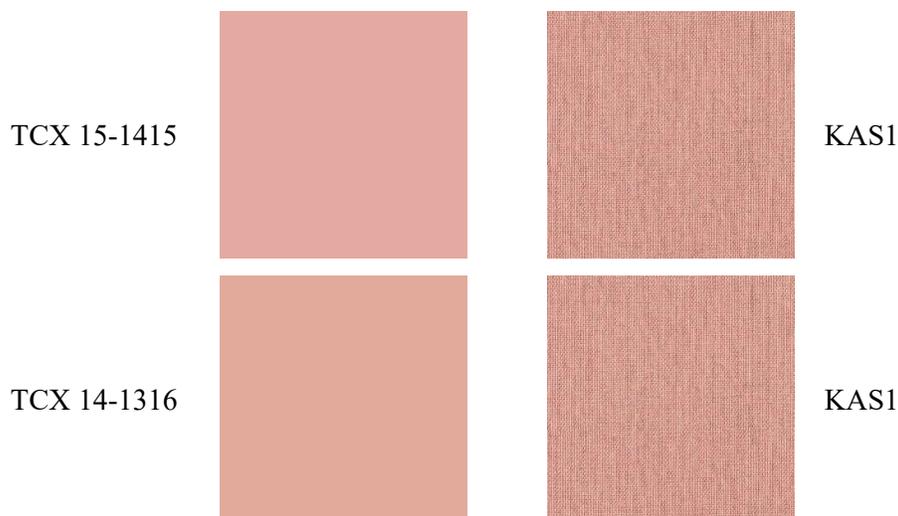
Figure 4.67: Shade matching with PANTONE numbers

4.3 Color Fastness Tests

Color fastness properties were evaluated for selected samples. In colorfastness tests, color fastness to washing, color fastness to light, and color fastness to rubbing were done. The samples were chosen from pure dyes, binary, and tertiary combinations. A sample of dye concentration of 24% owf was tested for every primary dye. For binary and tertiary combinations, sample number 5 from set I was chosen for each combination. A total of 26 samples were tested for color fastness.

(A)   Color Fastness to Washing

Colorfastness to washing test was done for 26 samples using the AATCC test method 61-2009 (1B). The test was conducted on laundr-o-meter, make-Ramp Impex Pvt Ltd. Utilizing the geometric greyscale, the multi-fiber strip's staining and the dyed samples' color change were visually evaluated. The color difference between stained and white fabric was compared and quantified using a standardized scale. The evaluation of color change entailed quantifying the difference in color between the tested sample and the original fabric using a scale.

Wash color fastness ratings for pure dyes, binary, and tertiary combinations are shown in Table 4.66 to Table 4.70. It shows the color change on samples and color staining on various fiber components. It was observed that the Marigold showed very good fastness and

good fastness was shown by Babool and Pomegranate dyes. Katha, Annatto, and Madder dyes showed average color fastness properties. It was also observed that the Madder stained nylon fibers and almost no staining on any other fiber by any other dye. It may be attributed to the high affinity of Madder dye towards nylon material as mentioned by Sadeghi-Kiakhani, (2015)

In the case of binary combinations, the Pomegranate/Babool mixture showed very good fastness. Babool/Annatto, Marigold/Babool, and Babool/Madder mixtures showed good fastness properties, while all other mixtures showed average results.

In tertiary combinations, the Pomegranate/Babool/Madder mixture showed very good fastness, and the Pomegranate/Babool/Annatto showed good fastness, while other mixtures showed average fastness.

Table 4.66: Color fastness to washing for pure dyes

Test Sample	Color change	Color Staining					
		Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Katha	3-4	4-5	4-5	4-5	4-5	4-5	4-5
Babool	4	4-5	4-5	4-5	4-5	4-5	4-5
Pomegranate	4	4-5	4-5	4-5	4-5	4-5	4-5
Marigold	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Annatto	3	4-5	4-5	4-5	4-5	4-5	4-5
Madder	3-4	4-5	4-5	4-5	4	4-5	4-5

Table 4.67: Color fastness to washing for binary combinations

Sample Code	Color change	Color Staining					
		Wool	**Acrylic**	**Polyester**	**Nylon**	**Cotton**	**Acetate**
PA	3-4	4-5	4-5	4-5	4-5	4-5	4-5
KA	3	4-5	4-5	4-5	4-5	4-5	4-5
BA	4	4-5	4-5	4-5	4-5	4-5	4-5
PB	4-5	4-5	4-5	4-5	4-5	4-5	4-5
MK	3	4-5	4-5	4-5	4-5	4-5	4-5
PK	3	4-5	4-5	4-5	4-5	4-5	4-5
MD	3-4	4-5	4-5	4-5	4	4-5	4-5
MA	3-4	4-5	4-5	4-5	4-5	4-5	4-5
MB	4	4-5	4-5	4-5	4-5	4-5	4-5
BD	4	4-5	4-5	4-5	4	4-5	4-5
KD	3-4	4-5	4-5	4-5	4	4-5	4-5
PD	3-4	4-5	4-5	4-5	3-4	4-5	4-5

