

Colorimetric Quantification of virgin and recycled cashmere fibers: equilibrium, kinetic and thermodynamic studies

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This is a pre-print version of the article published on Journal of Natural Fiber:

<https://www.tandfonline.com/doi/abs/10.1080/15440478.2021.2009399>

Abstract

Cashmere is byword for soft, luxury, and expensive stylish clothes. Objective and quantitative methods to identify and possibly quantify recycled cashmere are crucial to discourage adulteration of high-quality virgin cashmere with cheaper recycled fibers.

Available analytical methods for the identification of recycled and virgin fibers are currently confined to subjective assays. This work investigates objective and reliable methodologies to quantify the amount of recycled cashmere in blend with virgin one, based on the different dye absorption capacity of recycled and virgin fibers. Pure virgin and recycled cashmere fibers were stained with different amounts of C.I. Direct Red 7 in different conditions, and the exhaust dyebaths were analysed by UV-visible Spectroscopy in order to quantify the residual unabsorbed dye. Then, the method was applied to blends of different proportions of virgin and recycled cashmere with a correlation of $R^2 = 0.95$. This approach could provide a system to protect companies and customers against frauds.

Keywords: cashmere, recycling, recycled fibers, quantification, adsorption kinetics, thermodynamics

Introduction

Cashmere is generally known as a luxury fiber for having special properties of softness, thinness, warmth, smoothness and rarity (McGregor 2018). These special characteristics made cashmere widely used in textile, especially in fashion industries (Asheim and Eik 1998). Cashmere is usually produced in extensive grazing system with tradition and nomadic management and its universal popularity has led to over-rearing of cashmere goats in their native countries and it is causing desertification (Ansari-Renani *et al.* 2013; Mueller *et al.* 2015). It is principally produced in Northern China, Mongolia, Tibet and Afghanistan, but also in smaller quantities in Iran, Australia and New Zealand (Bishop and Russel 1994). Each goat is able to produce from 100 to 160 g of fiber forming the downy undercoat of the fleece and the world production is estimated of 9000-10000 tons per year of which 50-60% comes from China and Tibet. Even if the cashmere represents only a small share of the world fiber consumption (less than 0.01% of annual world fiber), its price has an overriding influence of world fiber market (McGregor 2018). Indeed, a fine white knitting cashmere costs US\$ 120-130 per Kg (Kargar *et al.* 2017).

Recycled cashmere is made of fibers reclaimed from post-factory scraps and post-consumer textile wastes, mostly worn knitwear, that have been sorted, shredded, and re-spun through standardized

mechanical process (Niinimäki and Karell 2020). The yarns are washed, rinsed and dried, and then wound onto spools for further processing to create new clothes.

The practice of mechanical recycling goes back hundreds of years; it was especially developed in the area of Prato, Italy, to produce woolen garments, rebranded as “regenerated wool” (Tarantini *et al.* 2009). Through recycling, the material value of textile wastes can be maintained at different levels (Singh and Ordoñez 2016). Nevertheless, recycled fibers quality cannot be compared to virgin fibers since the mechanical processes of recycling cause some extent of detriment to their morphological and mechanical properties (Yuksekkaya *et al.* 2016). Fibers are mainly shortened through shredding and thus deteriorate, but the quality can still sufficiently fulfil the requirements of most clothing applications, actually because they were often added with virgin fibers to create yarns (Bhatia, Sharma, and Malhotra 2014). The use of recycled cashmere as feedstock is already established and technologies are in use (as well as the use of recycled wool and wool blends), mainly as it can be 40-60% cheaper than virgin cashmere.

Current legislation in the U.S. already provides for the requirement to indicate the presence of recycled fibers on the labelling or marking of textile products containing such fibers. It is likely that similar provisions will be adopted also in the EU, in order to counter frauds, and try to warn consumers over products which may be inferior in integrity and performance. However, regulations and laws require recognized and reliable methodologies (Hole and Hole 2020).

