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β -CYCLODEXTRIN: DISPERSE YELLOW 211 COMPLEXES IMPROVE COLORISTIC INTENSITY OF POLYAMIDE DYED KNITS

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Abstract

Dyes are complex molecules that can, sometimes cause damage to the aquatic environment and harm human health. They are often not completely removed from the effluent by the usual treatments, therefore, efforts have been made to increase their exhaustion from dyeing through with chemical and physical processes. In this context, the use of β -cyclodextrin (β -CD) as dyeing auxiliary agent promotes the reduction of harmful products also increasing color intensity of the fabric. In this paper, β -cyclodextrin (β -CD) was used as a complexing agent to dye polyamide (PA) using the dye C.I. Disperse Yellow 211 (DY211) in order to improve dye exhaustion and color intensity using the β -CD:DY211 complex. Conventional dyeing process and β -CD:DY211 dyeing process by exhaustion were compared and adsorption kinetics, isotherms and the coloristic intensity were evaluated. The chemical shifts in the FTIR spectra and the thermal stability evidence the formation of the β -CD:DY211 complex. Regarding dyeing kinetics and isotherm, the pseudo-first order model was the most appropriate to describe the process, while Nernst isotherm was the one that best represented the adsorption results. Categorically, the samples dyed with the β -CD:DY211 complex obtained higher coloristic intensity in comparison with the conventional process. With this evidence, it is possible to conclude that cyclodextrin is a suitable replacement for environmentally harmful textile aides without further steps into the dyeing process or the need for additional equipment.

Key-words: dyeing; cyclodextrin; polyamide; color.

1. INTRODUCTION

Textile dyes are complex, potentially carcinogenic and genotoxic chemicals. They often lead to several complications for human health and damage to aquatic life.¹ The treatment of wastewater from the textile industries is a difficult and costly process², due to the high chemical demand for oxygen and the excess of suspended solids.³ Therefore, cyclodextrins (CDs) have been gaining prominence due to their potential for application in textile dyeing⁴⁻⁷ and finishing.⁸⁻¹⁴ This tendency promotes the sustainability of textile processing since the textile industry is highly polluting.¹⁵

Polyamide (PA) is an important fiber for the textile market used in curtains, carpets, nets and sportswear¹⁶. Several studies seek to increase the dyeability of this fiber, using techniques such as ozonation, plasma, surface chemical groups change, and others.¹⁷⁻¹⁹ However, these techniques can increase the process costs, reducing the viability for some companies. Thus, in this work, β -CD will be used as a dyeing auxiliary.

The cyclization of linear glucanopyranose linear chains from starch by cyclomalto-dextrin-glucanotransferase (CGTase) produces CD. The number of glucanopyranose units classifies α -CD, β -CD and γ -CD, respectively with 6, 7 and 8 D-(+) glycopyranose linked by α -1,4 bonds.²⁰⁻²² These host molecules can be used in the most diverse industries, such as food,²³ cosmetics²⁴, textile²⁵, treatment of wastewater²⁶ and others. In the textile industry, cyclodextrin is used in textile dyeing,^{7,27,28} as a finish^{13,15,29} and in the wastewater treatment³⁰⁻³².

In textile dyeing, CDs can be used as auxiliary agents for dyeing or grafted into the fabric²⁵. In both cases, the aim is to increase the color intensity of the product after dyeing. The advantage of using them as auxiliaries is related to the replacement of non-biodegradable products by CDs, which comes from a biodegradable source, positively impacting the process as a sustainable product.

CDs are capable of producing complexes with dye molecules that change their properties.^{6,7} It is possible to obtain complexes with a 1:1 (CD:host) molar ratio when the host molecule is well adjusted to the CD cavity. When the host molecule is long enough to be accommodated into the CD cavity, the other extremity of the molecule, can also form complexes with different molar stoichiometries (e.g. 1:2, 2:1, 2:2, 3:1, 3:2).³³

