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Parametric Model of Absorbance Spectra for NIR and SWIR Dyes and Dye-Mixtures in Fabric Using Gaussian Functions

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14. ABSTRACT This study describes parametric modeling of near-infrared (NIR, 0.7-0.9 μm) and shortwave infrared (SWIR, 0.9-1.7 μm) absorbance spectra, which is for optimizing NIR-SWIR reflectance of dyed fabrics with respect to given illuminations and background environments. The parametric models are linear combinations of gaussian functions, which are for modeling dyes in fabric whose absorption spectra span the NIR/SWIR spectral range. In general, decomposition of an absorbance spectrum in terms of linear combinations of gaussian functions is not unique. This suggests investigating what are optimal linear combinations of gaussian functions for modeling given spectra. Prototype modeling is applied to NIR/SWIR absorbing dyes, and their mixtures, in fabric samples, which consist of a cotton blend. The results of this study demonstrate parametric modeling using linear combinations of gaussian functions for simulating NIR/SWIR absorbance spectra, which are for variable dye and dye blend concentrations in fabrics.					
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1. Introduction

Experiments with NIR/SWIR-absorbing dyes in fabric have demonstrated the ability to adjust NIR/SWIR reflectances of materials to match specified spectral response, i.e., reflectance spectra. There exists a need to develop and apply NIR/SWIR signature reduction treatments to existing and future military uniforms. One solution is the development of parameter spaces for process optimization of dyed fabrics. Optimization algorithms would use parameter spaces to determine optimum dye-fabric combinations and fabrication processes given a target reflectance spectrum and the constituent materials available. To reach the point of process optimization, various NIR and SWIR absorbing dyes, military fabrics, fabrication processes, and parametric reflectance models should be examined.

Optimizing reflectance spectra of dyed fabrics with respect to given specifications poses the problem of optimizing diffuse reflectance of materials. Diffuse reflection defines a separate regime for spectroscopic analysis of material surfaces and layers. The physical processes underlying diffuse reflectance are discussed in references [1-6]. Parametric models applied for these analyses include those based on multiple reflections from layered systems (i.e., scattering matrix formulations) [7,8], the Kubelka-Munk theory of diffuse reflectance (and formulations derived from it) [9-12], and exponential-function representations (formally similar to the Beer-Lambert Law) [3]. The parametric model of diffuse reflectance presented in this study, which is for analysis and characterization of dyed fabrics, is based on the Beer-Lambert model of diffuse reflectance [9-12] and procedures for background-normalized (or background-subtracted) reflectance spectra [13].

2. Materials and Methods

Dyes. Dyes were chosen for their unique absorption features in the NIR/SWIR bands and ease of sample preparation due to their solubility in common laboratory solvents. These dyes have wavelengths of maximum absorption in either the NIR or SWIR bands, with appreciable spectral features extending into the visible spectrum. The dyes used in this study are: FHI10312 (see Reference [14]), which is a cyanine dye, soluble in acetone, and has an absorption maximum at 1030 nm; and ADS775PI, chemical formula $C_{36}H_{44}ClN_2I$ (see reference [15]), which is soluble in methanol, and has an absorption maximum within 773-783 nm (in MeOH). Within this study dyes FHI10312 and ADS775PI are designated Dye 1 and Dye 2, respectively.

Fabric. The base fabric considered for dye application was a cotton-blend fabric. The parametric model considered in this study assumes a rough surface, finite and non-uniform thickness, and a heterogeneous composition, which is based on the characteristic microstructure of cotton-blend fabrics.

Dye and Dyed-Fabric Sample Preparation. For each dye and corresponding solvent, a stock solution was made, followed by serial dilutions of each stock solution, for the purpose of adjusting concentration of dye deposited. Dye-fabric samples were prepared by pipetting 1 mL of each dye solution onto the centers of 2×2 (in)² fabric pieces. The pipetting speed was adjusted as to avoid pooling of the dye solution on the fabric surface. Dye-fabric samples were given 24 hours to dry before total reflectance measurements were made.

Spectral Measurements of Dyed-Fabric Sample. Measurements of total reflectance were made using a Perkin-Elmer® Lambda™ 1050 UV/Vis/NIR/SWIR spectrophotometer (Waltham, MA, USA) in combination with Perkin Elmer® UV WinLab™ software (version 6.0.3). Reflectance was measured from 250 nm to 2500 nm at 5-nm stepping increments. All measurements were 8 degree hemispherical in total reflectance collection mode. The Lambda 1050 incorporated a double beam, 150 mm integrating sphere housing a photomultiplier tube (PMT) detector for the UV-Vis (175 – 860 nm) region and an Indium Gallium Arsenide (InGaAs) detector for the NIR-SWIR (860 - 2500 nm) region. Radiation sources included a deuterium lamp for operation in the UV (175 – 319 nm) and a tungsten halogen lamp for use in the Vis-NIR-SWIR (319 – 3000 nm). A light source change at 319.2 nm and a detector change at 860.8 nm occurred automatically during monochromator slewing. For UV-Vis wavelengths, the slit width was fixed at 4 nm. For NIR-SWIR wavelengths, the slit width was set to “Servo” mode, which automatically adjusted the slit width during scanning to maintain constant energy at the detector. Shown in Figure 1 are reflectance spectra of dyes under analysis as a function wavelength for a given dye concentration deposited, and the reflectance spectrum of the control fabric containing no dye.

3. Parametric Model of NIR-SWIR Reflectance Spectra for Dyed Fabrics

A model that combines physically consistent trend features of diffuse reflection with background-subtraction and normalization procedures for removal of host-fabric spectral features is given by

$$A_s(\lambda) = \sum_{j=1}^{N_j} A_j \exp\left(-\frac{(\lambda - \lambda_j)^2}{2\sigma_j^2}\right) \quad (1)$$

$$Z_A(\lambda) = \sum_{n=1}^N w_n (A_M(\lambda_n) - A_s(\lambda_n))^2 \quad (2)$$

$$A_M(\lambda) = \ln\left(\frac{1}{R_d(\lambda)}\right) \quad (3)$$

$$R_d(\lambda) = \frac{R_{d+s}(\lambda)}{R_s(\lambda)} \quad (4)$$

The formal procedure underlying inverse analysis based on Eqs.(1)-(4) entails adjustment of the parameters A_j , λ_j and σ_j , $j=1, \dots, N_j$, according to constraint conditions on the calculated absorbance. This approach defines an optimization procedure where the absorbance spanning the range of wavelengths is adopted as the quantity to be optimized. Constraint conditions are imposed on the absorbance by minimizing the objective functions defined by Eq. (2), where $A_M(\lambda_n)$ is the measured or target absorbance for wavelength λ_n . The quantities w_n ($n=1, \dots, N$) are weight coefficients that specify relative levels of influence associated with constraint conditions $A_M(\lambda_n)$. A significant aspect of least-squares parameter optimization, as defined by Eq.(2), is the choice of a sufficiently complete set of basis functions. This implies that all possible modes of a given

process can be modeled parametrically by linear combinations of these functions. Accordingly, the parametric model defined by Eqs. (1)-(4) adopt gaussian functions as basis functions, whose general form is consistent with spectral features of diffuse reflectance. The quantity R_d is the background-normalized reflectance [13]. The quantities R_s and R_{d+s} are the reflectivities of the base and dyed fabrics, respectively.

The parametric model defined by Eqs. (1)-(4) consists of linear combinations of basis functions. Diffusely reflected radiation is related to changes in scattering, absorption, and thickness of a dyed fabric layer. The parametric model assumes an infinitely thick layer. Due to the complex nature of diffuse scattering, and uncertainty with respect to dyed fabric microstructure, the absorbance function $A_S(\lambda)$ defined by Eq.(1) represents the combined influence of absorption, scattering and all other underlying physical processes occurring within the dyed fabric layer that contribute to reflectance. In addition, this function represents the influence of statistical variations in fabric thickness and dye concentration within the fabric. For the purpose of parametric modeling, the function $A_S(\lambda)$ defines a parametric representation of absorbance spectra, which are intrinsic to each dye within a known fabric. The parameters λ_j and σ_j are determined using measured diffuse reflectance for dyes within fabrics of known dielectric response, while the coefficients A_j are adjustable parameters accounting for other physical characteristics, including relative concentrations for dye mixtures in fabrics.

4. Prototype Simulations

A series of prototype simulations of spectra for pure dyes and dye mixtures, Dye 1 and Dye 2, in fabric spectra were considered for the purpose of model validation. Shown in Figure 2 are background-normalized absorbance spectra of dyes in fabric, as function of dye concentration. Each experimental absorbance spectrum was modeled by adjusting parameters A_j , λ_j and σ_j , $j=1, \dots, N_j$, until the objective function (Eq. (3)) achieved reasonable minimization (see Tables 1 through 5). Shown in Figure 3 are Gaussian basis functions for decomposition of absorbance spectra of Dyes 1 and 2 with respect to Eq.(1). Shown in Figures 4 and 5 are basis-function decompositions of absorbance spectra for Dye 1 and Dye 2, respectively, in fabric with respect to basis-function expansion Eq.(1). Figures 6 and 7 show comparisons of absorbance functions, which have been determined by inversion, using Eqs. (3) and (4), and calculated using basis-function expansion Eq.(1), for Dye 1 and Dye 2 in fabric, respectively.

Shown in Figure 8 are diffuse reflectance spectra of Dye 1 and Dye 2 mixtures in fabric. Shown in Figure 9 are background-normalized absorbance spectra of Dye 1-Dye 2 mixtures in fabric, as function of relative dye concentrations. Shown in Figure 10 are basis-function decompositions of absorbance spectra for Dye 1 and Dye 2 mixtures with respect to basis-function expansion Eq.(1). Figure 11 shows comparisons of absorbance functions, which have been determined by inversion, using Eqs. (3) and (4), and calculated using basis-function expansion Eq.(1), for Dye 1 and Dye 2 mixtures in fabric. Referring to Figure 11, the agreement between absorbance functions demonstrates that the reflectance spectra for combinations of dyes can be represented parametrically by linear combinations of basis functions, Eq.(1), where influence associated with the relative concentration of dye molecules as well as the influence of processes other than absorption and scattering, can be represented by phenomenological coefficients A_j .

Table 1. Gaussian Basis Functions for Dye 1

Basis Function	λ_j	σ_j
1	560	100
2	1070	50
3	820	100
4	1260	150
5	1600	100
6	950	70

Table 2. Gaussian Basis Functions for Dye 2

Basis Function	λ_j	σ_j
7	750	60
8	800	30
9	460	30
10	880	40
11	650	70

Table 3. Gaussian Basis-Function Coefficients for Dye 1 Deposited in Fabric

Concentration	A_1	A_2	A_3	A_4	A_5	A_6	Correlation
0.03 g/L	-0.01382	0.065657	0.019004	0.027205	-0.04254	0.053789	0.944
0.15 g/L	0.083217	0.202751	0.106994	0.277486	-0.00477	0.18593	0.994
0.30 g/L	0.161195	0.266978	0.179991	0.421514	0.023774	0.25559	0.992
0.75 g/L	0.196976	0.283022	0.22345	0.477678	-0.00751	0.287424	0.987
1.5 g/L	0.372072	0.349672	0.370922	0.602839	0.052649	0.353103	0.970
3.0 g/L	0.663106	0.443148	0.619771	0.685865	0.148364	0.399084	0.926

Table 4. Gaussian Basis-Function Coefficients for Dye 2 Deposited in Fabric

Concentration	A_7	A_8	A_9	A_{10}	A_{11}	Correlation
0.03 g/L	0.018554	0.046522	-0.01501977	-0.0149203	-0.0115792	0.835
0.15 g/L	0.070856	0.100409	-0.053141	-0.02322	-0.018024	0.929
0.30 g/L	0.1641	0.248449	0.002163	-0.046653	-0.006961	0.986
0.75 g/L	0.403573	0.464459	0.042737	-0.056098	0.035558	0.991
1.5 g/L	0.663098	0.641542	0.131971	0.016354	0.151794	0.989
3.0 g/L	1.0795298	0.916238	0.754395	1.11319	1.122199	0.980

Table 5. Gaussian Basis-Function Coefficients for Dye 1-Dye 2 Mixture Deposited in Fabric

Dye 1 & Dye 2 Concentrations	A_1	A_2	A_3	A_4	A_5	A_6
5 % - 95 %	-0.02455	0.009003	-0.51617	-0.00107	-0.0139	0.154765
25 % - 75 %	-0.00549	0.003521	-0.10636	-0.02696	-0.04496	0.02157
50 % - 50 %	0.012079	0.087158	-0.41027	0.044151	-0.00741	0.188774
75 % - 25 %	0.012521	0.023507	-0.15115	0.005249	-0.0157	0.065528
95 % - 5 %	0.01998	0.161599	-0.24952	0.056627	0.004002	0.196678

Dye 1 & Dye 2 Concentrations	A_7	A_8	A_9	A_{10}	A_{11}	Correlation
5 % - 95 %	0.581477	0.592417	0.027969	0.296308	0.074549	0.988
25 % - 75 %	0.226986	0.250363	0.020171	0.07617	0.03578	0.991
50 % - 50 %	0.421141	0.435497	0.011511	0.264546	0.040511	0.987
75 % - 25 %	0.203862	0.231501	0.00123	0.09055	0.027104	0.988
95 % - 5 %	0.206473	0.219878	-0.00871	0.159544	0.027526	0.984

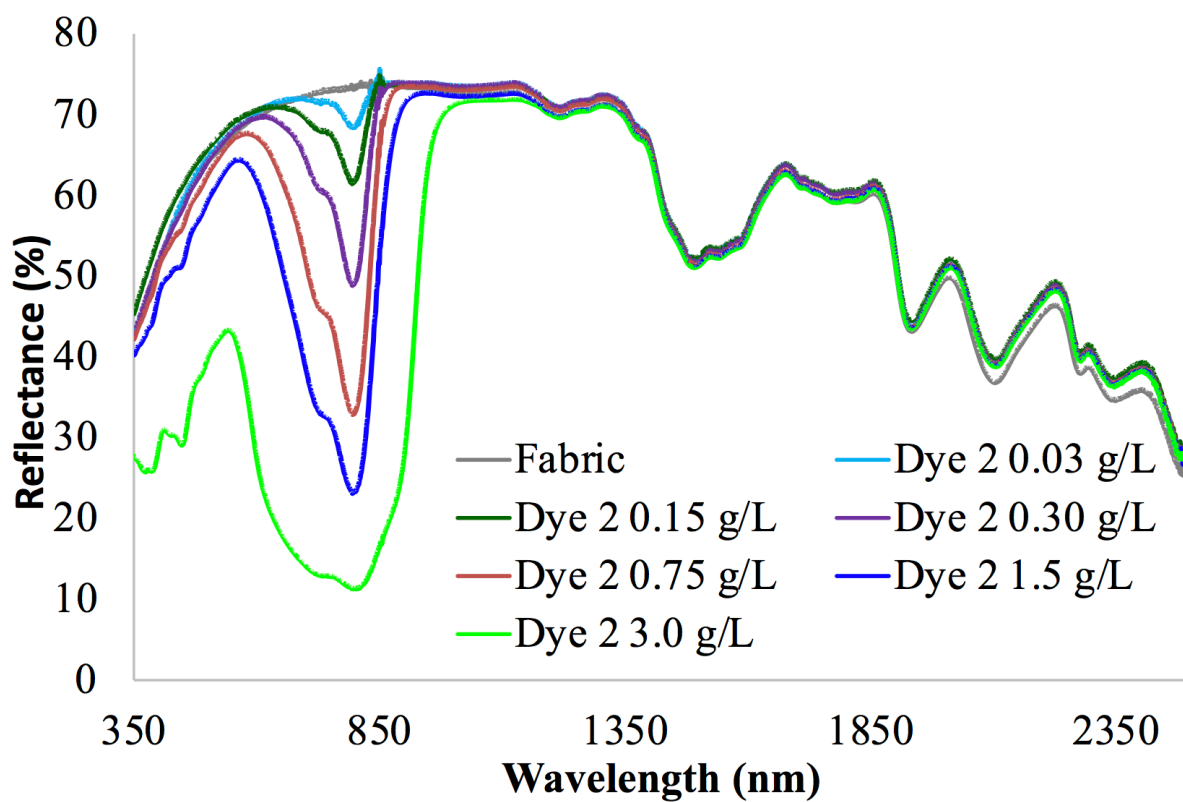
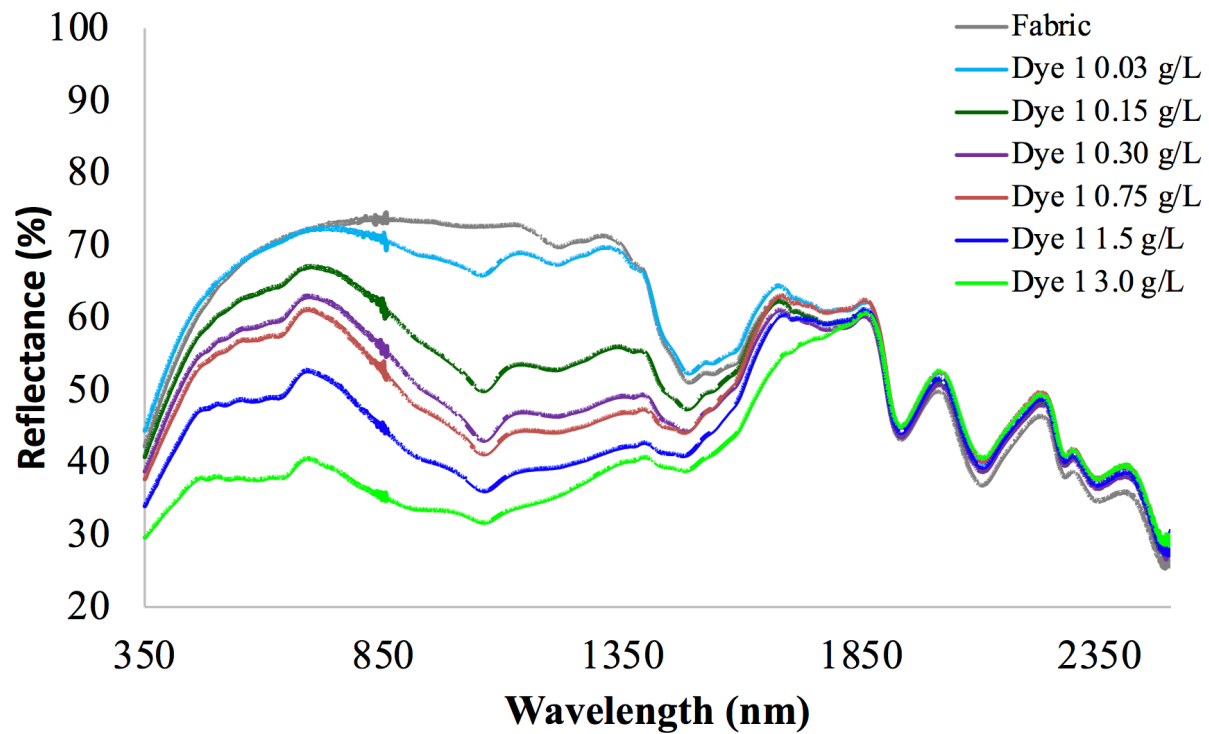


Figure 1. Diffuse reflectance spectra of dyed fabrics and of control fabric containing no dye.