Nowadays, the most common way for the identification of recycled fibers is based on morphological studies by microscope observation method (Guifang *et al.* 2015) based on the investigation of typical fiber abrasion and breakages (ASTM D4510-18 Standard Methods for Counting Partial Cleavage in Wool and Other Animal Fibres 2018) that can be affected by possible evaluation errors. Therefore, effective and real-time identification processes are urgently required in order to minimize measurement uncertainty. For fiber identification, a well-assessed strategy is the staining with selected dyes (Hubbe *et al.* 2019). More in general, staining methods are simple, fast and low-cost and do not require complex equipment and they are widely used in industries for different materials such as wood, pulp and paper, but also for fiber and textiles (Vazquez-Cooz and Meyer 2002; Jablonský *et al.* 2015; Anheuser and Roumeliotou 2003). Lai *et al.* successfully applied a staining test for the identification and quantification of fibers in polyester/cellulose blends using Kayastain Q (Lai *et al.* 2002). Different blends were differently stained as function of blend ratio and the data collected were fitted by a regression model resulting in precise quantification of polyester and cellulose fiber amounts. Jablosky *et al.* (Jablonský *et al.* 2015) used the zinc-chloride-iodine stain to discriminate cellulose fiber. The fibers could be stained from 1 to 2 minutes and they were identified using RGB (red, green, blue) vector with discriminatory analysis.

Migliavacca *et al.* proposed the xanthoproteic reaction, the reaction between wool keratin and concentrated nitric acid responsible for wool yellowing, as a suitable chromatic test to detect chemical changes induced on wool fibers by oxidative treatments (Migliavacca, *et al.* 2014). Similarly, Shirlastain A test is usually used for qualitative analysis of antifelting treatments on wool top. The test is based on the colorimetric reaction of wool with a reagent consisting of an aqueous solution of picric acid, Chlorazol Blue G150, and Scarlet Crocein 3BS (Greaves 1985). The undyed wool combed sliver is dipped at room temperature into the reagent solution; untreated wool turns to yellow, while wool samples subjected to oxidative processes range from orange to red depending on severity of the treatment. Chandra and co-workers described a staining method using a direct blue and a direct orange dye for the microscopic investigation of fibrillation and mechanical damages of cellulosic fibers, for example the enzymatic treatment on recycled fibers (Chandra and Saddler 2012). It was found out that when the fiber wall is more accessible, one of the selected dyes much easier penetrates inside the fiber due to its higher affinity for the inner part of the material. In a similar way, the mechanically recycled cashmere fibers, shortened and damaged are supposed to be more accessible to dyes.

With regard to the recycled fibers, in recent years many research groups are focused on the development of recycled materials for removing dyes due to the intrinsic physical characteristic of the recycled materials. Mahar and co-workers reported the dyeing of recycled PET using two disperse dyes without a further decreasing of the mechanical properties and Ghafar *et al.* investigated the ability of the recycled viscose in the methylene blue adsorption (Mahar *et al.* 2017; Abdel Ghafar *et al.* 2019). In another research, nylon fibers were recovered from textile waste and the methylene blue was used as a model substrate for evaluating the thermodynamic and kinetic parameters related with the adsorption process on PA recycled fibers (Metwally *et al.* 2018).

Since no studies can be found out in literature about the discrimination of recycled and virgin fiber by the use of dyes, this work describes preliminary results on quantification of recycled cashmere fibers, based on objective and reliable methodologies. A traditional microscopy investigation has been applied to identify and record recycled cashmere fibers, with their typical morphological features. Moreover, an objective method for the quantitative analysis of virgin and recycled cashmere fiber blends has been developed, based on their different dye absorption capacity.

Pure virgin and recycled cashmere fibers were stained with different amounts of C.I. Direct Red 7 in different conditions, and the exhaust dyebaths were analyzed by UV-visible spectroscopy in order to quantify the residual unabsorbed dye. In order to accomplish this examination, physicochemical characteristics of the virgin and recycled cashmere were highlighted. Process parameters were optimized (staining time, dye concentration and temperature) and isotherms and kinetics were studied for both virgin and recycled cashmere fibers. Then, the optimized method was applied to blends of different proportions of virgin and recycled fibers, in order to evaluate the detection limits. This approach could provide a system to protect companies and customers against frauds.