Table 4.68: Color fastness to washing for tertiary combinations

Sample Code	Color change	Color Staining					
		Wool	**Acrylic**	**Polyester**	**Nylon**	**Cotton**	**Acetate**
MBD	3	4-5	4-5	4-5	3-4	4-5	4-5
MKA	3	4-5	4-5	4-5	4-5	4-5	4-5
PKD	3	4-5	4-5	4-5	4-5	4-5	4-5
MKD	3	4-5	4-5	4-5	4-5	4-5	4-5
MBA	3	4-5	4-5	4-5	4-5	4-5	4-5
PBD	4-5	4-5	4-5	4-5	4-5	4-5	4-5
PKA	3-4	4-5	4-5	4-5	4-5	4-5	4-5
PBA	4	4-5	4-5	4-5	4-5	4-5	4-5

The current study examined the wash fastness of samples dyed individually, in binary and ternary combinations, with respect to their compatibility and incompatibility. The findings are presented in Table 4.69 and Table 4.70. It shows the color fastness of mixtures with respect to the component dyes in the mixtures. It was observed in most cases that the color fastness to washing for mixtures was in accordance with the fastness of component dyes. However, in some instances, the mixture's fastness was found to be lower or higher than the component dyes. **By examining the results, it was visible that there was no relation between compatibility/non-compatibility and color fastness.**

Table 4.69: Colorfastness to washing of binary mixtures with respect to component dyes

| Sample Code (AB) | Mixture | | Individual Dyes | | | |
| | | | Component A | | Component B | |
	Color Change	Color Staining (Nylon)	Color Change	Color Staining (Nylon)	Color Change	Color Staining (Nylon)
PA	3-4	4-5	4	4-5	3	4-5
KA	3	4-5	3-4	4-5	3	4-5
BA	4	4-5	4	4-5	3	4-5
PB	4-5	4-5	4	4-5	4	4-5
MK	3	4-5	4-5	4-5	3-4	4-5
PK	3	4-5	4	4-5	3-4	4-5
MD	3-4	4	4-5	4-5	3-4	4
MA	3-4	4-5	4-5	4-5	3	4-5
MB	4	4-5	4-5	4-5	4	4-5
BD	4	4	4	4-5	3-4	4
KD	3-4	4	3-4	4-5	3-4	4
PD	3-4	3-4	4	4-5	3-4	4

Table 4.70: Colorfastness of washing tertiary mixtures with respect to component dyes

Sample Code (ABC)	Mixture		Individual Dyes					
			Component A		Component B		Component C	
	Color Change	Color Staining (Nylon)	Color Change	Color Staining (Nylon)	Color Change	Color Staining (Nylon)	Color Change	Color Staining (Nylon)
MBD	3	3-4	4-5	4-5	4	4-5	3-4	4
MKA	3	4-5	4-5	4-5	3-4	4-5	3	4-5
PKD	3	4-5	4	4-5	3-4	4-5	3-4	4
MKD	3	4-5	4-5	4-5	3-4	4-5	3-4	4
MBA	3	4-5	4-5	4-5	4	4-5	3	4-5
PBD	4-5	4-5	4	4-5	4	4-5	3-4	4
PKA	3-4	4-5	4	4-5	3-4	4-5	3	4-5
PBA	4	4-5	4	4-5	4	4-5	3	4-5

(B)   Color Fastness to Light

Light color fastness ratings for pure dyes, binary, and tertiary combinations are shown in Table 4.71 to Table 4.73. It was observed that the Babool and Madder showed good fastness. Pomegranate, Katha, and Marigold dyes showed average light fastness properties, while Annatto showed average to poor light fastness.

In the case of binary combinations, the Pomegranate/Madder mixture showed good fastness, while Marigold/Annatto and Marigold/Katha showed average to poor and poor light fastness, respectively. All other binary mixtures showed average ratings.