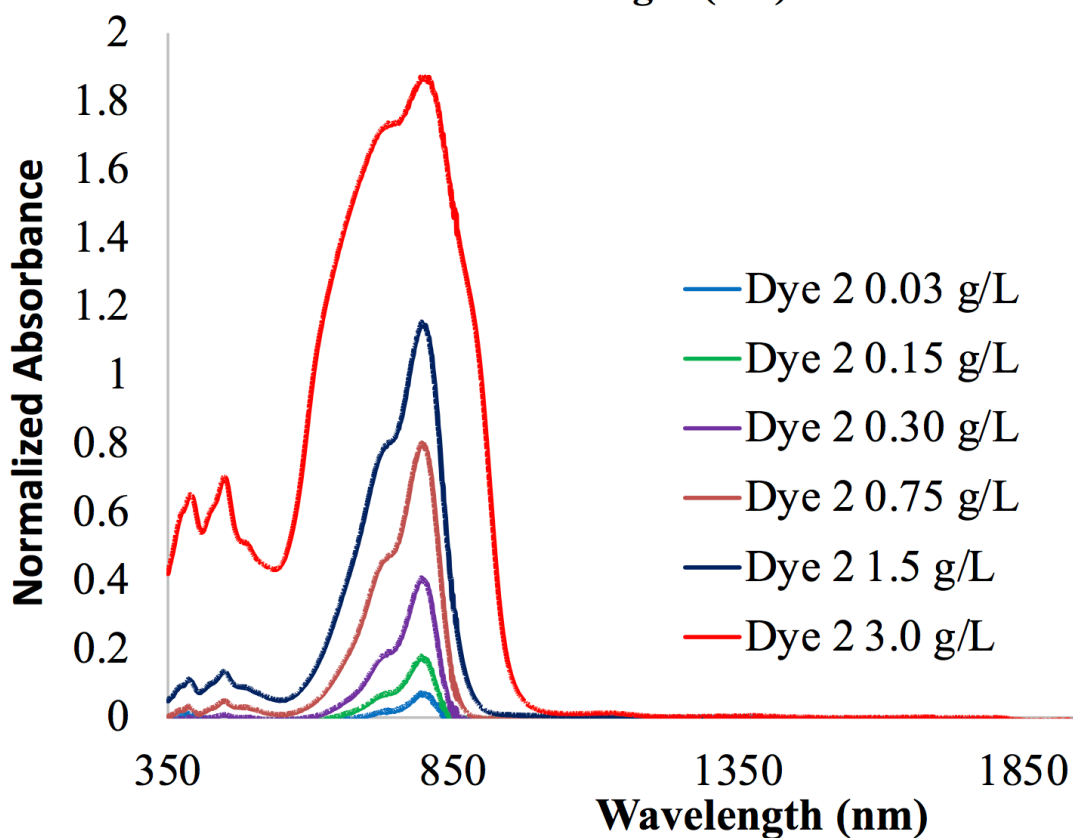
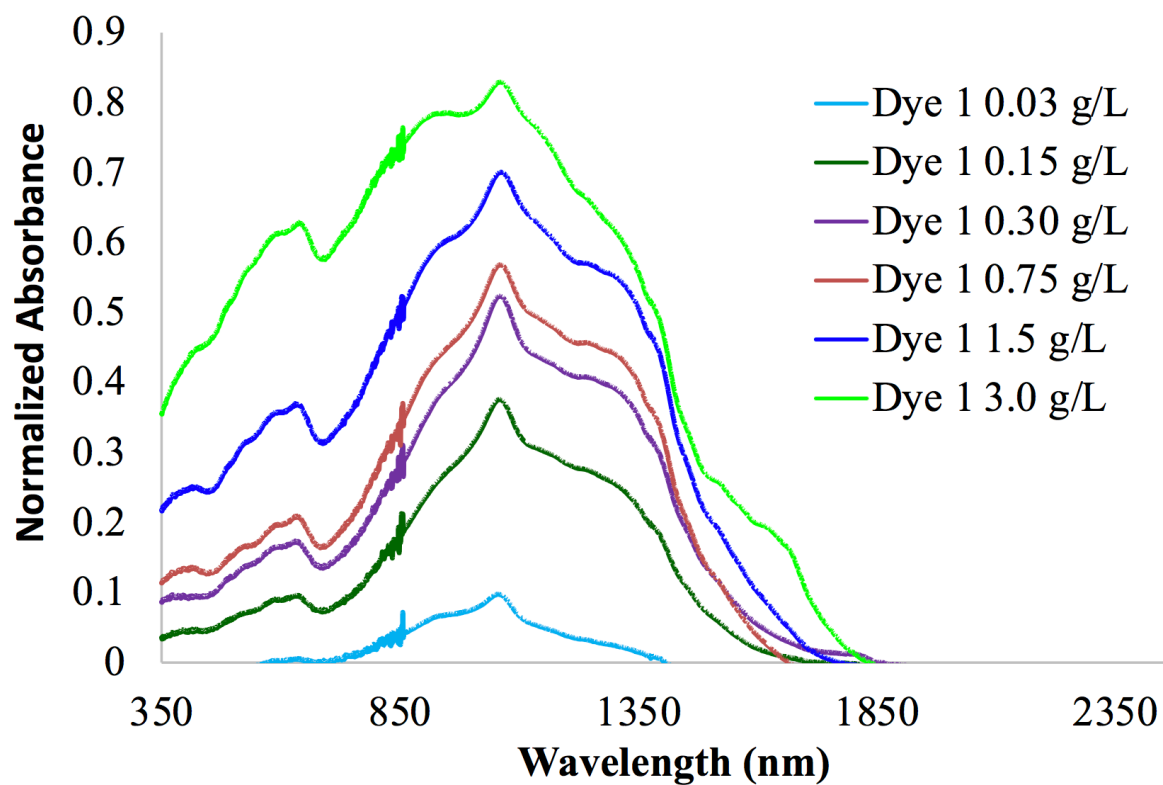


Figure 2. Background-normalized absorbance spectra of dyes in fabric, as function of dye concentration.

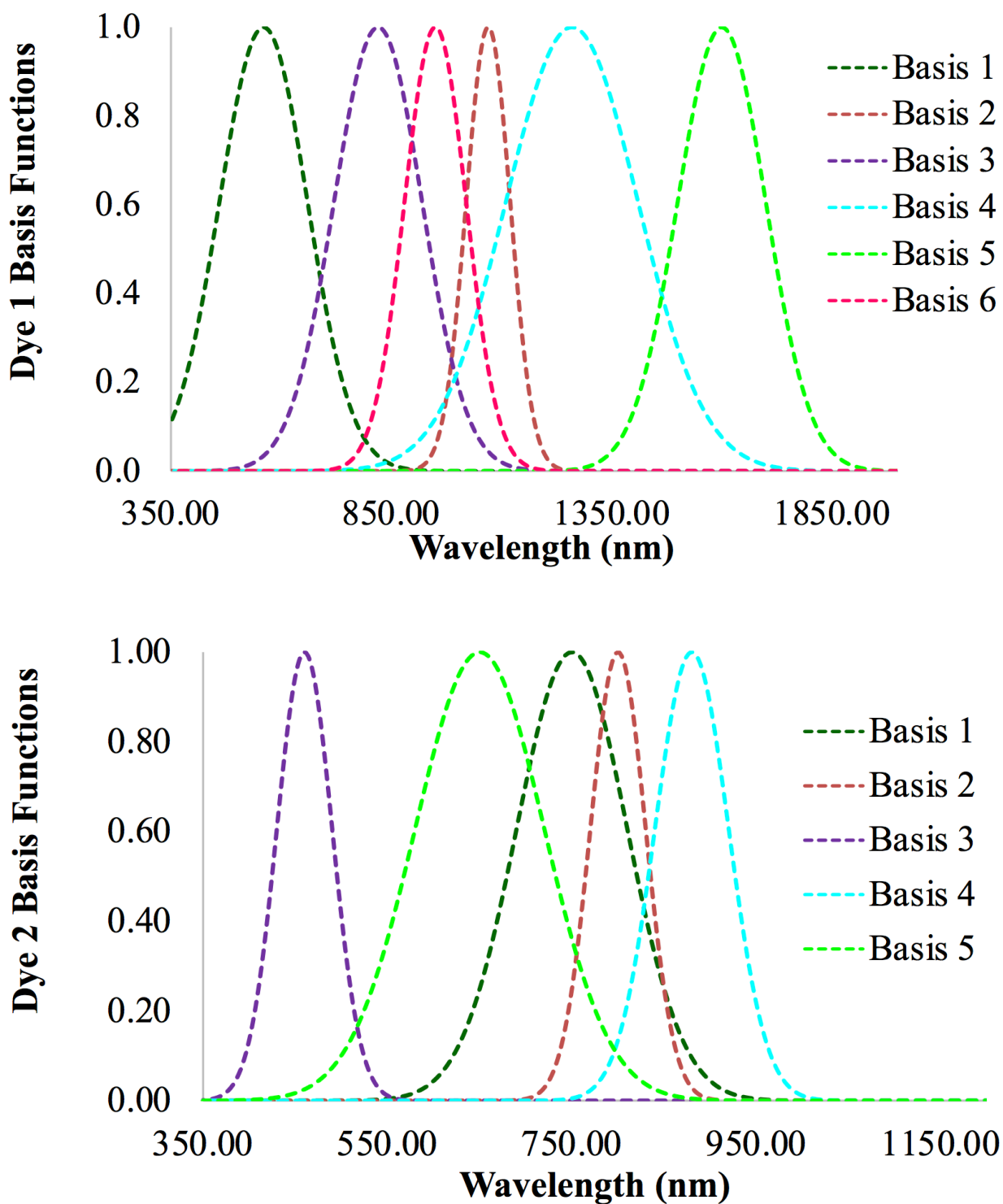
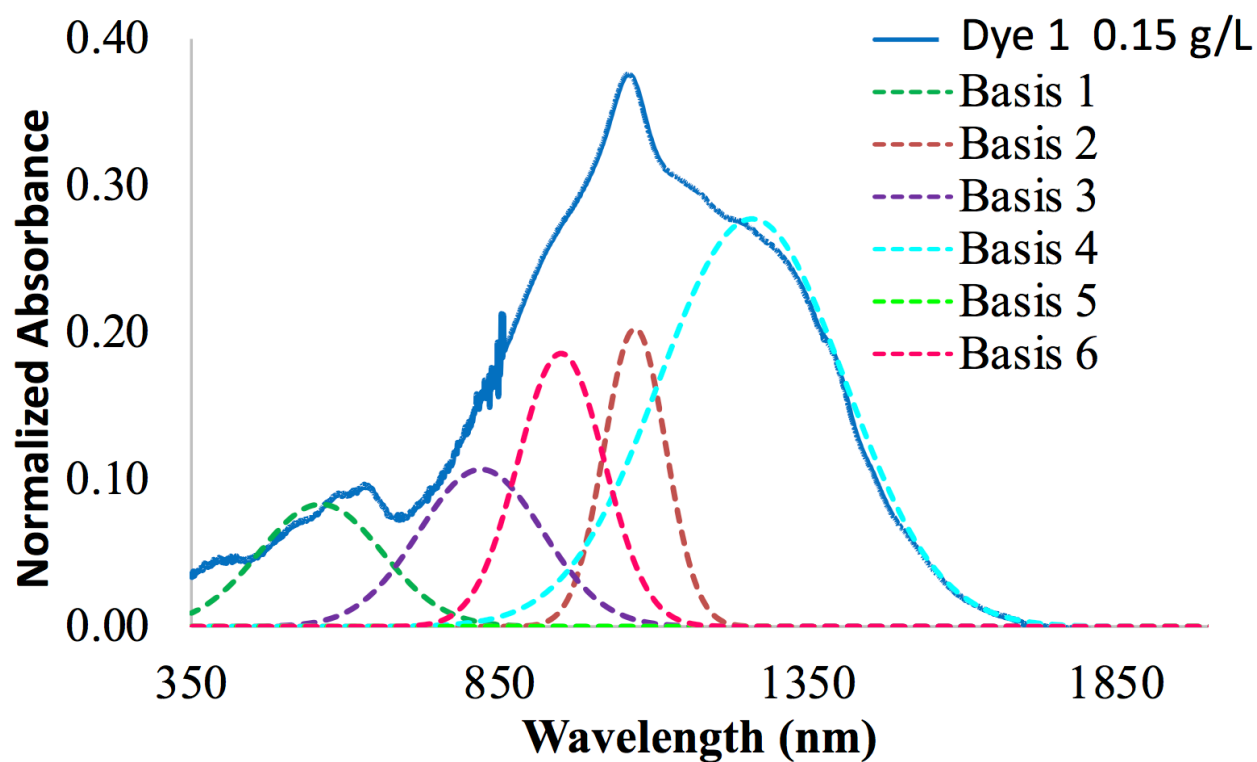
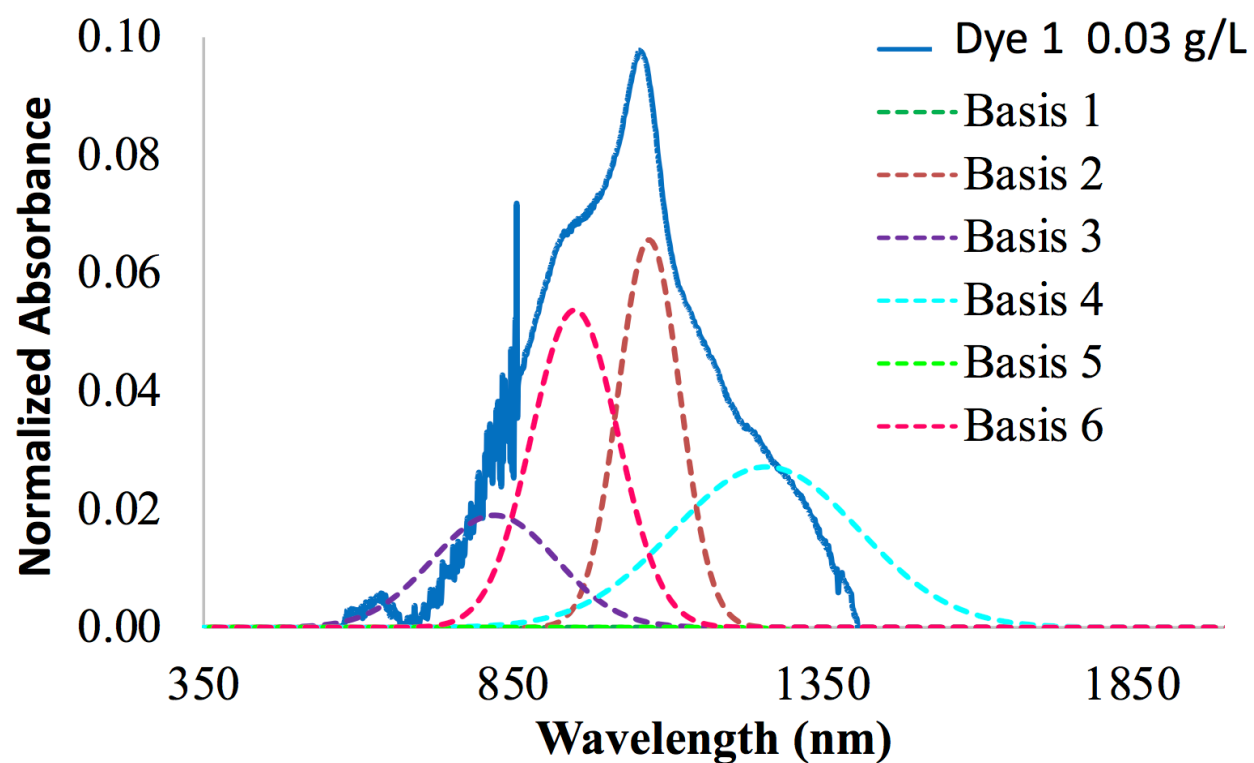
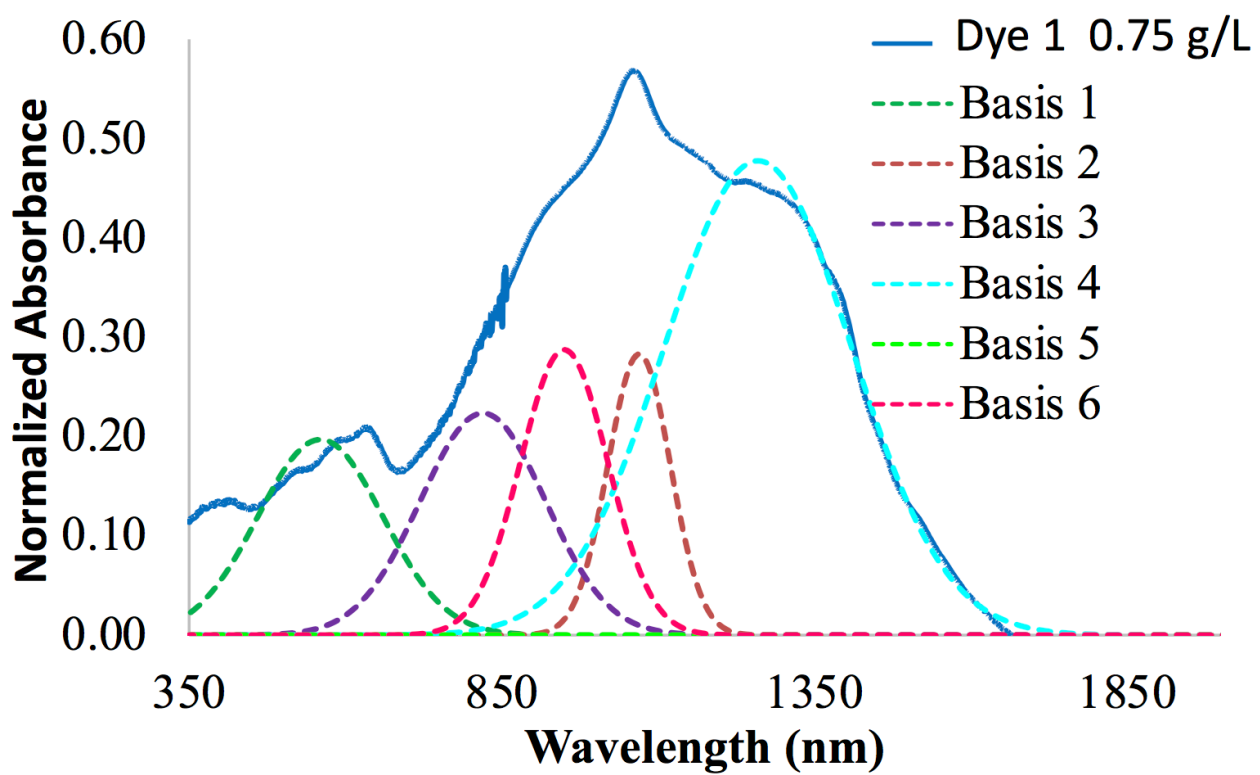
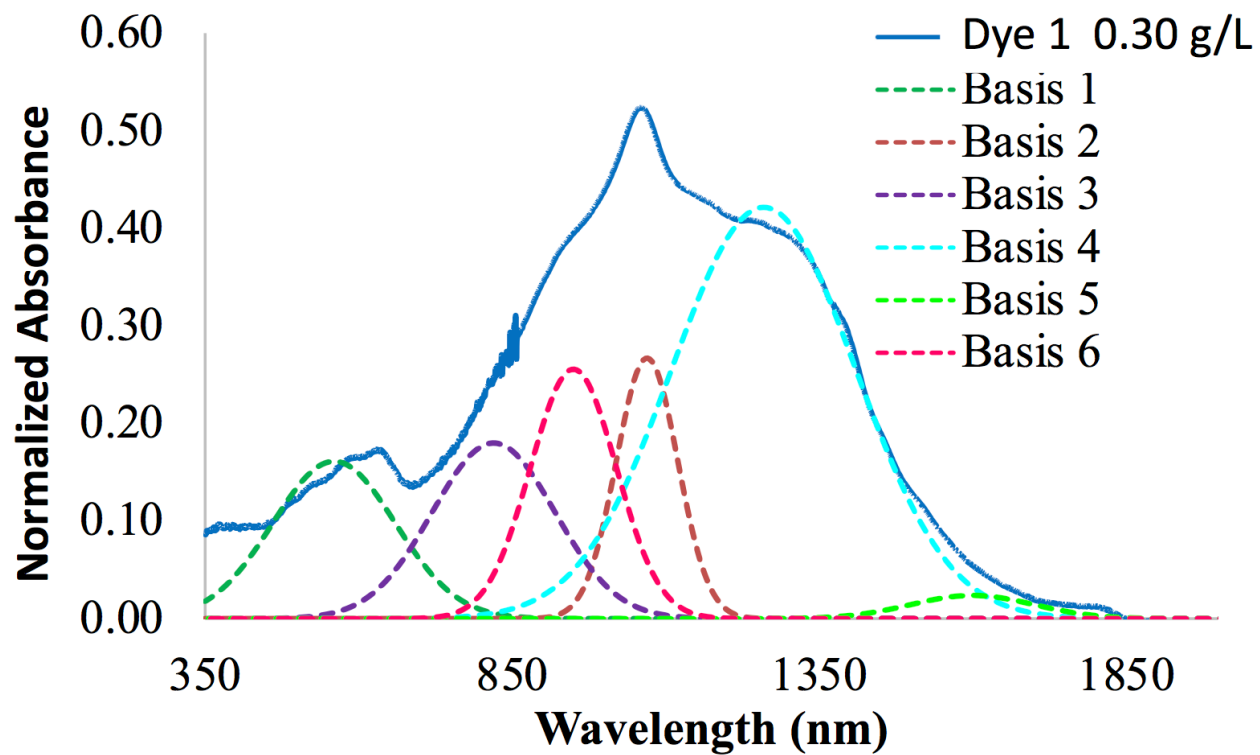