Materials and methods

Materials

Samples of virgin and recycled cashmere were provided by different textile companies (Biella, Italy).

Direct Red 7, hydrochloric acid, dichloromethane and ethanol were purchased by Sigma Aldrich.

The cashmere samples were extracted in Soxhlet with dichloromethane and ethanol for 4h, dried in an oven at 105 °C until constant weight and finally conditioned for 24 h (20 °C, 65% RH).

Morphological characterization

Morphological investigation was carried out by a Zeiss EVO 10 Scanning Electron Microscope. SEM operated with an acceleration voltage of 15-20 kV, 50 pA probe and 20-30 mm working distance. Samples were mounted on aluminium specimen stubs with a double-sided tape, then sputter coated with a gold layer 20-30 nm thick in rarefied argon, using an Emitech K 550 sputter coater with a current of 20 mA for 180 s.

Moisture uptake

Moisture uptake *versus* time of virgin and recycled cashmere samples, previously dried to constant mass at 105 °C, was determined by weighting samples over time in standard conditions (20 °C, 65% RH).

Thermal analyses

Thermogravimetric analyses were carried out in a TGA Mettler Toledo, models Star^e system under nitrogen atmosphere (gas flux 100 mL min⁻¹). Analyses were performed by weighting about 10 mg of sample mass in an alumina open pan, following the subsequent thermal program: heating (10 °C min⁻¹) from room temperature up to 800 °C.

Differential Scanning Calorimetry analyses (DSC) were performed with a Mettler TA 3000 apparatus equipped with a DSC 20 cell purged with nitrogen. The temperature program was set in the range from 30 to 270 °C, with a heating rate of 10 °C min⁻¹.

Fourier Transformed Infrared Spectroscopy (FT-IR)

The FT-IR spectra of virgin and recycled cashmere were acquired with Attenuated Total Reflection (ATR) technique in the range from 4000 to 650 cm⁻¹ with 50 scans and 4 cm⁻¹ of resolution by means of a Thermo Nicolet Nexus spectrometer equipped with a ZnSe crystal.

Colorimetric quantification and adsorption evaluation

Virgin and recycled cashmere samples were dried in an oven at 105 °C until constant weight. Fiber blends (with a content of recycled cashmere ranging from 10% to 90%) were prepared.

Different staining solutions were prepared in the range of 5-500 ppm of Direct Red 7. The fibers samples were dipped in the staining solution with a liquor ratio 1:50, under continuous stirring varying the contact time (from 30 s to 10 min). Then, the fibres were rinsed with distilled water and dried in an oven at 50 °C.

The dyebath was filtered using a PTFE syringe filter with pore diameter of 45 µm and analyzed using a double-beam Perkin Elmer 200 UV-Vis spectrophotometer at 515 nm. The dye amount remained in the dyebath was quantified using the calibration curve previously prepared. The amount of dye adsorbed $q_e = \frac{V(C_0 - C_e)}{m}$ at the equilibrium (q_e , mg g⁻¹) was quantified by applying the following equation:

1)

V is the volume of the solution analyzed (10 mL), C₀ is the initial concentration of the dye in solution (expressed in mg L⁻¹), C_e is the concentration of non-adsorbed dye at the equilibrium (expressed in mg L⁻¹), whereas m is the amount of sorbent (50 mg).

$$C_e/q_e = C_e/q_m + 1/K_L q_m$$

In this study, the equilibrium experimental data for adsorbed Direct Red 7 on virgin and recycled cashmere samples were analyzed using the Langmuir and Freundlich models. These isotherms are as follows:

2)

where C_e is equilibrium concentration of Direct Red 7 (mg/L) and q_e is the amount of the dye adsorbed (mg) per unit by virgin or recycled cashmere (g). q_m and K_L are the Langmuir constants related to the adsorption capacity (mg/g) and the equilibrium constant (L/g), respectively.