Thus, complexation for its use in dyeing is only possible if there is compatibility between the CD and the dye. β -CD is the most suitable type of cyclodextrin for use in the

textile industry due to its ease of production, its ability to fix on textile surfaces and its suitability for encapsulation.²⁵ Ming Lu and Yiping Lu³⁴ showed that the formation of the β -CD:dye complex may happen with many dyes depending only on the size of the molecule. Capignano⁷ studied the application of β -CD with dispersive dyes applied to polyester (PES) dyeing. In another study, dye complexes with CD positively affected the color uniformity, intensity and bath exhaustion when compared to the usual additives.³⁵ Parlat³⁶ dyed cotton using a reactive dye complex: cyclodextrin complex that improved the uniformity of the dyed product. Several other papers show positive results with different fibers.^{6,37-40}

The objective of this paper was to dye PA using a green innovative process using β -CD and dispersive yellow dye 211 (DY211) complex (β -CD:DY211) and to evaluate its influence on the dyeing process of PA knit when compared to conventional dyeing. The complexes will be employed directly in the dyeing bath without the need for further steps, a feasible concept for conventional industrial setups. To date, no literature studies were conducted with polyamide, and β -CD:DY211 emphasizing the novelty of this study.

2. MATERIALS AND METHODS

2.1. Materials

CAVAMAX W7 β -CD with molar mass 1135 g/mol was purchased from Wacker, Germany. C.I Disperse Yellow 211 dye from Golden Technology, Brazil. ($C_{15}H_{12}ClN_5O_4$). Other analytic grade products from Sigma Aldrich, Germany. The substrate for impregnation of β -CD:DY211 was a knit 100% PA (236.67 ± 1.29 g/m²) from INTEXTER, Spain.

2.2. Methods

2.2.1. Molecular Modelling

The models of the tridimensional molecular structure of the DY211 were made using the Avogadro and MOPAC 2012 software packages. These models were considered as a reference for detecting the possible interactions between β -CD and dye molecules using the atom-molecule longitudinal and transversal measurements.

2.2.2. Complexing and dyeing process

The inclusion complex β -CD:DY211 was prepared by kneading.^{41,42} In this method β -CD was wetted in ceramic mortar with distilled water, at room temperature and pH 7. DY211 was added, (1:1 molar) slowly while grinding. The slurry was kneaded for about 30 min. Then, the product was dried at room temperature for 12 h.

2.2.3. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared Spectroscopy (IR) spectra for β -CD, DY 211 and β -CD:DY211 were obtained using KBr pellets, in the region from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} and 64 scan accumulations in the transmission mode, using the Nicollete Avatar apparatus and the OMNIC 6.2 software, USA. The samples were pre-conditioned for 24h prior to the test at 60 °C.

2.2.4. Thermogravimetric Analysis (TG)

The thermal stability and microstructural differences of the β -CD:DY211 were evaluated using the thermogravimetric apparatus (Shimadzu TG 50, Japan). Samples were pre-conditioned at 60 °C for 24 h. From, the experimental results, the thermal behavior was verified for β -CD, DY211, as well as for the complex β -CD:DY211. The heating rate was set to 10 °C/min between 30 °C and 600 °C in an Argon atmosphere.

2.2.5. Dyeing – Adsorption Kinetics and Adsorption Isotherms.

Adsorption experiments were carried out using 25 mL of dye solutions (180 mg/L) and 1 g of PA knit. The experiments with the β -CD, were performed using the β -CD:DY211 molar ratio of 1:1.

The textile dyeing process, was performed via dye exhaustion using the KIMAK AT1-SW apparatus (Brazil) for 60 minutes at 90 °C. After that, the PA knit sample was removed from the bath. The samples were diluted and analyzed by spectrophotometry (Lambda 750 PerkinElmer, USA) at 498 nm. Equation (1) was used to evaluate the quantity of adsorbed dye in the adsorbent phase at equilibrium and Equation (2) was used to evaluate the percentage of dye exhaustion.

$$qt = \frac{V(C_i - C_t)}{m} \quad (1)$$

$$E(\%) = \left(\frac{qt \times m}{C_i \times V} \right) \times 100 \quad (2)$$

Where: C_i is the initial concentration of dye (mg/L), C_t is the concentration of dye at the pre-set time (mg/L), V is the volume of the dye solution and m the mass of the adsorbent (g).

The adsorption kinetics was adjusted according to the pseudo first-order and intra-particle diffusion models.