Figure 3. Basis functions for Dyes 1 and 2 in fabric.





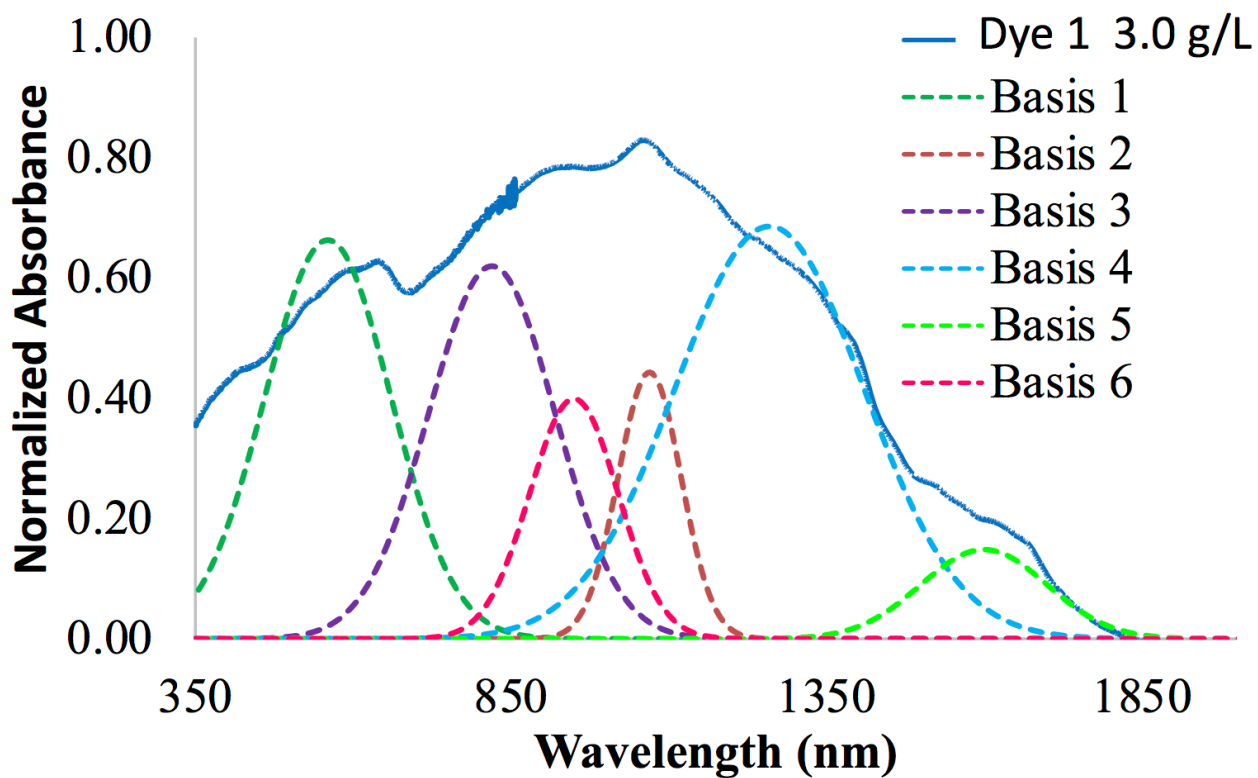
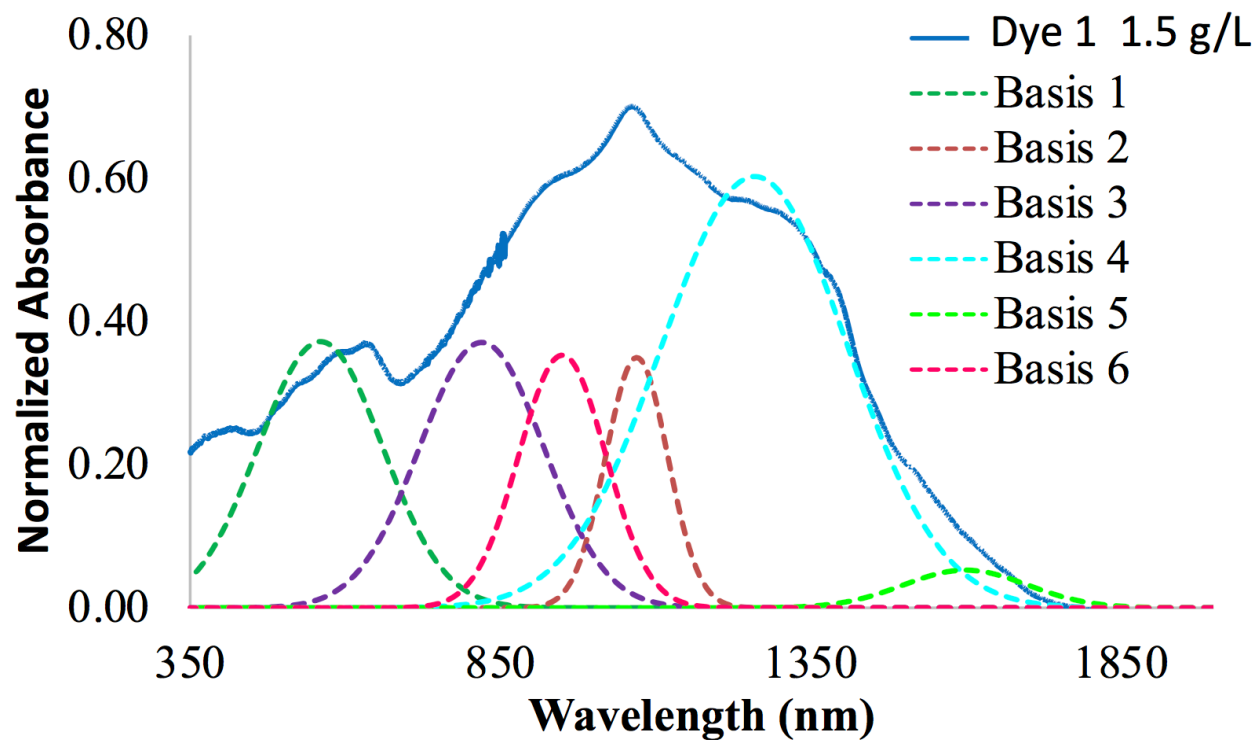
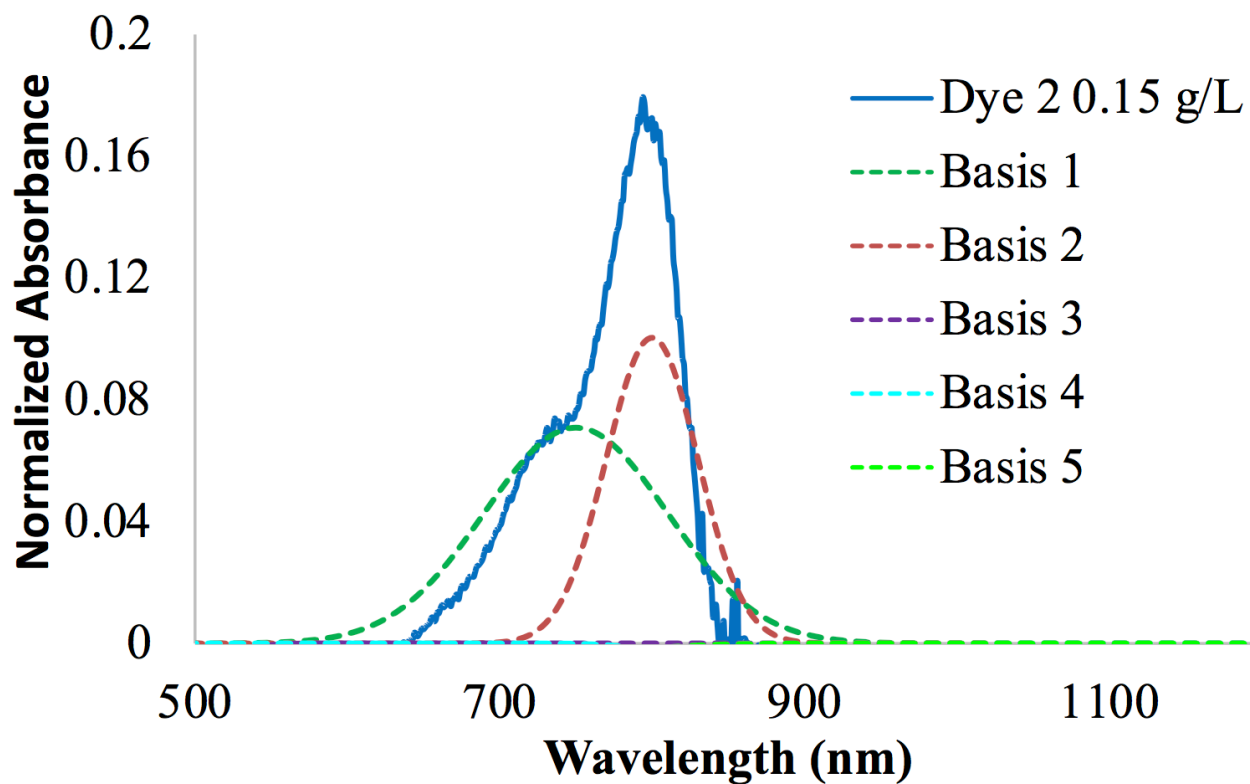
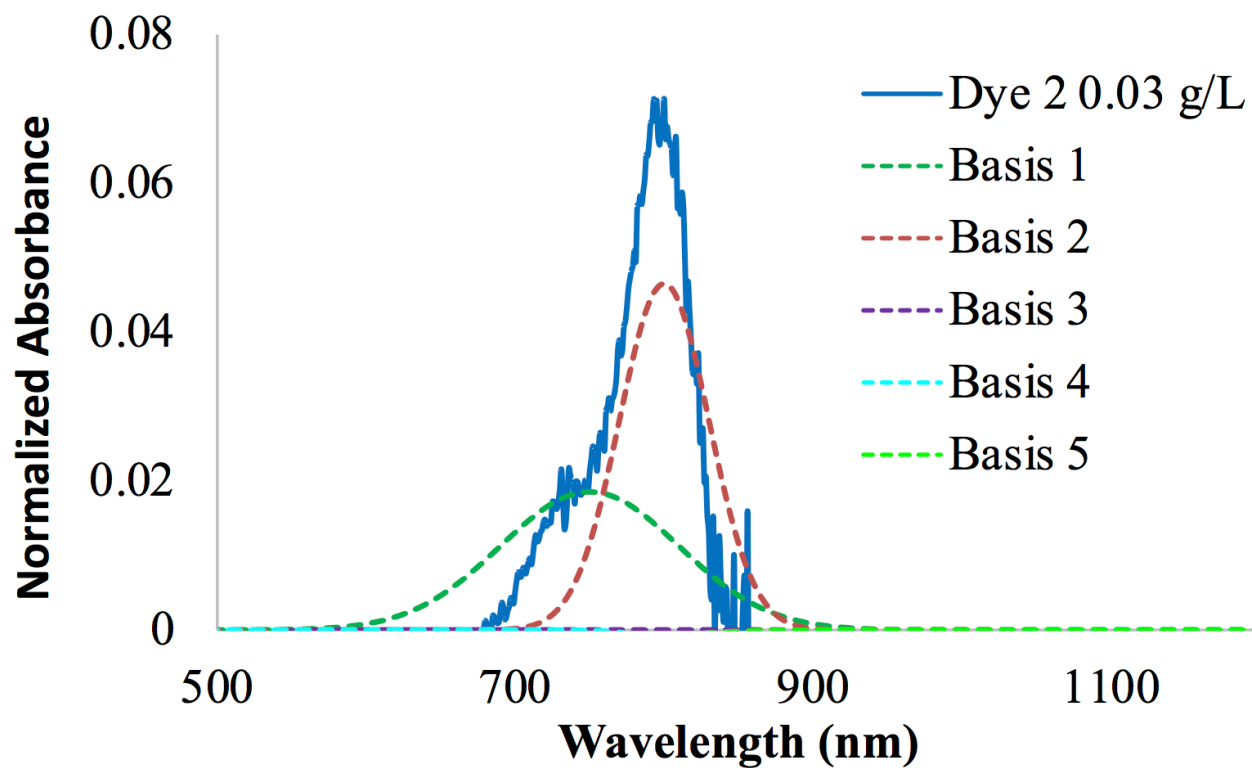
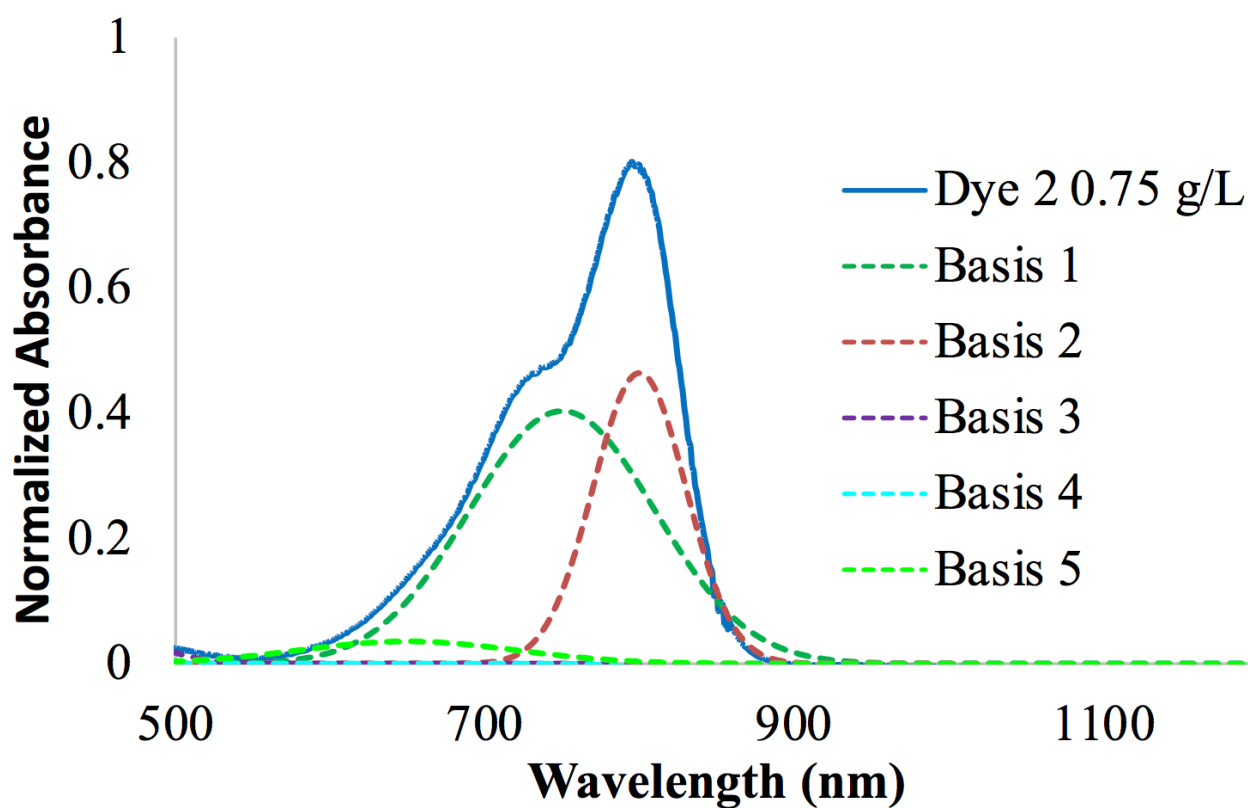
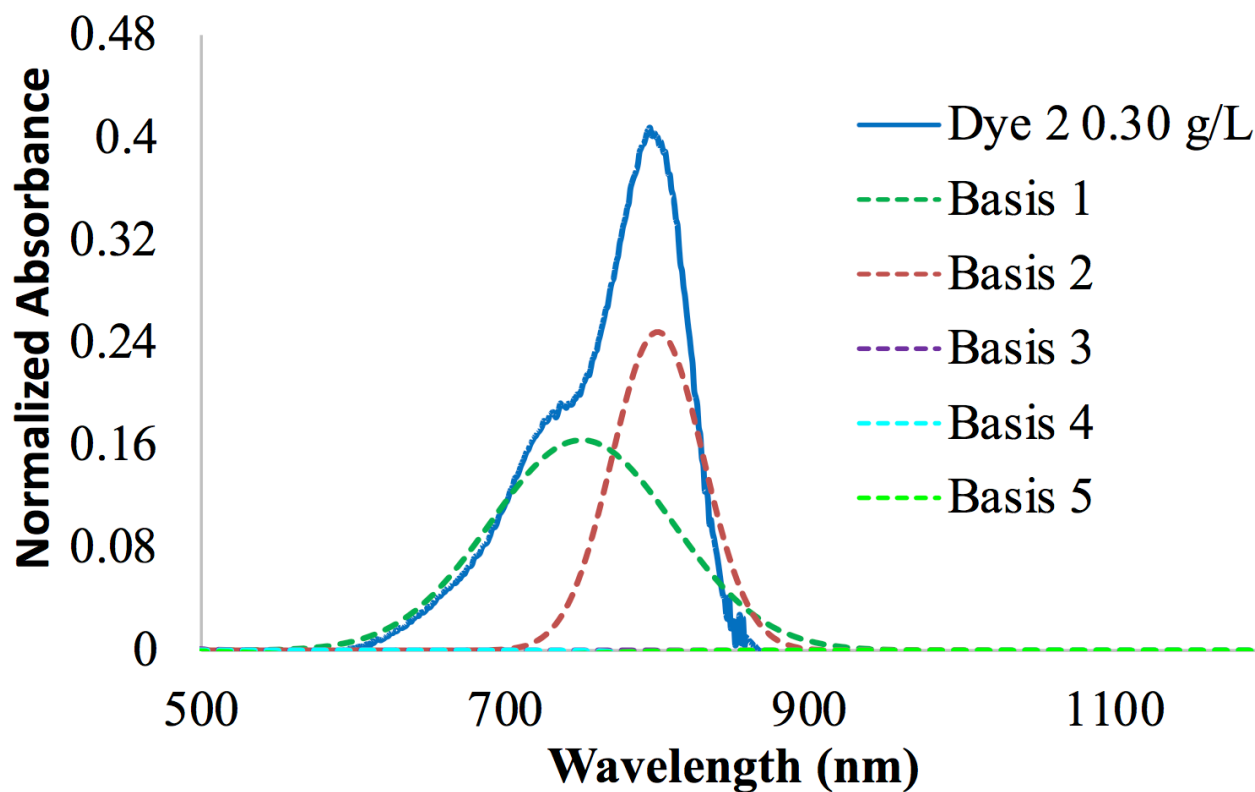