3)

where K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

In the present work, the $\log(q_e - q_t) = \log q_e - (K_1/2.303)t$ adsorption data were analyzed using three kinetic models, the pseudo-first-order and pseudo-second-order kinetic. For the pseudo-first-order model is expressed as follows (Balouch *et al.* 2013):

4)

where q_e and q_t are the amounts of dye (mg/g) adsorbed on cashmere fibers at equilibrium and at time t , respectively, and k_1 is the rate constant (1/min). The rate constant, k_1 was obtained from slope of the linear plots of $\log(q_e - q_t)$ versus t .

For the pseudo-second-order mechanism, and McKay 1999):

$$h = k_2 q_e^2$$

the data were elaborated as follow (Ho

5)

And the initial rate of adsorption h is:

6)

where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min), h is the initial rate of adsorption (mg/g min). If plot of t/q_t against t of Eq. 6 should give a linear relationship from which the constants q_e , h and k_2 can be determined.

$$K_c = \frac{C_{Ae}}{C_e}$$

second-order adsorption (g/mg min), h is second-order kinetics is applicable, the

$$\Delta G^0 = -RT \ln K_c$$

linear relationship from which the

To calculate the thermodynamic parameters such as enthalpy of adsorption, ΔH^0 , entropy of adsorption, ΔS^0 , and free energy of adsorption, ΔG^0 , the following equations were applied (Santos and Boaventura 2008):

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

parameters such as enthalpy of ΔS^0 , and free energy of were applied (Santos and

7)

$$\log q_e = \log K_F + (1/n) \log C_e$$

8)

9)

Results and discussion

Morphological characterization

Cashmere samples were observed with a Scanning Electron Microscopy (SEM), in order to evaluate morphology differences in virgin and recycled fibres. Figures 1a and 1b show virgin cashmere fibers, whereas figure 1c and 1d show recycled cashmere fibers with typical breakings due to mechanical re-processing.

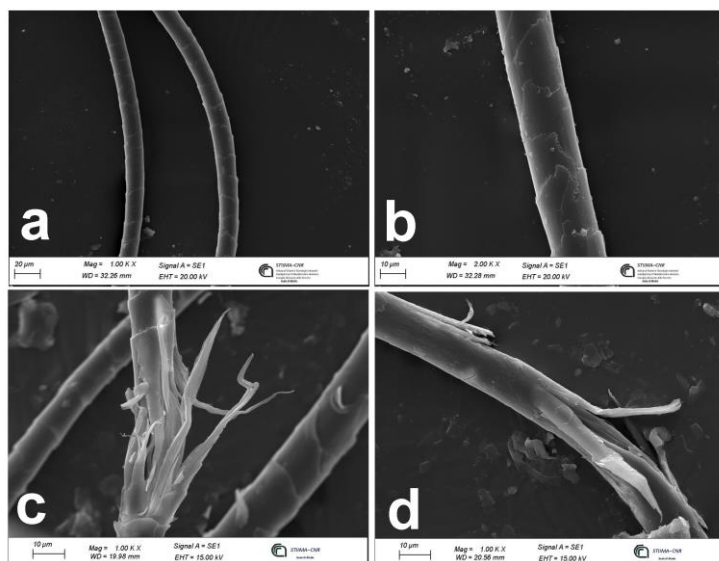


Figure 1: SEM micrographs of virgin (a-b) and recycled (c-d) cashmere fibers

Figures 1a and 1b show the morphology of virgin cashmere fibers, which are extensively described in literature (Vineis *et al.* 2010): fibers are cylindrical with small and even diameter, and a typical surface scale pattern which overlap like tiles of a roof. Cuticle cells (scales) display relatively distant and smooth margins, often so wide that they appear to entirely envelop the fibers. The mean scale frequency is 6-7 per 100 μm and the thickness of the cuticle cells at the distal edge is less than 0.5 μm . In Figure 1 panel c and d, recycled cashmere fibres with typical breakings due to mechanical re-processing are shown. The SEM pictures better display the breaking morphology: many fibers show partial cleavages (semi-ruptures) in the typical forms called “brushes” (Figure 1 panel c) and “knees” (Figure 1 panel d), with run-off of spindle-shaped cortical cells from the inner cortex structure. The number of semi-ruptures counted per meter of fiber is used for acceptance testing of commercial shipments of wool and other animal fibers, according to the ASTM D4510-18 standard. However, this method is non quantitative, highly subjective and information on between-laboratory precision is limited.