Isotherms were carried out under the same conditions and with the same equipment, varying the amount of dye, with a dye concentration range between 10 and 200 mg/L. The adsorption isotherms were adjusted according to the Nernst, Freundlich and Langmuir Models. using the software Origin 8.5.1. The standard affinity of a dye for a fiber was calculated by Equation (3):

$$-\Delta\mu = RT \ln K_n \quad (3)$$

Where, R is the universal gas constant, T represents the temperature (K) and K_n is the Nernst constant of the isotherm

2.6 Color Evaluation

The color of the textile substrates was evaluated in both processes using the spectrophotometer Delta Vista 450G (Brazil) and the software i7 Delta Color. From the data provided by the equipment, coloristic coordinates and CMC color difference were obtained (Color Measurement Committee) (l:c) (1:1) (Eq. 4) and CIE (Comission Internationale de l'Eclairage) Lab 2000 (Eq. 5).

$$\Delta E_{CMC}^2 = \left(\frac{\Delta L^*}{lS_L}\right)^2 + \left(\frac{\Delta C^*}{cS_C}\right)^2 + \left(\frac{\Delta H^*}{S_H}\right)^2 \quad (4)$$

Where:

ΔL^* luminosity variation, ΔC^* saturation variation, ΔH^* hue variation, l light factor (1), c saturation factor (1), are constant in the adopted model (1:1), S_L , S_C and S_H are functions of L , C and H and C respectively.

$$\Delta E_{00}^2 = \left(\frac{\Delta L^*}{K_L S_L}\right)^2 + \left(\frac{\Delta C^*}{K_C S_C}\right)^2 + \left(\frac{\Delta H^*}{K_H S_H}\right)^2 + R_r \left(\frac{\Delta C^*}{K_C S_C}\right) \left(\frac{\Delta H^*}{K_H S_H}\right) \quad (5)$$

Where:

The factors K_L , K_C and K_H are correction parameters related to the observation conditions of the samples, and in the textile industry: $K_L = 2$ and $K_C = K_H = 1$.

In addition, the method ISO 105-A03/AATCC was applied to perform the washing fastness testing, regarding a multi-fiber fabric: acrylic, cotton, polyamide, polyester, triacetate and viscose. The evaluations were performed using a DataColor spectrophotometer (Spectraflesh model SF650X).

3. RESULTS AND DISCUSSIONS

3.1. Dye Molecular Geometry

The size of the dye molecule influences the production of β -CD:DY211 complexes.^{22,43} The complexation occurs due to the water displacement in the CD cavity that allows the CD to host the dye molecule. The dye molecule geometry may facilitate or hinder the complexation. The number of glucose units of cyclodextrin determines the internal diameter and the volume of the cavity.⁴⁴ β -CD has 7 glucopyranose units and the diameter of 6.5 Å. This size enables the encapsulation of aromatic and heterocyclic compounds such as the DY211 dye.²⁰

Figure 1 presents the highest transversal and longitudinal dimensions for DY211 and a tridimensional model.

Figure 1 - Transversal and longitudinal dimensions for DY211 and a tridimensional model

According to Andraus et al²⁰, the production of an inclusion complex depends on the geometric adjustment between the host molecule (dye) and the cavity of the host molecule (β -CD). The host should be planar to be allocated in the cavity. According to Figure 1, the maximum transversal size of the dye is 5.86 Å, inferior to the β -CD cavity diameter (6.5 Å), consequently enabling the formation of the β -CD:Dye complex.

Rekharsky and Inoue⁴⁵ showed that Van der Waals interactions occur regardless of the size and shape of the molecule to be hosted but they are critically related to the distance between molecules. Another important factor mentioned by Takahashi³³ is the longitudinal size of the host molecule because the β -CD cavity has a cone-like geometry with an internal length of approximately 7.9 Å. Thus, when the host molecule is too long to fit in a cavity, the other side of the molecule would be responsible for creating the

molecular interactions that conform to the first step in the formation of the complex. The dye molecule has a longitudinal section of 12.11 Å. According to Szejtli⁴⁶, the complexes may be formed following the ratios CD: host 1:2, 2:1, 2:2, 3:1, 3:2, etc. Agreeing with Cromwell and coworkers⁴⁷, the formation of the CD complexes depends basically on the longitudinal size and the cylindrical volume of the CD cavity. CDs have 6.5 Å longitudinal size and 7.9 Å deepness, corresponding to 350 Å³ of cylindrical volume approximately. Assuming that the DY211 molecule has a cylindrical volume of approximately 435 Å³, it is expected that the interaction between the dye and CD occurs in a ratio of 1:1 and a small piece of the host molecule will stay out of the CD cavity. Thus, the 1:1 ratio with respect to the reagents was used in order to favor the formation of the 1:1 complex.