Figure 4. Basis-Fuction decomposition of absorbance spectra for Dye 1 in fabric with respect to basis-function expansion Eq.(1).





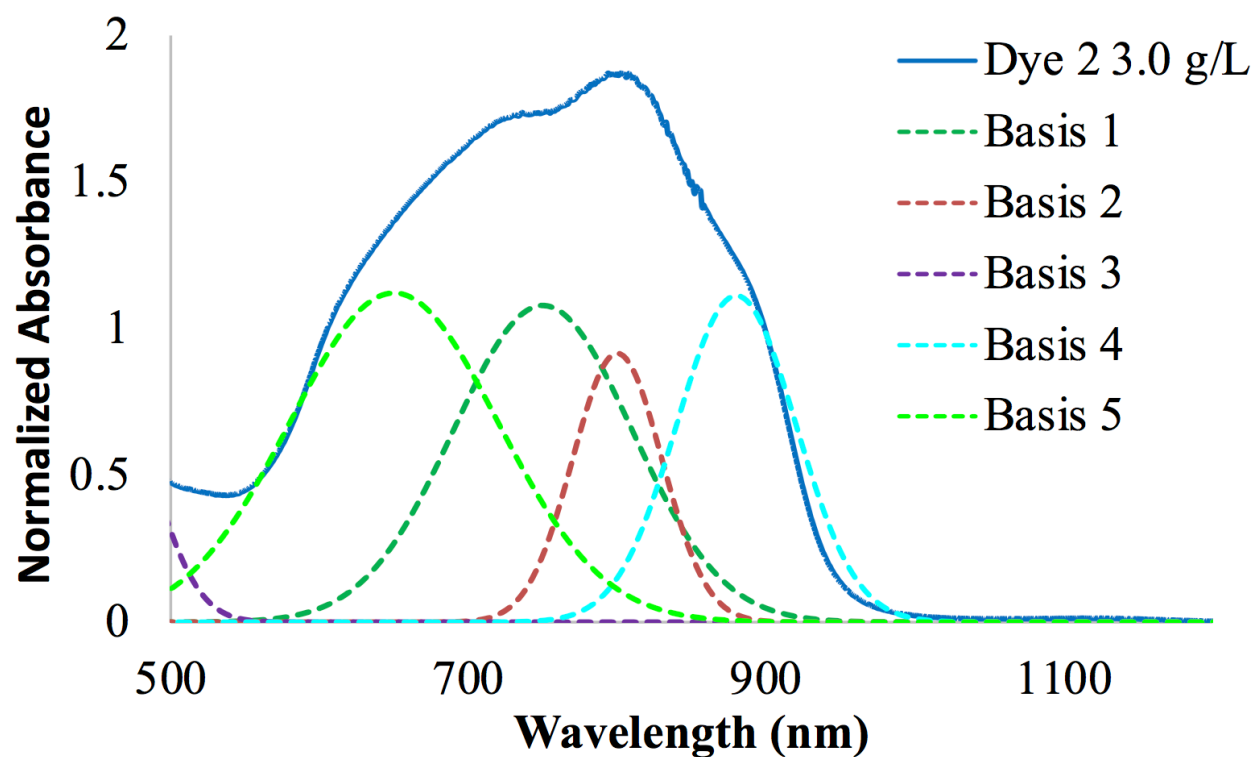
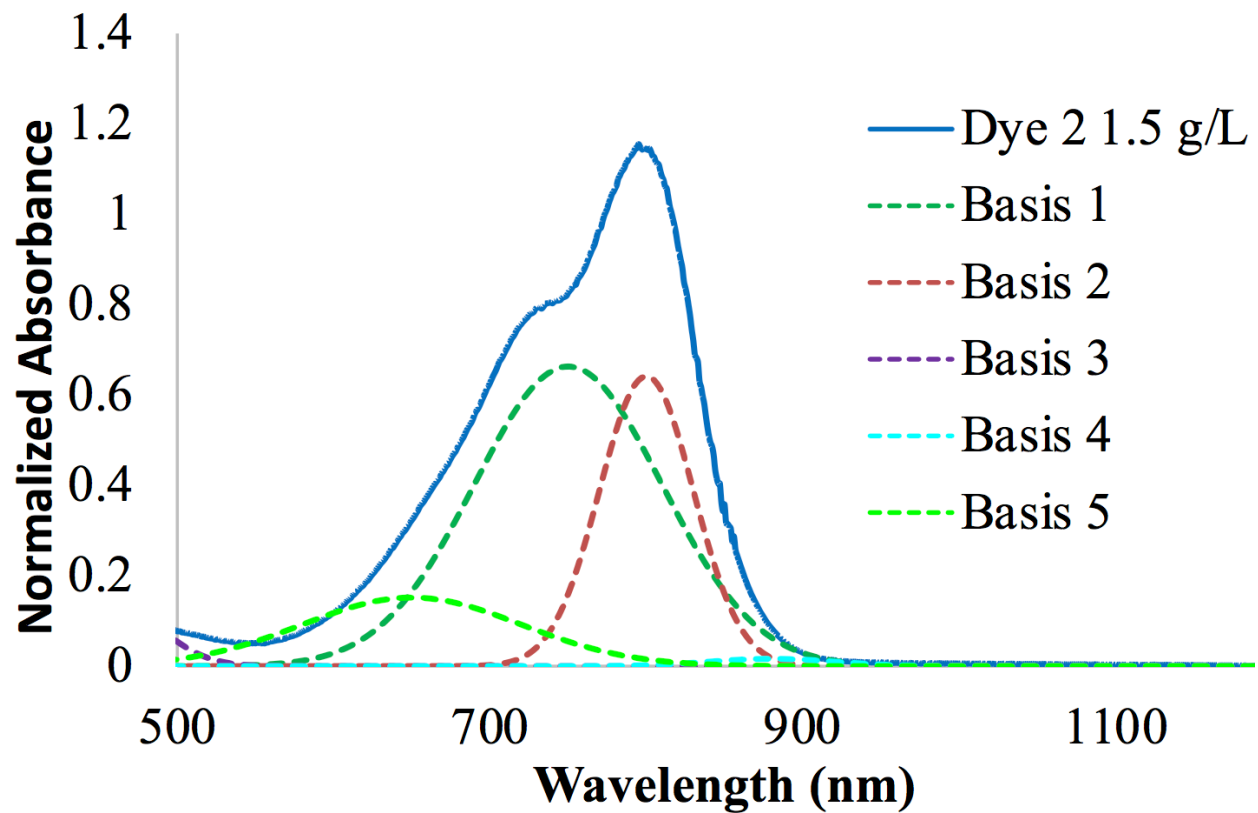
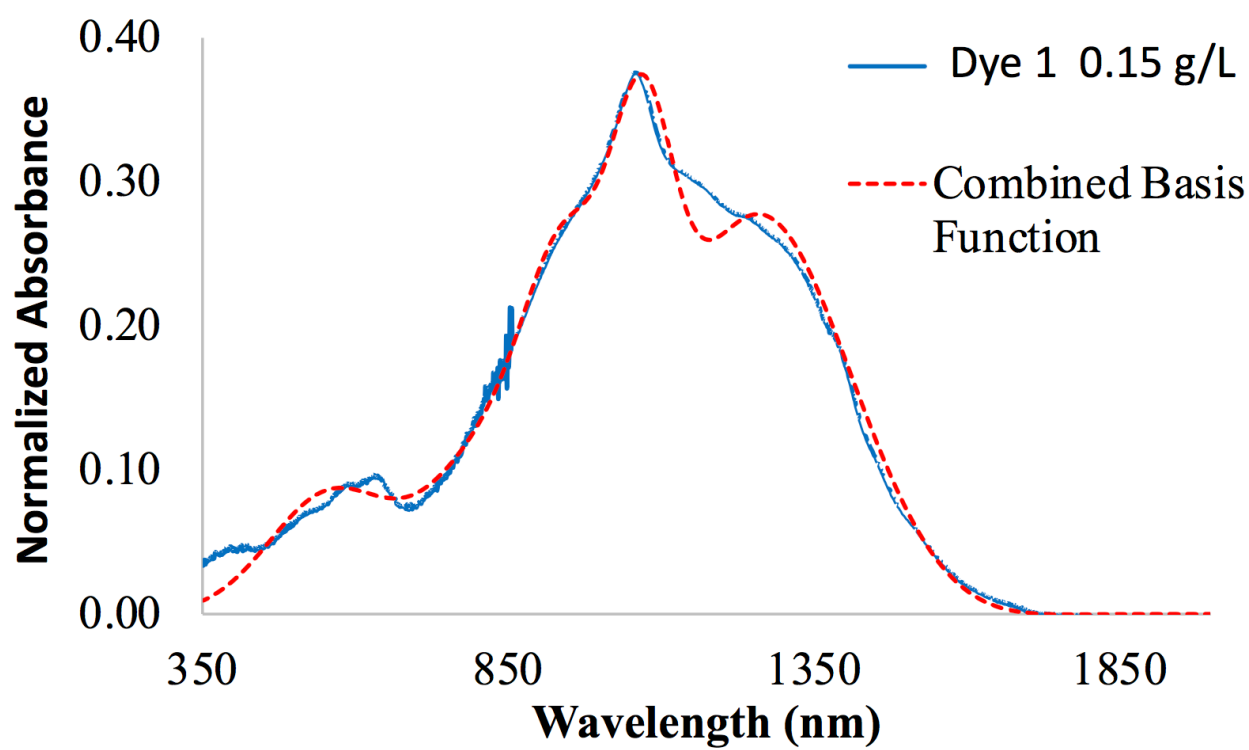
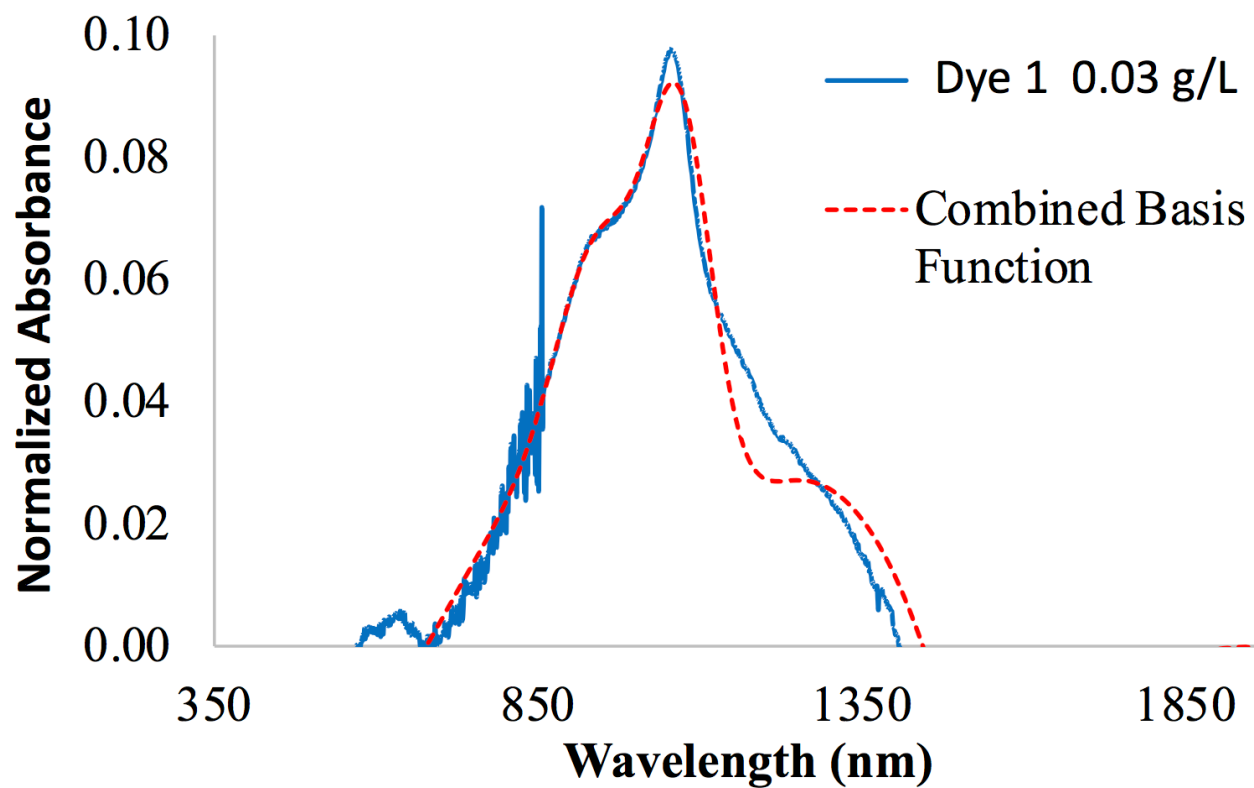
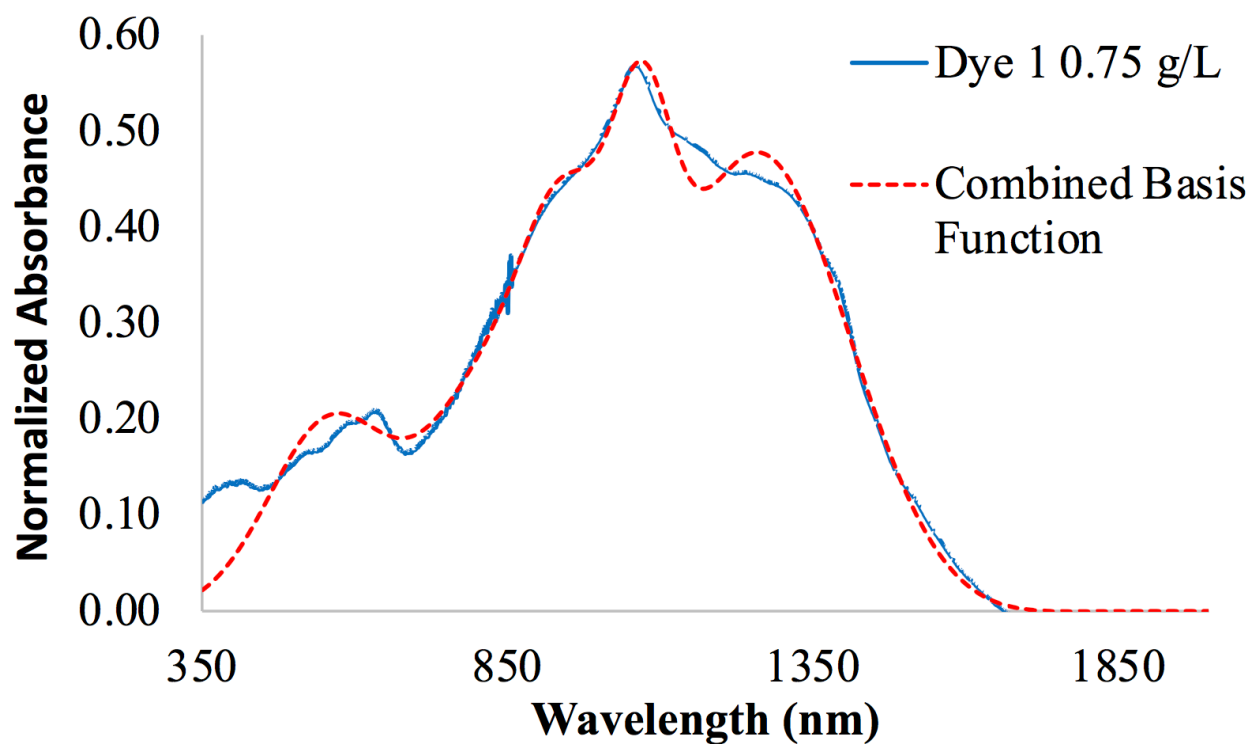
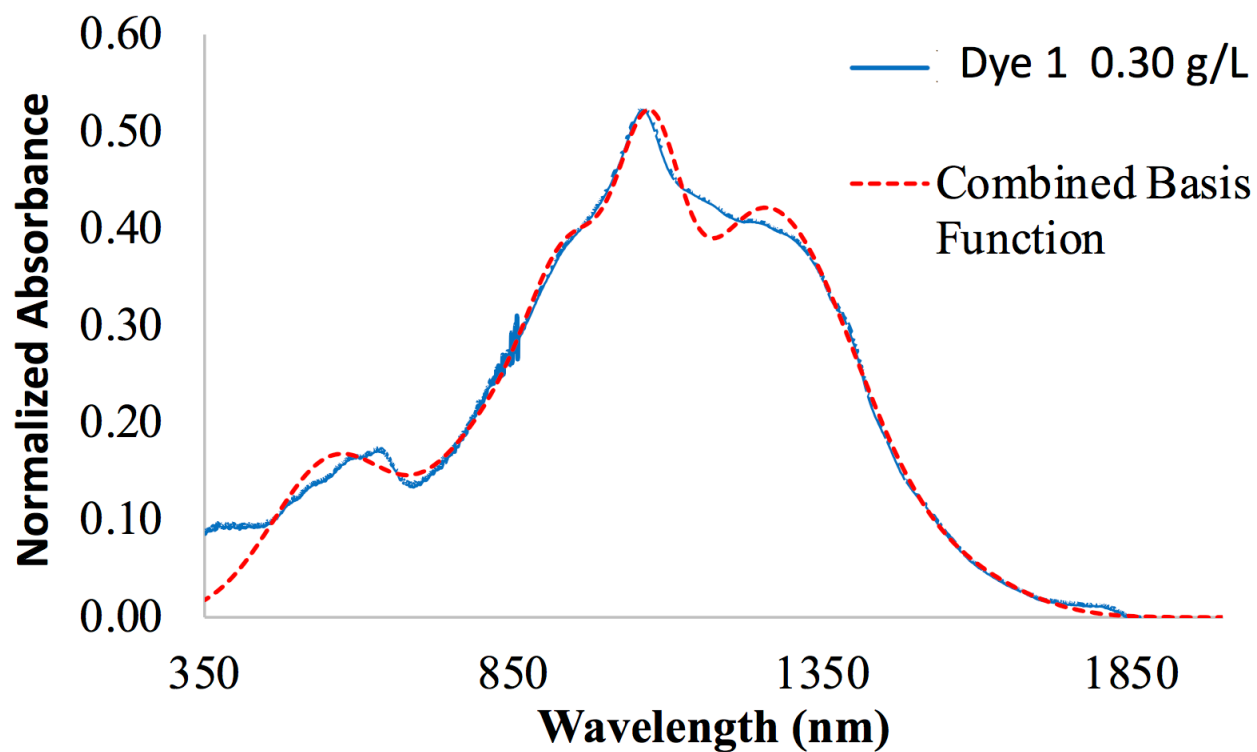


Figure 5. Basis-function decomposition of absorbance spectra for Dye 2 in fabric with respect to basis-function expansion Eq.(1).