Moisture uptake

Additional qualitative information has been obtained by the water uptake rate, which is related with the presence of breakages along the fibers due to the disruption of hydrophobic external cuticle layer (epicuticle). Figure 2 shows differences in moisture uptake rate between virgin and recycled cashmere, dried at 105 $^{\circ}\text{C}$ until constant weight and then stored in a conditioned atmosphere for up to 24 h.

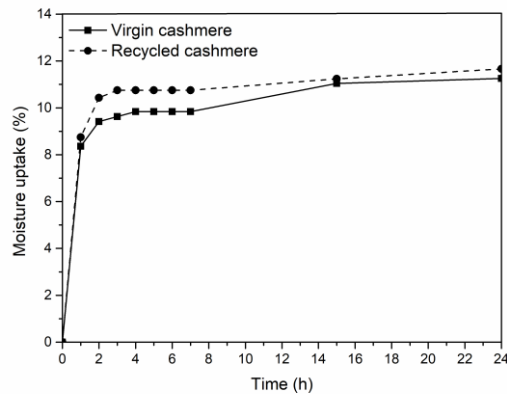


Figure 2: Moisture uptake versus time of virgin (black line) and recycled cashmere (dotted line)

After 4h, moisture uptake for virgin sample is 9.8% while recycled sample absorbs 10.8%. Nevertheless, after complete conditioning, the moisture uptake reaches a plateau for both the samples, as shown in Figure 2. Initially, the water absorption rate of recycled cashmere is higher than that of the virgin sample. The presence of ruptures and damages in the structure of recycled cashmere causes a less moisture resistance. The existence of fractures on the surface of the fiber or cracks inside the fiber matrix increase the exposed surface facilitating the diffusion of water and the moisture uptake. Anyway, after 15h of complete conditioning, the equilibrium between the absorbed/desorbed water is reached and the moisture uptake of virgin and recycled cashmere becomes equal. The adsorption of water before the equilibrium state can be used for distinguishing the two classes of cashmere.

Fourier Transformed Infrared Spectroscopy (FT-IR)

In order to evaluate the occurrence of some chemical modification in the structure of the recycled cashmere fiber caused by the recycling process, ATR analysis has been performed. The recorded spectrum is shown in Figure 3 and for a comparison, the spectrum of the virgin cashmere is also reported.

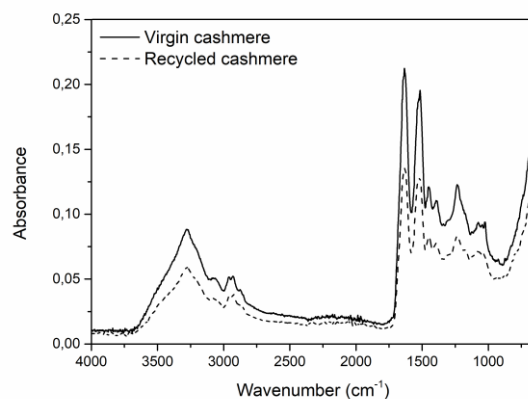


Figure 3: FT-IR spectra of virgin cashmere (black line) and recycled cashmere (dotted line)

In Figure 3 the infrared absorption spectra of virgin and recycled cashmere samples are shown. The spectra are very similar and characteristic absorption bands assigned mainly to the peptide bonds (CONH) are clearly visible. The vibrations in the peptide bonds, known as Amide A (3280 cm^{-1}),

Amide I (in the range 1700–1600 cm^{-1}), Amide II (close to 1520 cm^{-1}) and Amide III (in the range 1220–1300 cm^{-1}) are also present (Aluigi *et al.* 2007). Moreover, absorptions peaks between 1200 and 1000 cm^{-1} attributed to SO vibration from oxidation and sulfitolysis reaction of cystine in cashmere fibers are not present in both samples which indicates that fibers have been not submitted to chemical treatments during the recycling operations (Rajabinejad *et al.* 2017).