3.2. FTIR Analysis

Figure 2 shows the Fourier Transform Infrared Spectra for β-CD, DY 211 (dye) and β-CD:DY211 (Complex) with several relevant bonds attributed.

Figure 2: Fourier Transform Infrared Spectra for β-CD (black line), DY 211 (red line) and β-CD:DY211 (blue line) obtained in the range between 4000 and 400 cm⁻¹.

Figure 2 shows β-CD bands at 3375, 2925, 1641 and between 1060 and 1020 cm⁻¹ corresponding to the typical cyclodextrin vibrational modes of □OH, □CH, □COH and □COC in the ether, hydroxyl functional groups as well as the glycosidic bonds respectively.³⁰⁻³² The band at 1080 cm⁻¹ shows a secondary hydroxyl group stretch present in the β-CD molecule.¹⁰ Bands between 950 and 700 are ascribed to -CH and C-C bindings, respectively in the glycopyranose ring of the cyclodextrins structure.⁹ Dye bands were observed at 3427 cm⁻¹ from OH stretch, 2230 cm⁻¹ from C≡N, 1692 cm⁻¹ from C=O, 1641 cm⁻¹ from ring C-N. Typical NO₂ bands were noticed at 1498 and 1313 cm⁻¹.^{30,33-36} Azo group (N=N) stretch band is observed at 1480 cm⁻¹.³⁴

From the data, both materials comprise the complexes by the overlapping the of β-CD and DY211 bands. However, complex spectra (blue) show a tiny transmittance band intensity attenuation for the dye just as evidenced in other β-CD-based materials from literature.^{1,29} It is also possible to observe a small shift at -OH β-CD groups from 3375 to 3397 cm⁻¹ caused by the dye complexation at the β-CD cavity. As there are no

significant shifts of other bands, it is assumed that the interaction between β -CD and dye occurs by outer-sphere coordination without new chemical bond formation. The insertion of a host-molecule in the β -CD cavity creates a conformational restriction evidenced in the attenuation of the signal.⁴⁸ Bakkialakshmi & Menaka⁴⁹ and Stanghellini et al⁵⁰ also noted the slight chemical shifts in the –OH groups (stretching ascribed in β -CD to 3375 and to the complex at 3397) and confirmed that these interactions would stabilize the complex. As observed in the works cited, the FTIR spectra clearly evidence the complex β -CD:DY211 formation by outer-sphere complexation.

3.3. Thermogravimetric Analysis

Figure 3 shows the thermal behavior for β -CD, DY211 and the β -CD:DY211 complex evaluated from 30 to 600 °C at 10 °C/min. The thermogravimetric curve for β -CD (Figure 3) shows two thermal events: 1) at 91.0 °C, the dehydration of β -CD with 9% mass loss⁵¹; 2) at 359.5 °C (73% mass loss) from the decomposition of β -CD which is completed at 600.0 °C.⁹ Regarding the DY211 dye, three thermal events are observed: 1) up to 60.0 °C corresponding to moisture loss; 2) From 60.0 to 234.0 °C (summed to event 1.14% mass loss) common in azo aromatic dyes, attributed to the beginning of a molten phase of the material⁵² that will be intensified at 325.3 °C (with 26% mass loss).

Figure 3: Thermogravimetric curve for β -CD (black line), DY211 (red line) and β -CD:DY211 complexes (blue line) obtained in an Argon atmosphere, (a) TG and (b) DTG.