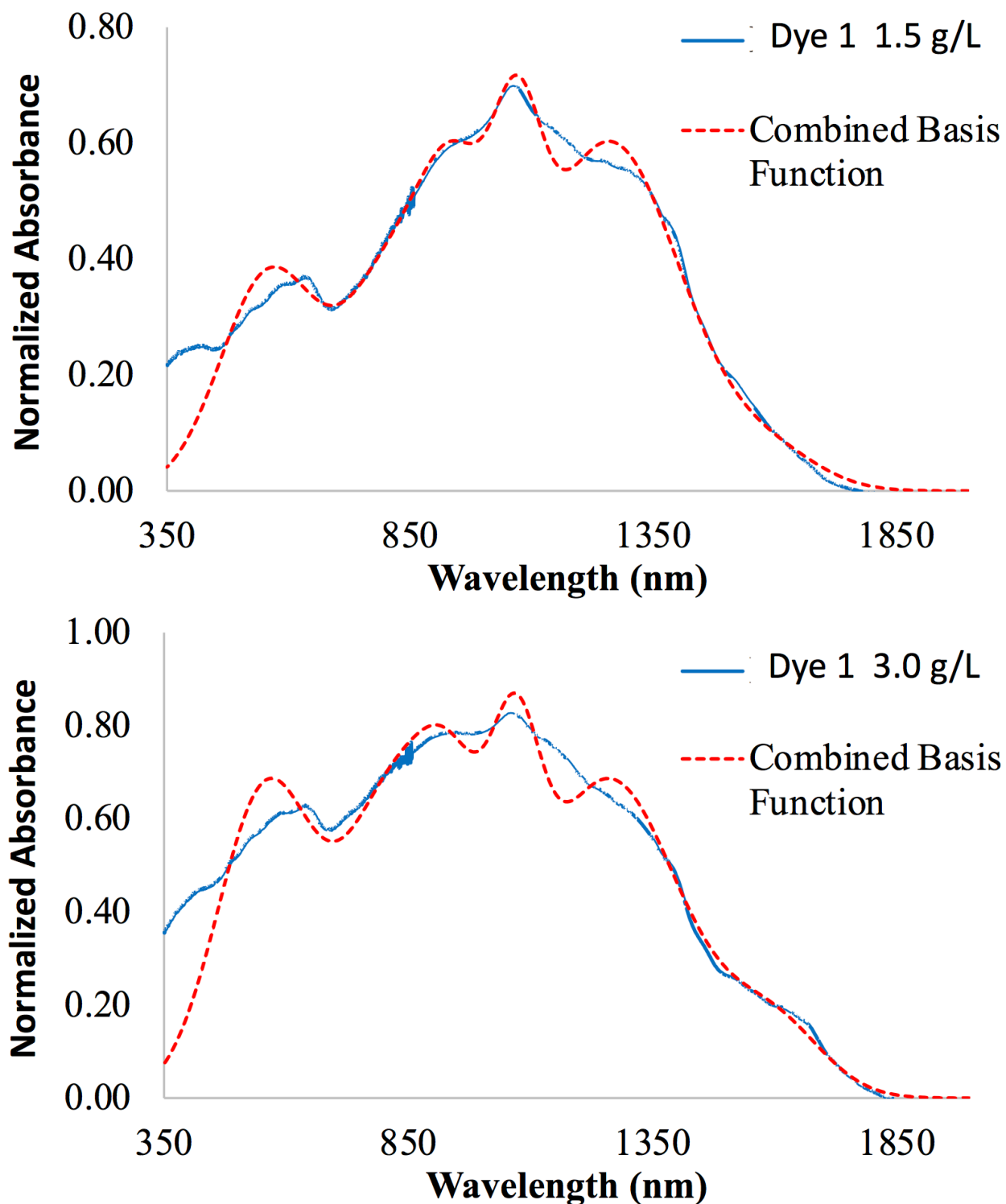
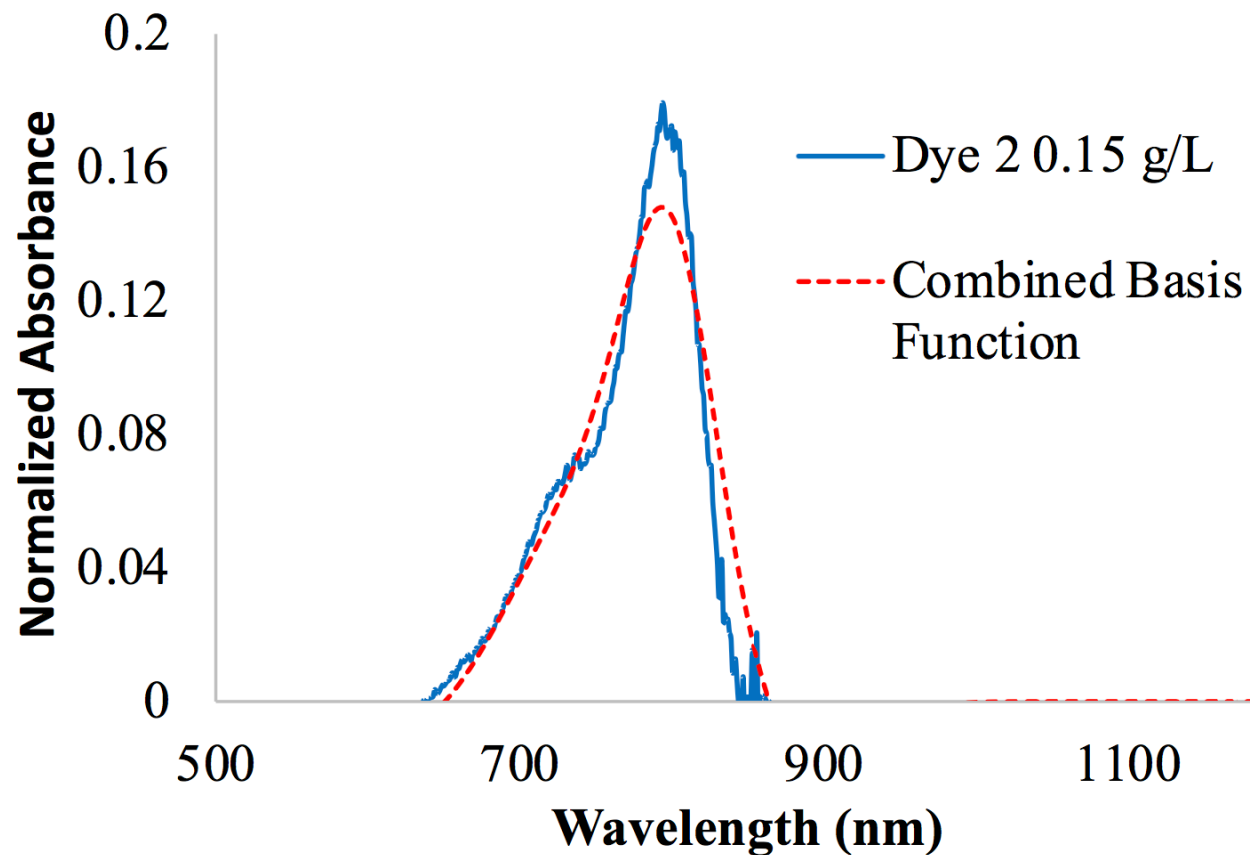
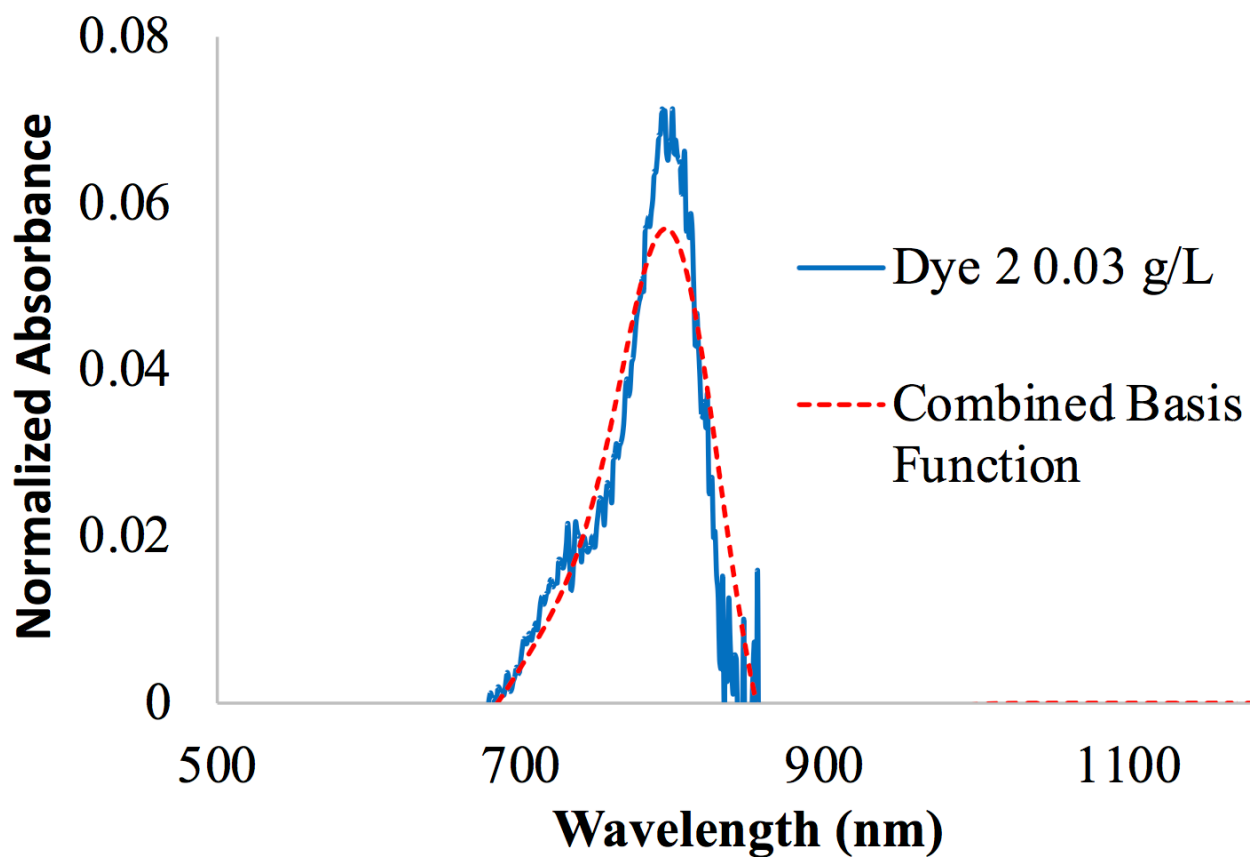
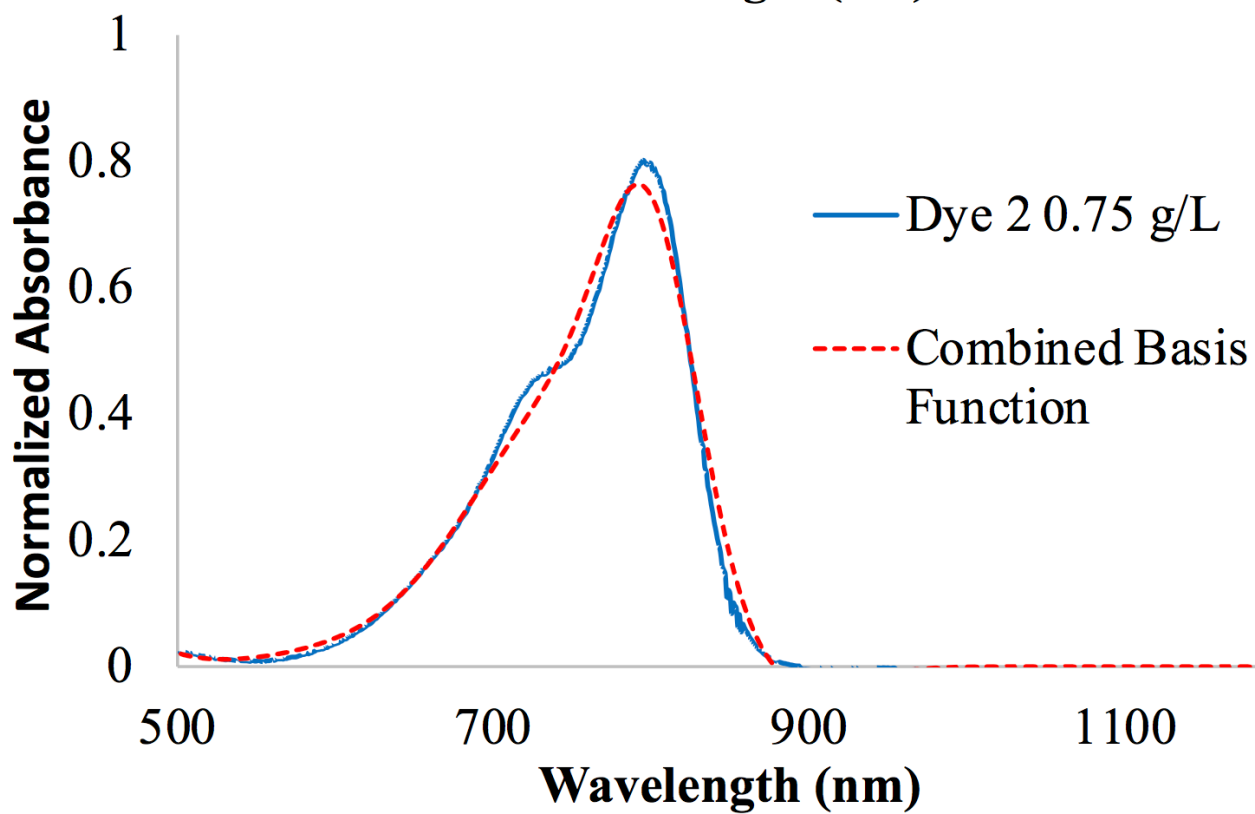
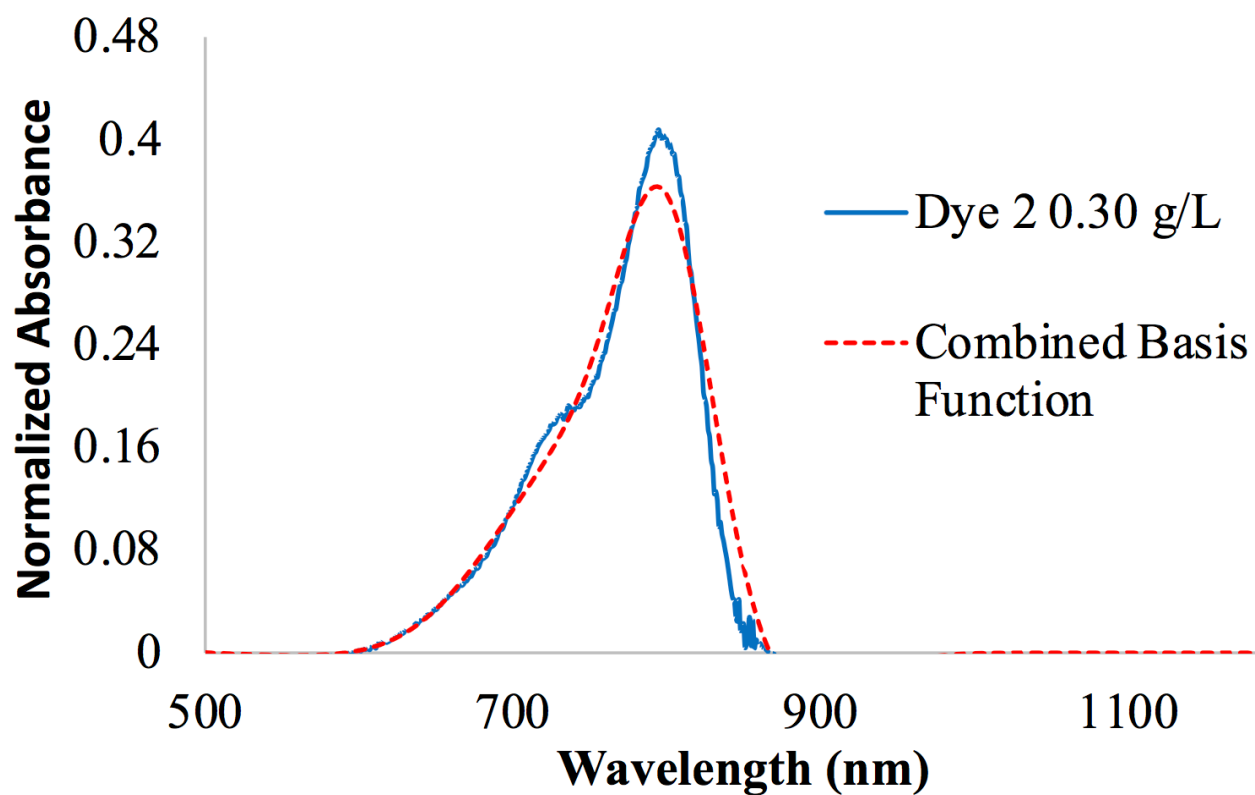


Figure 6. Absorbance spectra for Dye 1 determined by inversion (Eqs. (3) and (4)) and calculated using basis-function expansion Eq.(1).