Thermal analyses

Thermal analyses were used to study the stability of the virgin and recycled cashmere. Since recycled cashmere fibers are subjected to severe mechanical treatments, the thermal stability needs to be considered and compared with the virgin cashmere fibers. The TGA and the DSC results are reported in Figure 4:

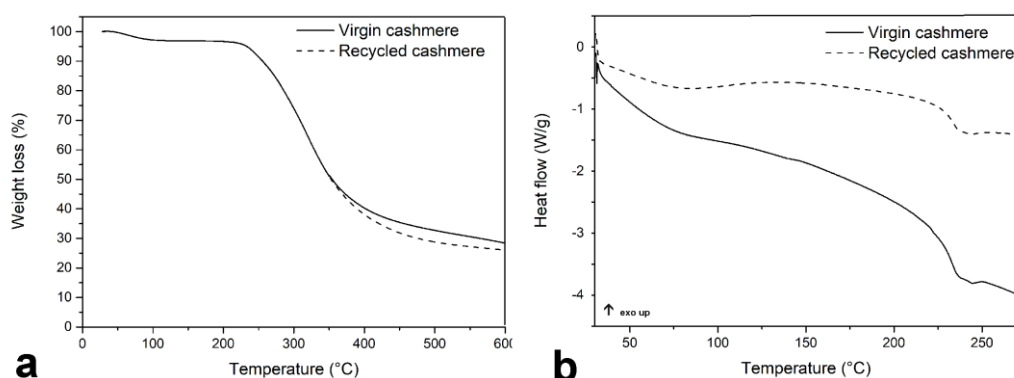


Figure 4: a) TGA of virgin (black line) and recycled cashmere (dotted line); b) DSC of virgin (black line) and recycled cashmere (dotted line)

As seen in Figure 4a, the shape of thermograms is similar for the two samples of cashmere analyzed. During heating, the thermal degradation in inert atmosphere takes place in two stages for all the samples. The initial stage of degradation occurs from 30 to 110 °C for both samples involving mass loss of 5%. The first stage of degradation can be attributed to the loss of water adsorbed by the cashmere samples as reported by other authors (Vineis *et al.* 2008). There are three kinds of water in the cashmere fiber: free water, chemically bonded water and loosely bonded water. During the first step of degradation, all these types of water are released. The main step of degradation appears between 220 °C and 400 °C for virgin cashmere with a mass loss of 59%. For the recycled cashmere, the main step of degradation occurs between 220 °C and 505 °C with a mass loss of 68%. This step is related with the breakdown of microfibril-matrix structure and disulphide bonds of cashmere keratin. The main step of degradation of the recycled cashmere results in a higher weight loss. Indeed, the presence of short and broken fibers can facilitate the volatilization reaction in recycled cashmere enhancing the degradation reaction.

The DSC depicted in figure 4b shows an endothermic peak for both cashmere samples in the range of 30 °C-100 °C attributed to adsorbed water evaporation, as already seen in the TGA thermograms. Endothermic peaks in the range of 230-255 °C are due to the denaturation of the crystalline α -helical structure of ortho- and para-cortical cells (Vineis *et al.* 2008), and they occur at the same temperature for both virgin and recycled cashmere. Thus, no significant differences can be observed for the DSC of virgin and recycled cashmere hence that no chemical modification of the inner structure of the fiber has been occurred during re-processing treatments.

Colorimetric quantification and adsorption evaluation

Since virgin and recycled cashmere have some physical differences attributed to the recycling process, their ability to adsorb dyes was investigated using Direct Red 7. In order to find the optimal condition for the quantitative staining test, the fibers were stained at different dye concentrations (from 5 to 500 ppm) at room temperature for 60 s. The results obtained for the virgin and recycled cashmere are listed in Table 1.