The thermal events of complex the β -CD:DY211 are observed in Figure 3(a) at 113.7, 277.1, 320.3, and 477 °C. This occurs due to the molar ratio 1:1 in the complex. At 277.1 °C the thermogram Figure 3 (a) and (b), shows a slight increase in dye decomposition, changing the descendent profile into a more intense angle (similar to CD). This indicates that the dye has a soft protection offered by the CD cavity. The sensibility of the azo bond is the responsible for the decomposition and no shifts were observed in the FTIR spectra. The final step of decomposition of the CDs occurs at 360°C. However, the complex presents an increase to 477 °C, which means that CDs and dye, in the complex, have extra-molecular interactions. As observed in the FTIR spectra, this small increase corroborates the dye insertion in the β -CD cavity through an outer-sphere coordination and without new chemical bonds formation.

3.4. Dyeing - Adsorption kinetics

Figure 4 shows the kinetic curves for the dyeing process: conventional (a) and with β -CD:DY211 complexes (b). From the data, Figure 4(a), it is observed that the system reaches equilibrium at about 20 minutes. The dye adsorption increases abruptly between 5 and 15 minutes; this may be unfavorable to the process because it implies a high diffusion coefficient, causing uniformity problems. The high substantivity of DY211 to PA fibers can be explained by the presence of electron donors in the PA structure ($-\text{OH}$ groups) and acceptors in the dye ($-\text{NO}_2$) group.⁵³

Figure 4: Kinetic Model adjustment for the dye DY211 in PA: (a) conventional process, without complex and (b) with β -CD:DY211 complexes.

Figure 4(b) presents the results obtained with the β -CD:DY211 complexes. The Figure shows that equilibrium is reached after approx. 20 minutes. Therefore, β -CD allowed a gradual adsorption process, acting as a controller agent.

Table 1 reports the kinetic constants, associated errors and correlation coefficients (R^2) for the models in Figures 4(a) and (b). In Table 2, for both processes the model that best fits is the pseudo-first order (PFO). The PFO reaction can be defined as a bimolecular reaction and occurs when one reacting material is present in excess or is maintained at a constant concentration compared with the other substance.⁴⁹

In the process that uses the complex, there is more dye adsorbed, 3.695 ± 0.015 , this represents $82.111 \pm 0.167\%$ exhaustion of the dye. In the conventional process, there is an exhaustion of $81.444 \pm 0.400\%$. The effect of the complex slightly improves the amount of dye adsorbed. However, as seen in the color analysis, this increase has a great effect on the final color of the product. Similar works report successful use of β -CD in textile dyeing. Singh and Sahu³⁵ claim that the CD increases dye affinity and exhaustion. In their work, CDs establish ionic and covalent bonds and Van der Waals intermolecular interactions with PA. Wan, Chen and Bai⁵⁴ have shown good dye affinity and fastness on polyurethane dyed with β -CD:Disperse Orange 31.

Table 1: Adsorption kinetics data for the dyeing processes - conventional and with the β -CD:DY211.

Process	Parameter	Pseudo first-order	Pseudo-second order	Intraparticle Diffusion
Conventional	q_{eq} (mgg ⁻¹)	3.665 ± 0.018	4.690 ± 0.463	--
	k_1 (h ⁻¹)	0.082 ± 0.014	--	--
	k_2 (g(mgh) ⁻¹)	--	0.016 ± 0.006	--
	k_{ia} (mg(gh ^{1/2}) ⁻¹)	--	--	0.556 ± 0.065
	R^2	0.9136	0.8850	0.7839
β -CD:DY211	q_{eq} (mgg ⁻¹)	0.9136	4.755 ± 0.423	--
	k_1 (h ⁻¹)	3.695 ± 0.015	--	--
	k_2 (mg(gh ^{1/2}) ⁻¹)	0.0773 ± 0.0109	0.015 ± 0.005	--
	k_{ia} (mg(gh ^{1/2}) ⁻¹)	--	--	0.557 ± 0.058
	R^2	0.9362	0.9106	0.8194

q_{eq} : amount of adsorbate adsorbed at time t ; k_1 : pseudo-first order speed constant; k_2 : pseudo-second order speed constant; k_{ia} : intraparticle diffusion speed constant.