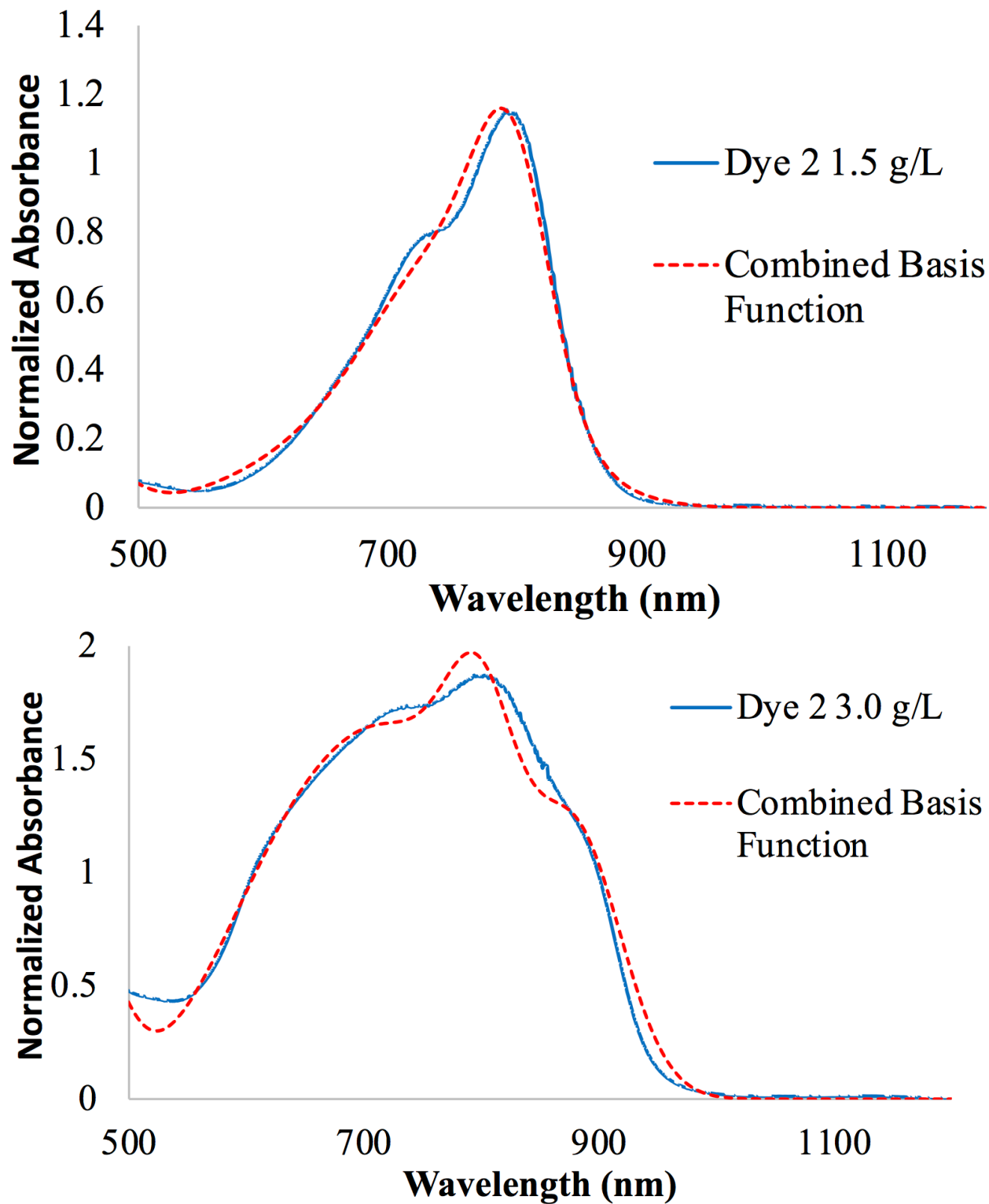


Figure 7. Absorbance spectra for Dye 2 determined by inversion (Eqs. (3) and (4)) and calculated using basis-function expansion Eq.(1).

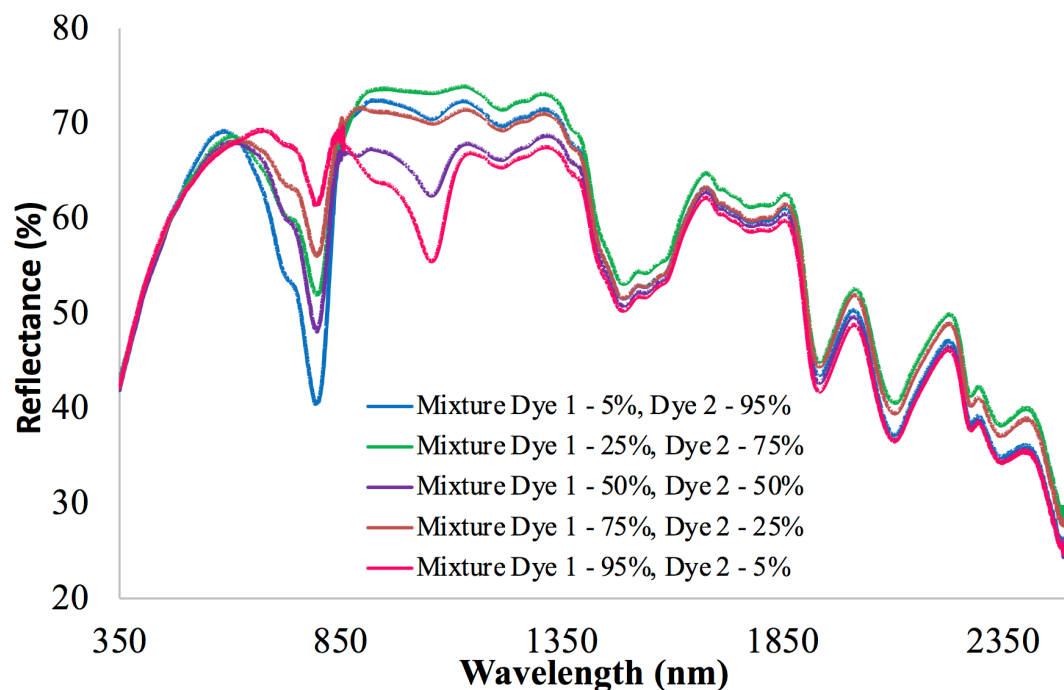


Figure 8. Diffuse reflectance spectra of dye mixtures in fabric.