In the case of tertiary combinations, the Marigold/Katha/Madder mixture showed good light fastness. Marigold/Katha/Annatto and Pomegranate/Babool/ Annatto showed average to poor fastness ratings, while Pomegranate/Katha/Annatto mixtures showed poor ratings. All other tertiary mixtures showed average ratings. Table 4.72 and Table 4.73 also show the light fastness of binary and tertiary mixtures with respect to the fastness of component dyes. The current study examined the light fastness of samples dyed individually, as well as binary and ternary combinations, with respect to their compatibility and incompatibility. It shows the color fastness of mixtures with respect to the component dyes in the mixtures. It was observed that in most cases, the color fastness to light for mixtures was in accordance with the fastness of component dyes. However, in some instances, the mixture's fastness was found to be lower or higher than the component dyes. **By examining the results, it was visible that there was no relation between compatibility/non-compatibility and color fastness.**

Table 4.71: Color fastness to light for pure dyes

Test Sample	Rating
Katha	3
Babool	4
Pomegranate	3-4
Marigold	3
Annatto	2-3
Madder	4

Table 4.72: Color fastness to light for binary combination with respect to component dyes

Sample Code (AB)	Mixture	Component A	Component B
PA	3	3-4	2-3
KA	3	3	2-3
BA	3	4	2-3
PB	3-4	3-4	4
MK	2	3	3
PK	3-4	3-4	3
MD	3-4	3	4
MA	2-3	3	2-3
MB	3-4	3	4
BD	3-4	4	4
KD	3-4	3	4
PD	4	3-4	4

Table 4.73: Color fastness to light for tertiary combination with respect to component dyes

Sample Code (ABC)	Mixture	Component A	Component B	Component C
MBD	3-4	3	4	4
PKD	3-4	3-4	3	4
MKD	4	3	3	4
MKA	2-3	3	3	2-3
MBA	3	3	4	2-3
PBD	3	3-4	4	4
PKA	2	3-4	3	2-3
PBA	2-3	3-4	4	2-3

(C)   Color Fastness to Rubbing

Rubbing color fastness ratings for pure dyes, binary, and tertiary combinations are shown in Table 4.74 to Table 4.76. The test samples were checked for color change and staining in the dry and wet states. The results show that all the samples of pure dyes obtained very good to good color fastness ratings except in the case of Madder. Madder showed some staining in wet conditions and got an average rating.

All the binary and tertiary mixture samples also showed very good to good rubbing fastness ratings. **It was visible that there was no relation between the compatibility/non-compatibility and color fastness to rubbing.**

Table 4.74: Color fastness to rubbing for pure dyes

Test Sample	Color change		Staining	
	Dry	**Wet**	**Dry**	**Wet**
Katha	5	4-5	5	4-5
Babool	5	4-5	5	4-5
Pomegranate	5	4-5	5	4-5
Marigold	5	4-5	5	4-5
Annatto	5	5	5	5
Madder	4-5	4	4-5	3-4

Table 4.75: Color fastness to rubbing for binary mixtures

Sample Code	Color change		Staining	
	Dry	**Wet**	**Dry**	**Wet**
PA	5	4-5	5	4-5
KA	5	4-5	5	4-5
BA	5	4-5	5	4-5
PB	5	4-5	5	4-5
MK	5	4-5	5	4-5
PK	5	4-5	5	4-5
MD	5	4-5	5	4-5
MA	5	4-5	5	4-5
MB	5	4-5	5	4-5
BD	4-5	4	4-5	3-4
KD	5	4	5	4
PD	5	4	5	4

Table 4.76: Color fastness to rubbing for tertiary mixtures

Sample Code	Color change		Staining	
	Dry	**Wet**	**Dry**	**Wet**
MBD	5	4	5	4
MKA	5	4-5	5	4-5
PKD	4-5	4	4-5	4
MKD	5	4-5	5	4-5
MBA	5	4-5	5	4-5
PBD	5	4-5	5	4
PKA	5	4-5	5	4
PBA	5	4-5	5	4-5

4.4 Anti-Microbial testing results

Anti- microbial test was done for each sample of primary dyed samples using AATCC 100:-2019 test method. The test results were assessed as the percentage of bacterial reduction for both bacteria used in the method.

The anti-bacterial results for six primary dyes are shown in Table 4.77. It shows that all the dyes show approx. 90% or above bacterial reduction.

Table 4.77: Anti-Microbial results

Dye	Bacteria (Percentage Bacterial Reduction)	
	Staphylococcus aureus	*Klebsiella pneumonia*
Marigold	89.6%	92.10%
Pomegranate	91.3%	90.90%
Babool	93.68%	89.23%
Katha	99.13%	99.10%
Madder	90.0%	90.60%
Annatto	96.8%	96.90%