As can be seen in Table 1, the lowest values of R^2 were obtained by adjusting to the intra-particle model, indicating that adsorption is governed by external mass transfer. With regards to kinetic models, PFO fits better both conventional and β -CD:DY211 dyeing ($R^2 > 0.91$). These results indicate that the adsorption of the complex, follows the kinetic model of PFO with fast adsorption and also governed by mass transfer. The pseudo-second order models are suitable to indicate the development of new chemical bonds. It is assumed that there is no chemical bond formation between dye and β -CD as the correlation coefficients (R^2) of this model are the lowest. The adsorption process is ruled by -OH intermolecular interaction. These data are consistent with the findings of the FTIR and thermogravimetric data also showing an outer-sphere kind of interaction.

3.5. Dyeing - Adsorption Isotherms

The adsorption isotherms are labelled by Q_e (adsorbed quantity at equilibrium / mg g⁻¹) vs. C_e (Dye concentration at equilibrium / mg L⁻¹) and represent dye equilibrium in the bath and in the fiber. It is possible to adjust the data according to the molecular interactions in three isotherms: Nernst, Freundlich and Langmuir, with the respective isotherms constants, k , written k_N , k_F , k_L .

Figure 5 fits the adsorption isotherm in the dyeing process, (a) conventional and (b) with β -CD:DY211 complexes.

Figure 5: Isotherm model adjustment for the dyeing process with DY211 dye on PA: (a) conventional process, without complex and (b) with β -CD:DY211. Q_e = Amount of DY211 dye adsorbed at equilibrium; C_{eq} = DY211 concentration at equilibrium

Table 2 shows the adjusted parameters of Langmuir, Freundlich and Nernst models as well as the respective experimental errors and correlation coefficients (R^2).

Table 2: Adsorption isotherms data for the dyeing processes - conventional and with the β -CD:DY211.

Process	Parameters	Langmuir	Freundlich	Nernst
Conventional	Q_{sat} (mgg^{-1})	64.420 ± 15.960	-	-
	k_L (Lmg^{-1})	0.004 ± 0.001	-	-
	k_F (Lg^{-1})	-	0.264 ± 0.004	-
	n_F	-	1.042 ± 0.007	-
	k_n	-	-	0.239 ± 0.001
	$-\Delta\mu$ ($KJmol^{-1}$)	-	-	-4.320
	R^2	0.9993	0.9996	0.9989
Complex (β -CD:DY211)	q_{sat} (mgg^{-1})	21.338 ± 2.905	-	-
	k_L (Lmg^{-1})	0.014 ± 0.003	-	-
	k_F (Lg^{-1})	-	0.348 ± 0.068	-
	n_F	-	1.129 ± 0.012	-
	k_n	-	-	0.266 ± 0.002
	$-\Delta\mu$ ($KJmol^{-1}$)	-	-	-3.998
	R^2	0.9979	0.9991	0.9979

Q_{sat} : amount adsorbed in saturation; k_L : constant of the Langmuir isotherm; k_F : constant of the Freundlich isotherm; n_F : adsorption intensity factor; k_n : constant of the Nernst isotherm; $-\Delta\mu$: The standard affinity of a dye for a fibre.

When compared to the conventional process correlation coefficients, in both cases they are similar. For the Langmuir model, the error associated with k_L is at the same magnitude as the parameter which suggests an absence of experimental data fit.

Thus, Freundlich and Nernst models fit with the process. However, as the n_F coefficient has a value of 1, the Freundlich model coincides with the Nernst model as two linear equations. Therefore, the adjustment that best represents the dyeing process is the Nernst model. In addition Eppers states that for dyeing synthetic fibers with dispersed dyes, the Nernst isotherm can describe the dyeing event.⁵⁰

The dye is transferred to the fiber, in which it is soluble, from the aqueous bath, in which it is only slightly soluble. It is generally true that the dye absorption isotherm is

linear at low dye concentrations. The dye molecules behave as if they were in a solution inside the fiber and are partitioned between the fiber and the dyebath. So that, at any temperature, the ratio of dye in the fiber to dye in the solution is constant. Differences commonly occur at relatively high concentrations, but the ideal linear behavior is observed with disperse dyes over a wide range of concentration.