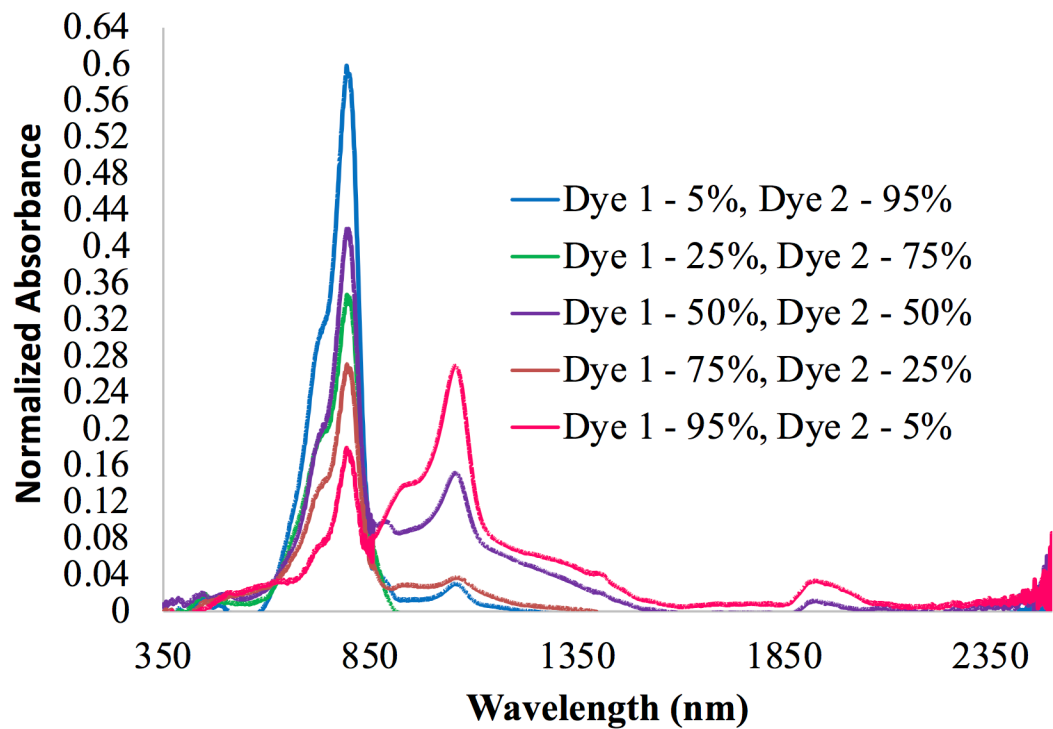
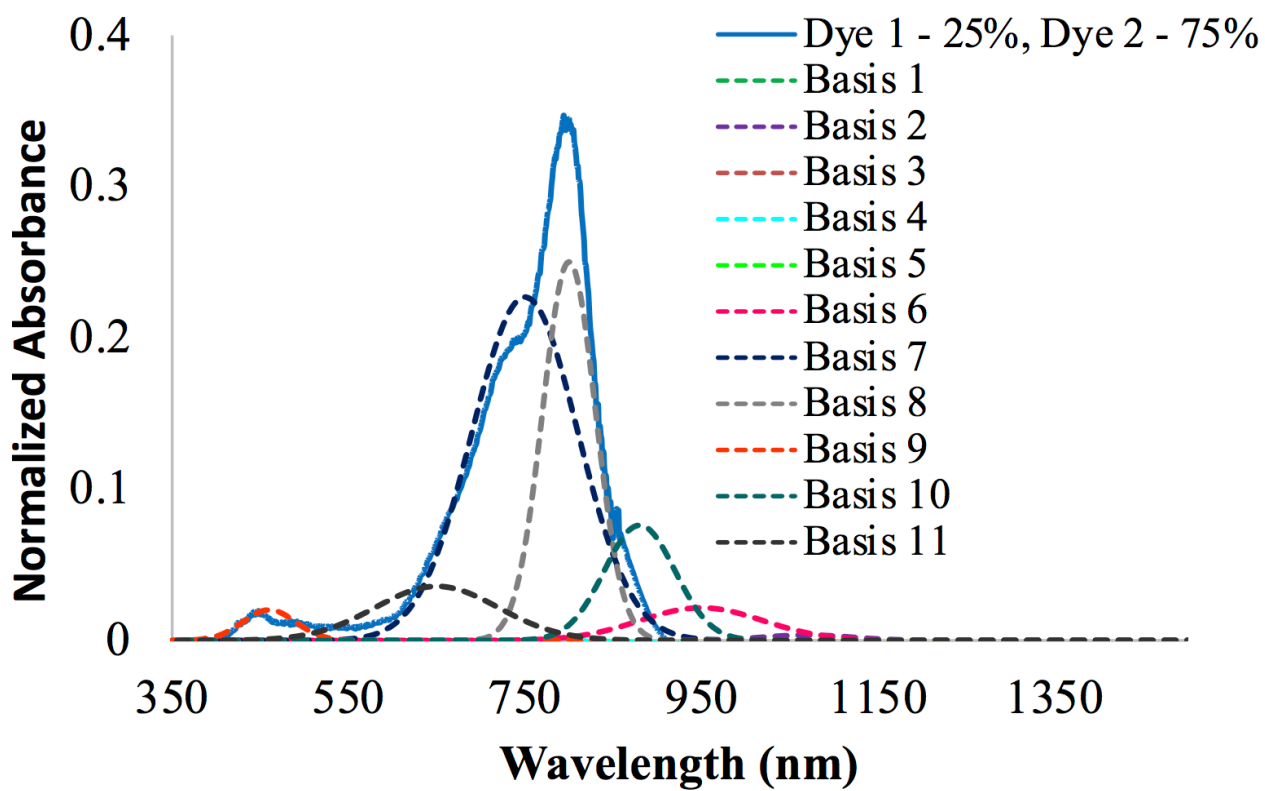
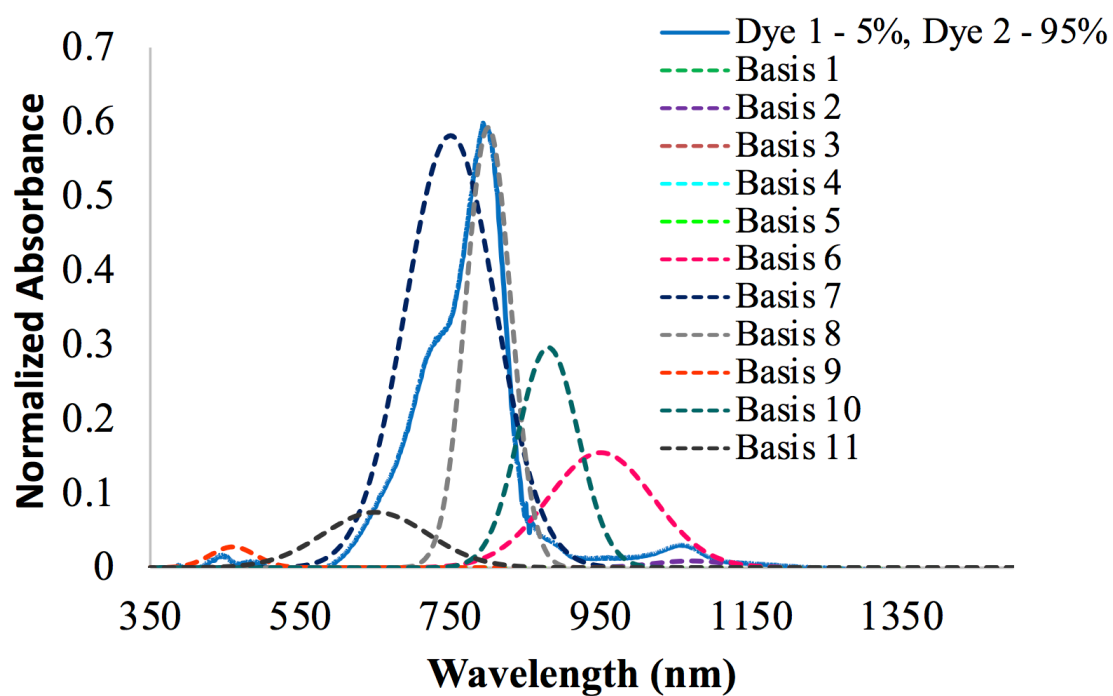
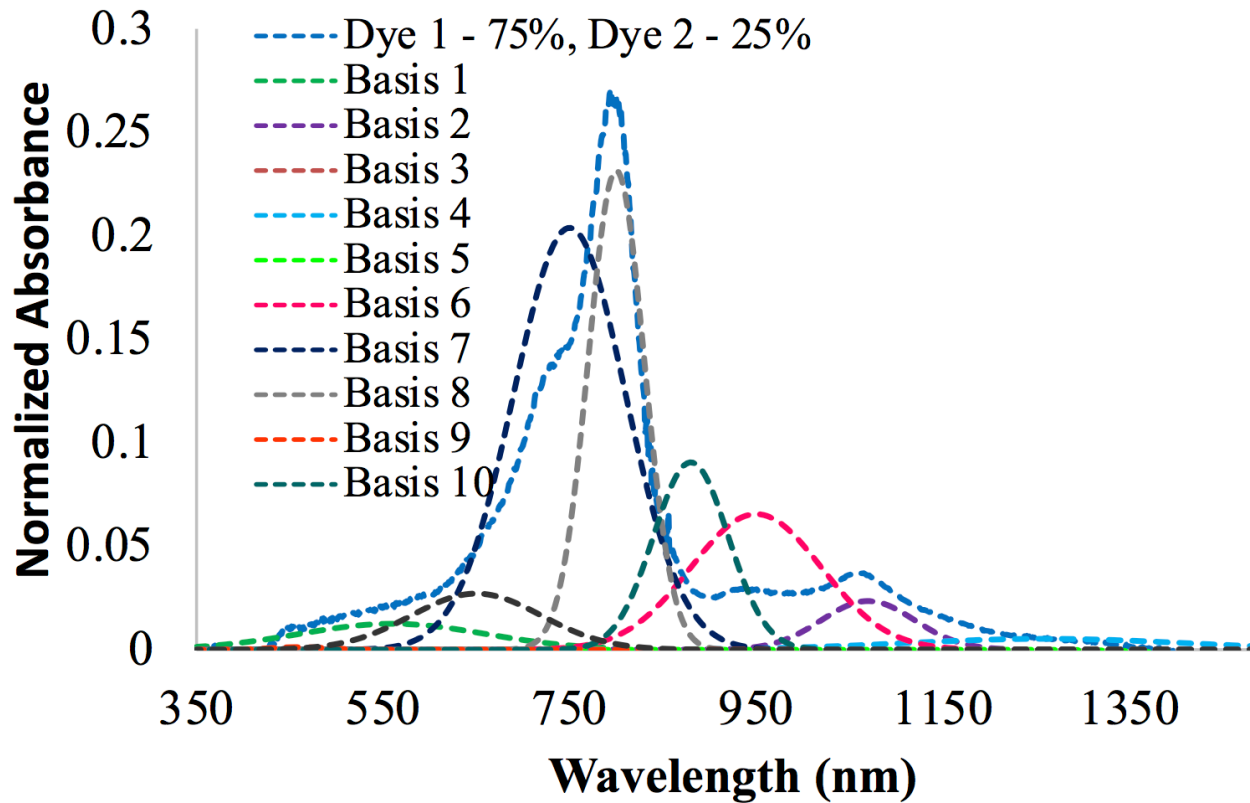
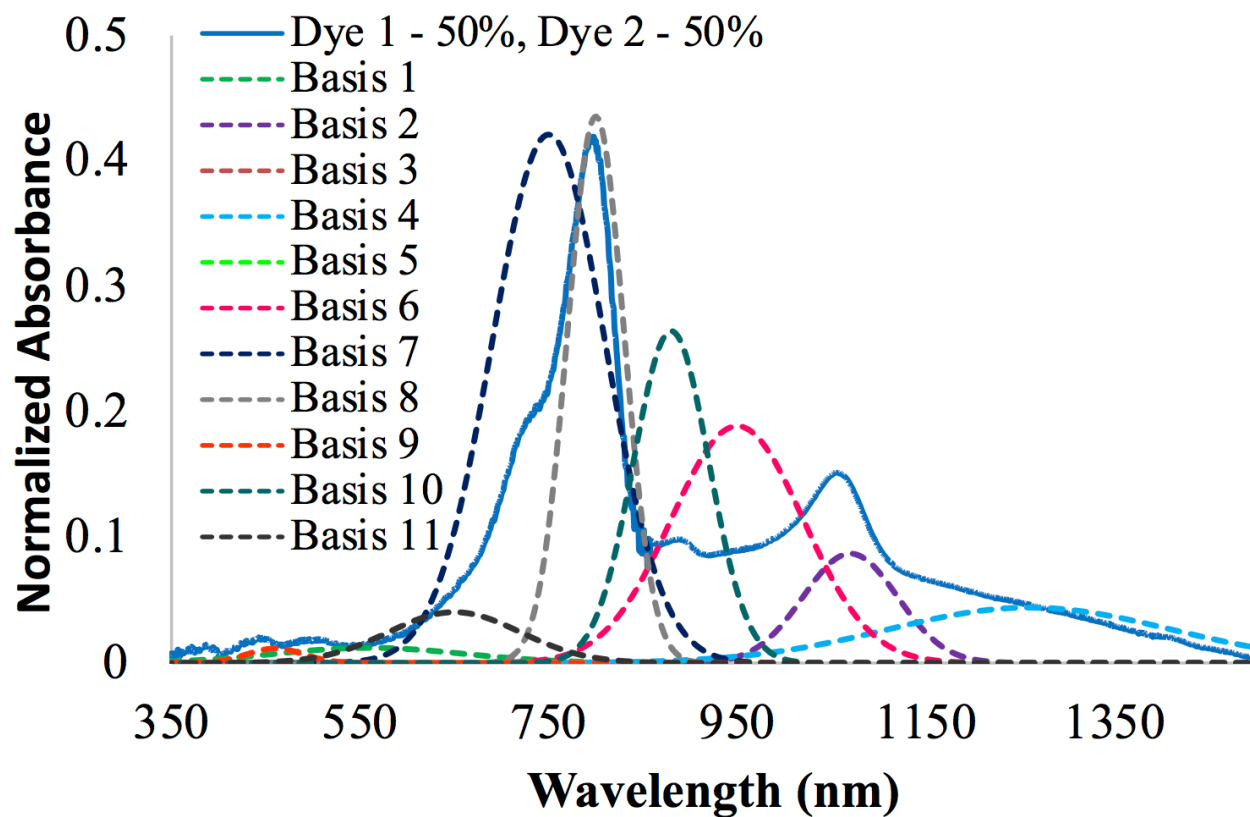


Figure 9. Background-normalized absorbance spectra of dye mixtures in fabric, as function of relative dye concentrations.