Sample	Initial dye concentration (ppm)	Dye adsorbed (ppm)
Recycled cashmere	5	2.59
Virgin cashmere	5	2.10
Recycled cashmere	50	29.67
Virgin cashmere	50	28.17
Recycled cashmere	500	263.61
Virgin cashmere	500	221.11

Table 1: Dye adsorbed by recycled and virgin cashmere samples at different dye concentrations (RT)

The amount of Direct Red 7 adsorbed is proportional to the initial concentration of Direct Red 7. Indeed, the amount of dye adsorbed by recycled cashmere is higher than the quantity adsorbed by the virgin cashmere due to the presence of ruptures and damages attributed to the recycling treatments. Despite the initial dye concentration provides the necessary driving force to overcome the resistance to the mass transfer of Direct Red 7 between aqueous phase and the solid phase, no differences can be detected due to an increase of the concentration gradient.

The contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. The amount of dye adsorbed by virgin and recycled cashmere were evaluated varying time from 30 to 5400 s and the results are reported in Figure 5.

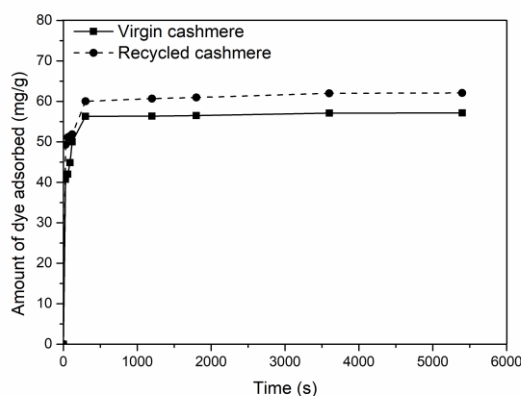


Figure 5: Amount of dye adsorbed (mg/g) by virgin (solid line) and recycled cashmere (dotted line) in function of contact time

Effect of contact time for the removal of Direct Red 7 by the virgin and recycled cashmere showed rapid increase of adsorption of dye in the first 300 s and, thereafter, the adsorption rate sharply decreases and the adsorption reached the equilibrium in about 300 s for both the samples, as shown in Figure 5. An increasing of contact time up to 1200 s resulted in about only 0.3% adsorption over those obtained for 300 s of contact time, hence that the equilibrium was reached.

Aggregation of dye molecules and the filling up of the reactive site on the surface of the virgin and recycled cashmere significantly affect the enhancement in adsorption after 300 s. Since the

difference in the adsorption values at 300 s and at 1200 s is very small, after 300 s of contact time, a steady-state approximation was assumed and a *quasi*-equilibrium situation could be accepted. Therefore, further thermodynamic experiments were conducted for 300 s of contact time only.

For better understand the difference in dye adsorption detected for virgin and recycled cashmere, the thermodynamic parameters were calculated. Thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) change of adsorption were evaluated from the equations 7), 8) and 9).

The values of ΔH^0 and ΔS^0 are determined from the slope and the intercept of the plots of $\log K_c$ versus $1/T$ at three selected temperatures (303 K, 313 K and 333 K) as shown in Figure 6 whereas the ΔG^0 values were calculated using the equation 9).