The results of the standard affinity of the dye for a fiber show that the dyeing using β -CD:DY211 presents higher values than those without cyclodextrin, suggesting that the cyclodextrin influences the affinity of the dye, highlighting the results of the kinetic study.

3.6 Color Evaluation

Table 3 shows the coloristic coordinates for the conventional dyeing and the dyeing using the β -CD:DY211 complex.

Table 3: Coloristic coordinates and color difference (CMC and CIE Lab 2000) for the conventional and β -CD:DY211 on PA.

Process	L*	a*	b*	ΔE_{00}	ΔE_{cmc}
Conventional	99.52	-1.43	17.9	5.54	3.35
β -CD:DY211	97.13	-0.99	22.88		

L luminosity, a chroma (+a red and -a green), b chroma (+b yellow and -b blue).

The results reveal that the fabrics dyed with the β -CD:DY211 complex were darker ($\Delta L < 0$), more saturated and more yellow ($\Delta b > 0$). Savarino et al⁵⁵ studied the dyeing of PA with β -CD complexes. According to the authors the higher coloristic intensity is obtained with the presence of complexes, since it changes the dyeing kinetic allowing better dyeing levelling as seen in the color difference values: $\Delta E_{00} = 5.54$ and $\Delta E_{cmc} = 3.35$, Table 3. Higher values indicate a proportional coloristic intensity (more dye in the fiber) and these results show the positive effect of β -CD:DY211 on dyeing, validating the initial hypothesis about the use of the complex for dyeing. In addition to the coloristic comparison, the washing fastness was evaluated Table 4.

Table 4 –Washing fastness performed in multi-fiber fabric according to ISO 105 A03/AATCC

Process	Washing fastness					
	Acrylic	Cotton	Polyamide	Polyester	Triacetate	Viscose
Conventional	4.43	3.84	1.91	3.25	3.20	4.19
β -CD:DY211	4.51	4.16	1.96	3.31	3.39	4.37

The results of the washing fastness indicate a slight improvement regarding the color of the fabric that was dyed using β -CD: DY211, indicating that cyclodextrin can be used as an additive in the dyeing process without impairing the fiber dye interaction.

Several studies have shown changes in the kinetics and thermodynamics of polyamide dyeing with CD as an additive, demonstrating that the formation of complexes with CD increases the adsorption of the dye by the fiber, justified by the increase in the intensity of the color, related to the increase in the dispersibility of the dye in the aqueous phase^{28,47,55,56} Kumbasar and collaborators⁵⁷ carried out a series of experiments using CD and acid dyes in order to observe the viability of CD as an equalizing agent in PA dyeing. The results showed that, for all the dyes used, the addition of CD improved the dyeing processes as long as some adjustments were applied according to the kinetic and thermodynamic studies. These results show that the addition of CD can be a source of substitution for additives from non-renewable sources. However, it is worth mentioning that the technical viability depends on the anchoring of the dye to the DC cavity.

4. CONCLUSIONS

From the results, it is possible to conclude that the use of β -CD:DY211 is favorable to dye 100% PA knits. The dye dimensions of the dye are compatible with the diameter of the β -CD cavity, allowing the formation of β -CD:DY211, evidenced by complex spectroscopy and thermogravimetric characterizations. Besides, the study of the kinetic parameters showed that there is a slight increase in the amount of adsorbed dye when dyeing with cyclodextrin complexes. The findings were statistically significant different. In addition, the dyeing can be represented by the PFO kinetic model, with rapid adsorption and without chemical bond formation. The results obtained through the coloristic coordinates confirm the kinetic study and validate the initial hypothesis of increased amount of adsorbed dye.

These findings implicate that β -CD:DY211 complexes are a sustainable alternative to a sustainable dyeing process. Furthermore, the complexes do not require additional steps, implying that industries can adapt their existing processes to adopt this technology in order to substitute additives from non-renewable sources. The results of this work show that the use of the complex is important, mainly because it allows the reduction of the concentration of dye necessary to produce the same shade in the substrate. This also

allows for a decrease in wastewater pollution from the dye, since cyclodextrin is biodegradable. Finally, cyclodextrin has proved to be an excellent substitute for environmentally harmful textile auxiliaries, without adding other steps to the dyeing process or the need for additional equipment.

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