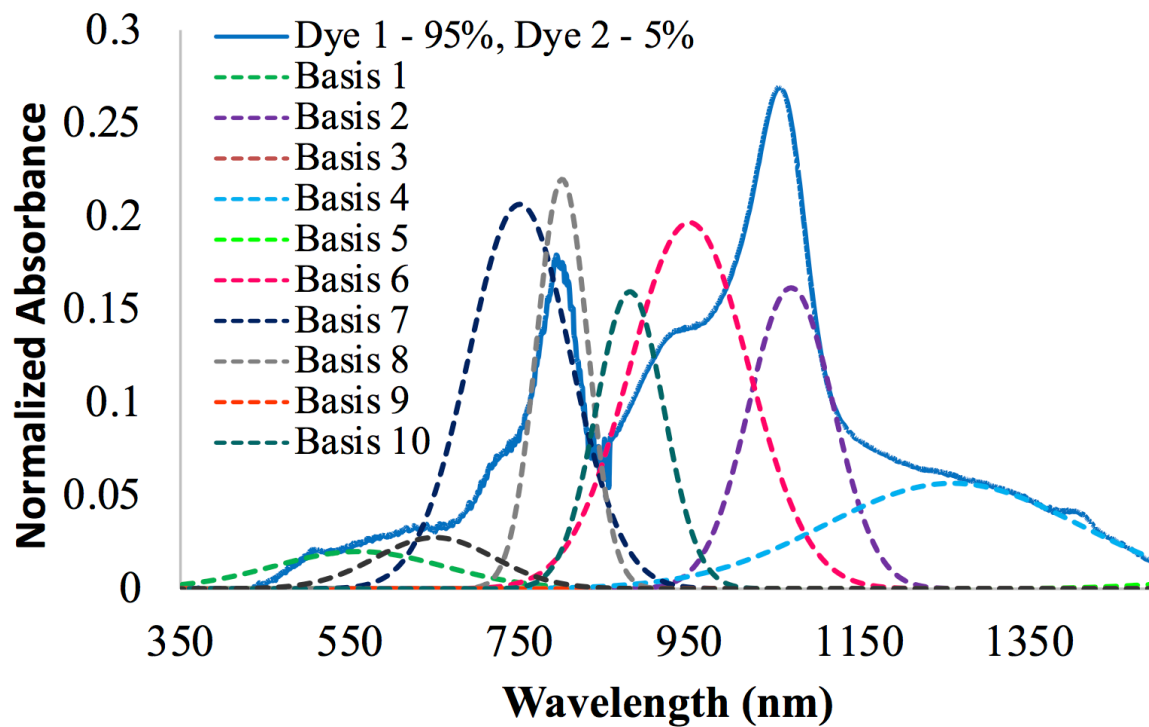
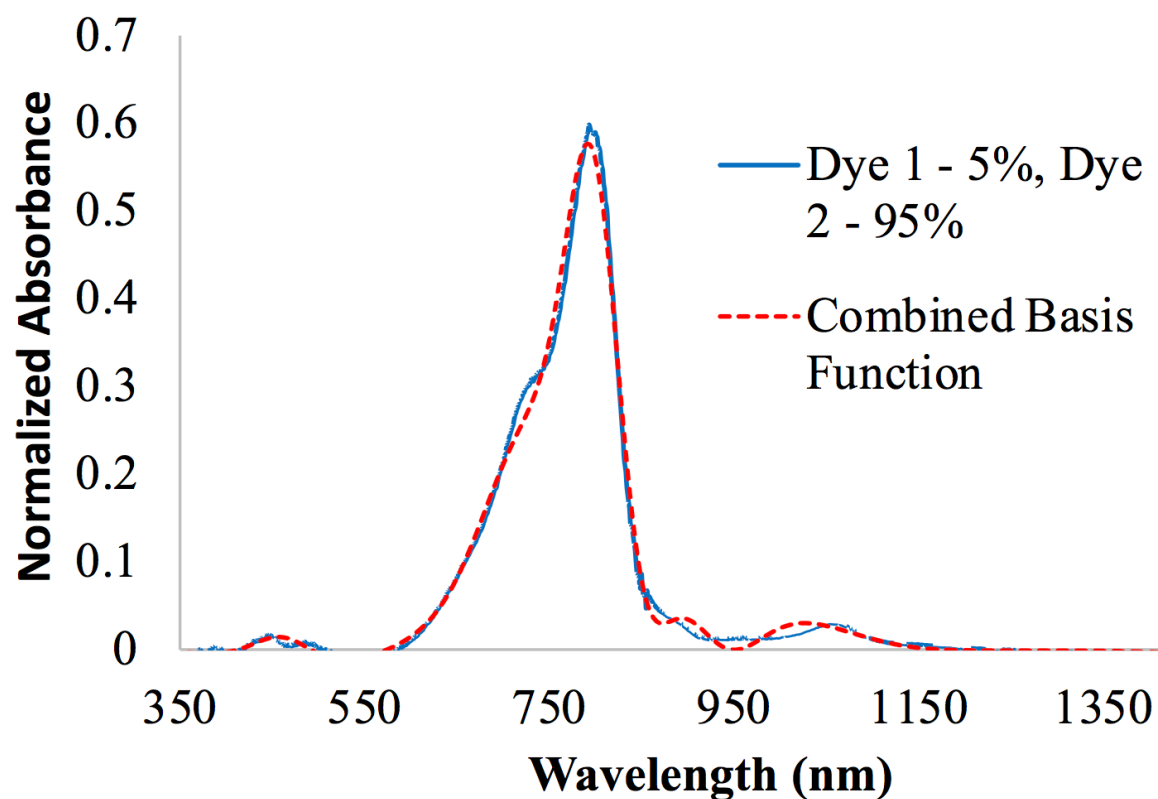
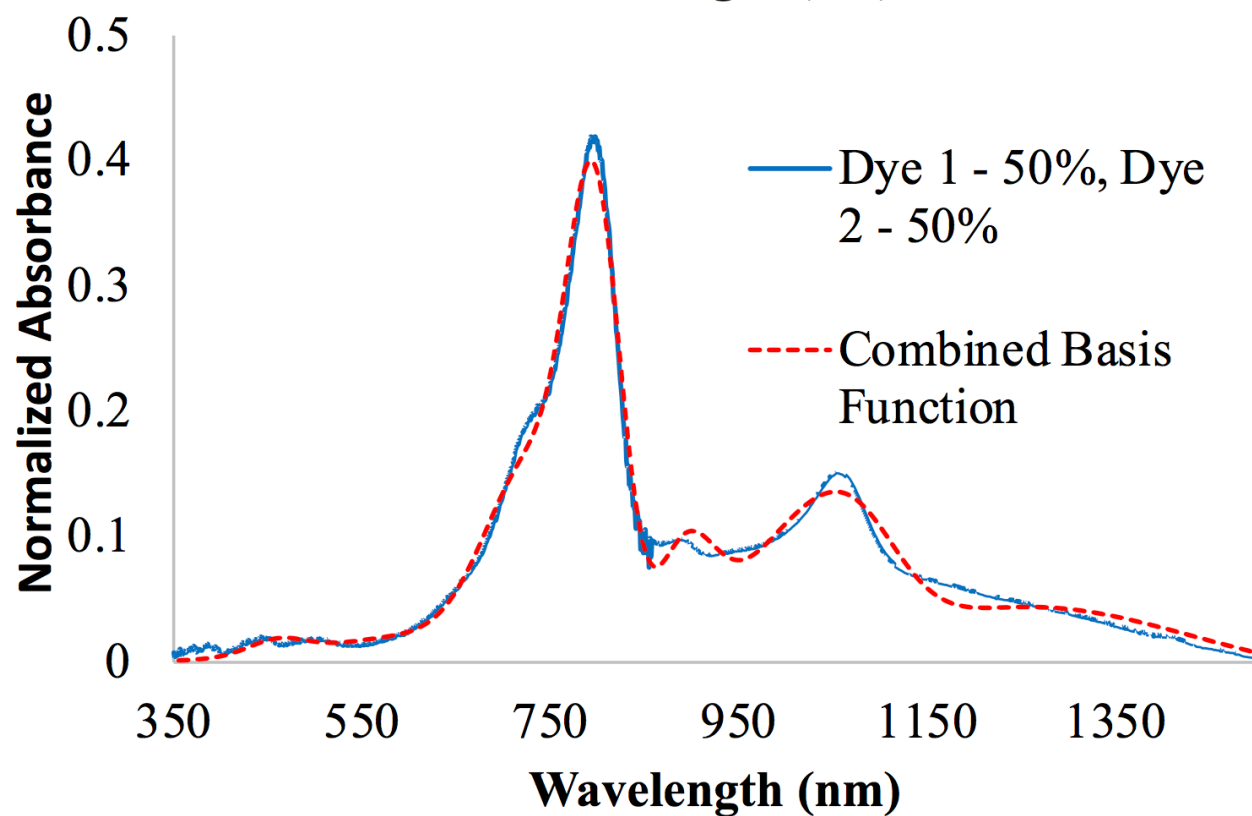
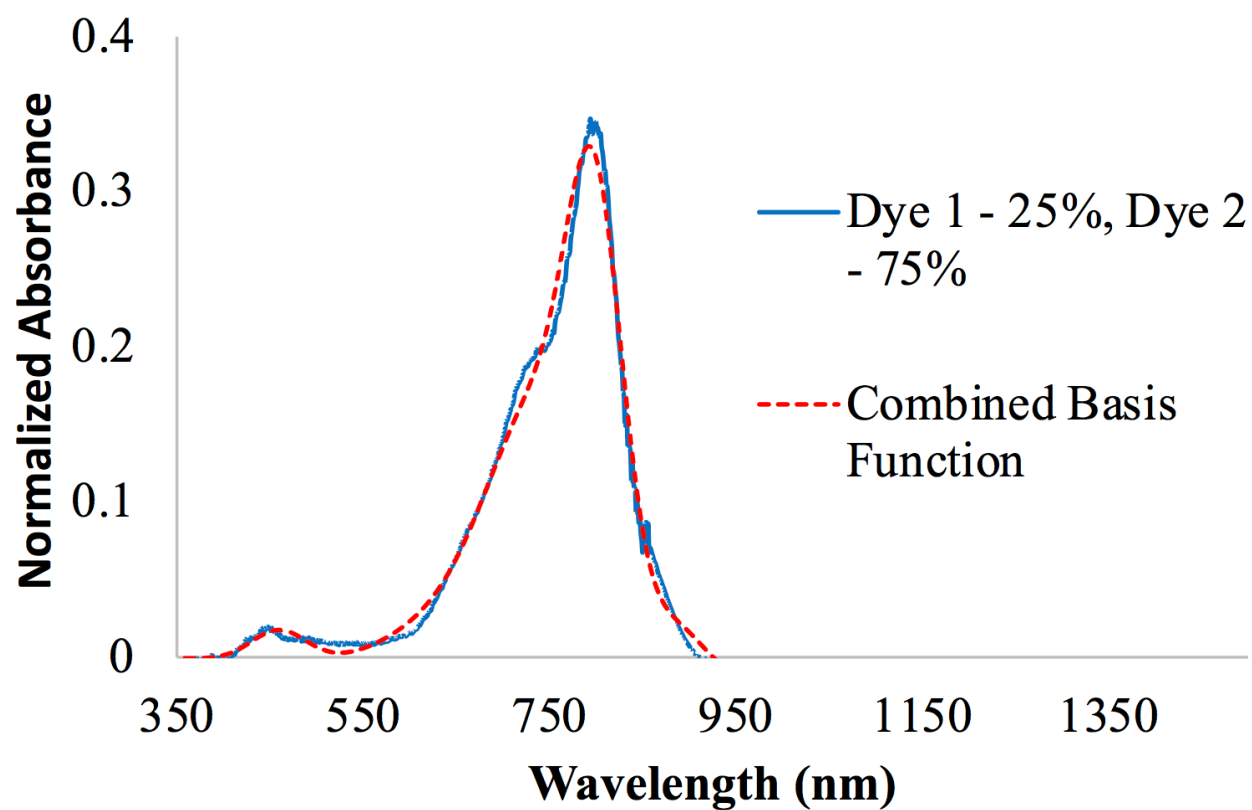


Figure 10. Basis-Function decomposition of absorbance spectra for Dye 1 and Dye 2 mixtures with respect to basis-function expansion Eq.(1).





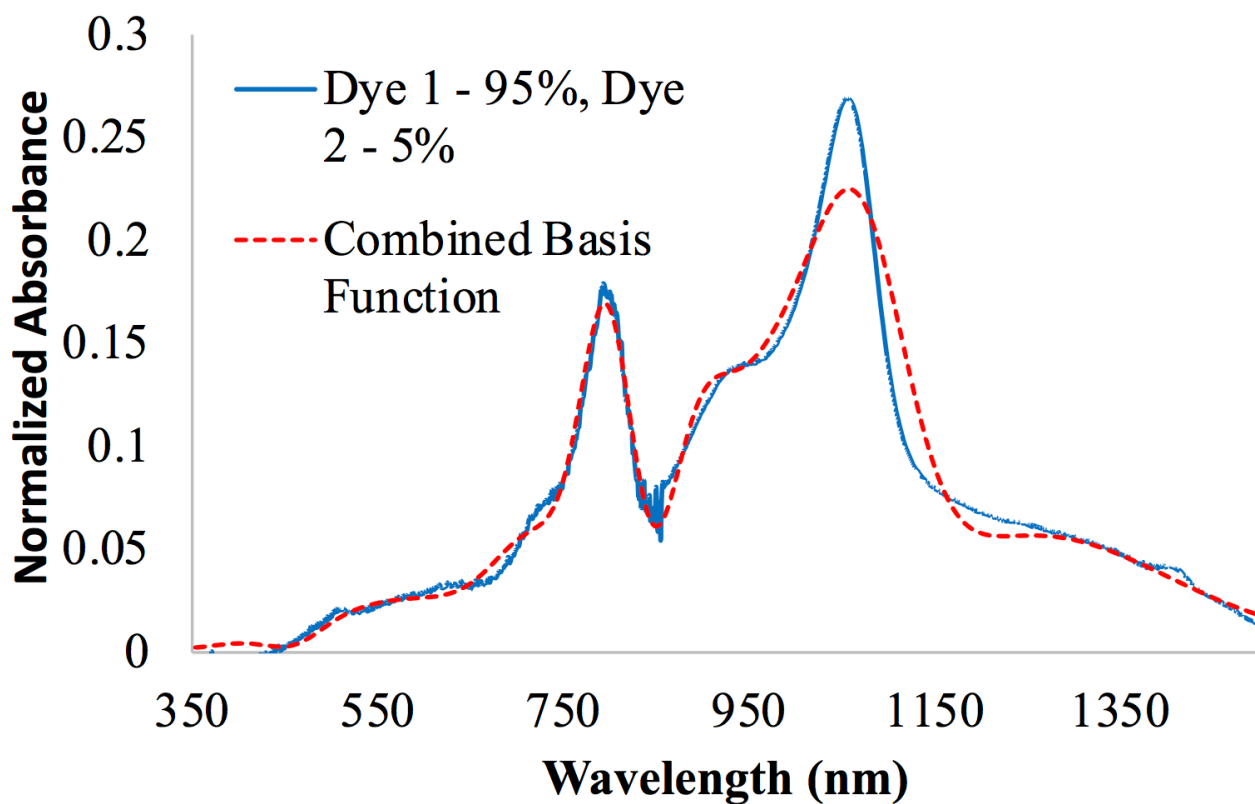
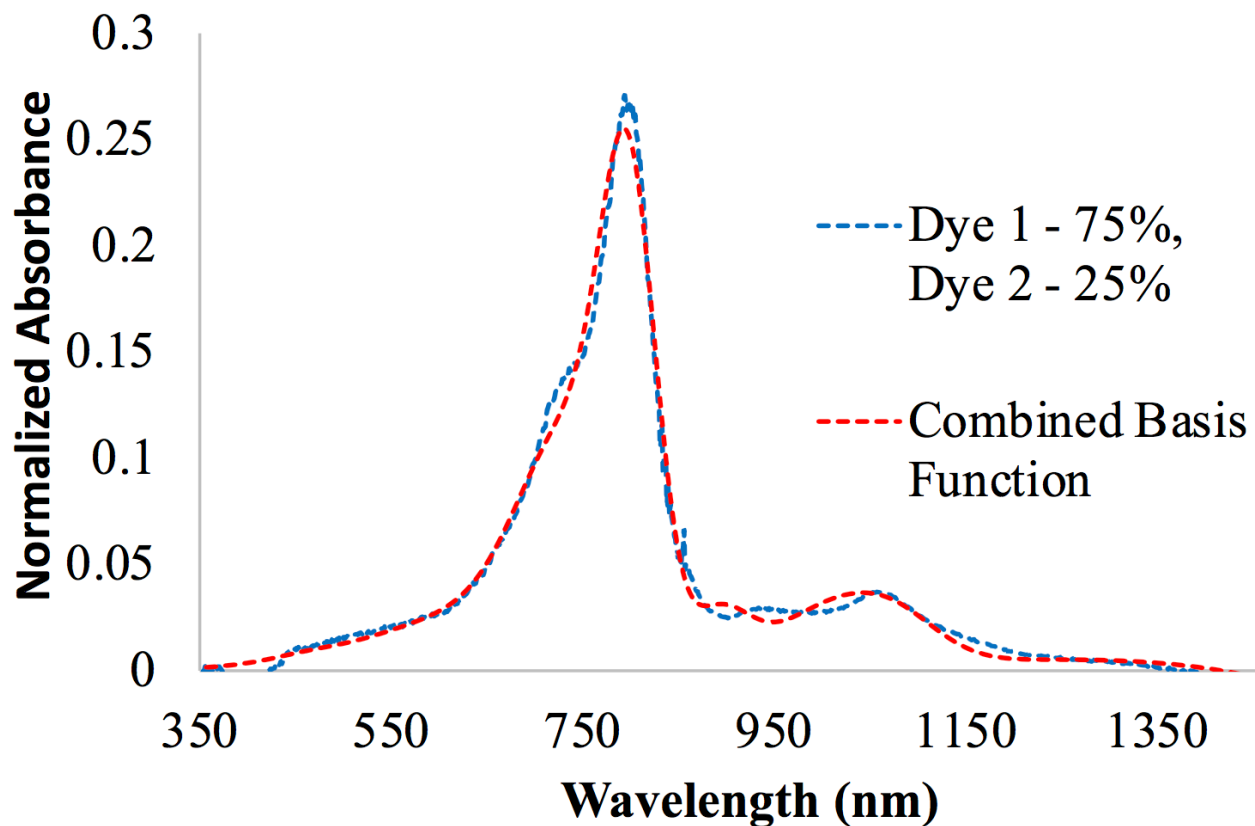


Figure 11. Absorbance spectra for Dye 1 and Dye 2 mixtures determined by inversion (Eqs. (3) and (4)) and calculated using basis-function expansion Eq.(1).

5. Conclusion

This study presents prototype simulations using a parametric model for diffuse reflectance characteristics of dyes and their mixtures in fabrics. The results of this study show good agreement between absorbance functions determined by inversion of experimentally measured reflectance spectra, using Eqs. (3) and (4), and spectra modeled using Eq.(1), for two NIR/SWIR absorbing dyes in a cotton-blend fabric as a function of concentration and wavelength. The relative agreement between modeled and experimentally constructed absorbance functions provides reasonable validation of the parametric model for simulating the diffuse reflectance of dye mixtures in fabrics. These results support proof of concept for construction of parameter spaces, which are for process optimization of dyed fabrics for NIR and SWIR applications. Parameter spaces, in combination with parameter optimization algorithms, would in principle determine optimal dyeing processes, combinations of dyes, and fabrics needed for achieving targeted dyed-fabric spectral response.

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