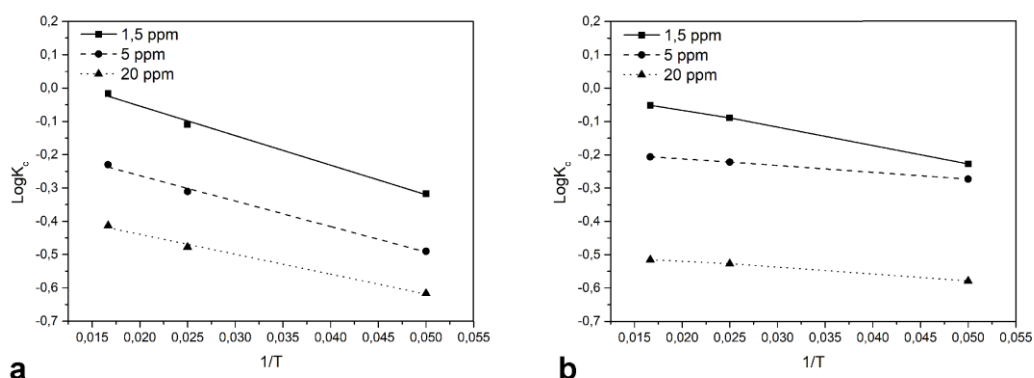


Figure 6: $\log K_c$ vs $1/T$ curves for a) recycled and b) virgin cashmere

These plots were used to compute the values of thermodynamic parameters for recycled and virgin cashmere as shown in Table 2.

Virgin cashmere					
Initial dye concentration (ppm)	ΔH^0 (j/mol)	ΔS^0 (j/molK)	ΔG^0 (j/mol)		
			303 K	313 K	333 K
1,5	-8.87	0.123	-1213	-841.9	-669.1
5	-7.66	-0.110	-1959	-1272	-922.9
20	-5.99	-0.320	-1483	-1532	-1068
Recycled cashmere					
Initial dye concentration (ppm)	ΔH^0 (j/mol)	ΔS^0 (j/molK)	ΔG^0 (j/mol)		
			303 K	313 K	333 K
1,5	-5.34	0.004	-1493	-1387	-730.6
5	-2.017	-0.172	-2052	-1561	-822.9
20	-1.946	-0.471	-2239	-1619	-845.9

Table 2: Thermodynamic parameters evaluated for virgin and recycled cashmere

From Table 2, ΔG^0 is negative, indicating that the adsorption is spontaneous for both the samples. The ΔG^0 evaluated is more negative for the recycled than for the virgin cashmere. The ΔG^0 values calculated for the recycled cashmere suggest that the adsorption of Direct Red 7 on the surface of recycled fiber is more feasible and spontaneous. The dye can easily penetrate inside the recycled

sample due to the presence of a large number of damaged fibers able to decrease the energy required for the dye adsorption process. Increasing the temperature, the value of ΔG^0 becomes less negative for both samples indicating that the spontaneity of the adsorption process decreases by increasing temperature. Furthermore, the magnitude of the ΔG^0 yields information on whether the adsorption is mainly physical or chemical. The low ΔG^0 evaluated indicates diffusion control and physisorption processes (Eren *et al.* 2010). The low negative values of ΔH^0 suggest that the process is slightly exothermic for both samples. The values of ΔS^0 reveals that the adsorption occurs with a slight increase in entropy of the systems. Increasing the initial concentration of dye, the ΔS^0 becomes more negative for both samples indicating a decreasing of randomness on the surface of virgin and recycled cashmere. Furthermore, it is found that $\Delta H^0 < T\Delta S^0$. This means that the contribution of ΔS^0 is not negligible for virgin and recycled cashmere and it affects the adsorption process. Overall, it can be concluded the ΔG^0 value indicates the process is feasible and spontaneous for both the sample, but increasing the temperature, the ΔG^0 gets more positive and the reaction is less spontaneous. The process occurs more spontaneity for the recycled cashmere respect to the virgin one and the negative ΔH^0 value suggests the exothermic nature of adsorption and the ΔS^0 can be used to describe the randomness at the cashmere-solution interface during the sorption.

For providing information about the capacity of adsorption of virgin and recycled cashmere, the adsorption isotherms were estimated. The equilibrium data for Direct Red 7 adsorption on recycled and virgin cashmere were fitted to the Langmuir and Freundlich equations 2) and 3). The Langmuir equation is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface and the energy of adsorption is constant without migration of adsorbate molecules on the surface. The Freundlich isotherm model describe the adsorption on heterogeneous surfaces with interaction between adsorbed molecules. The Langmuir (a) and Freundlich (b) isotherms are reported in Figure 7 for virgin and recycled cashmere.

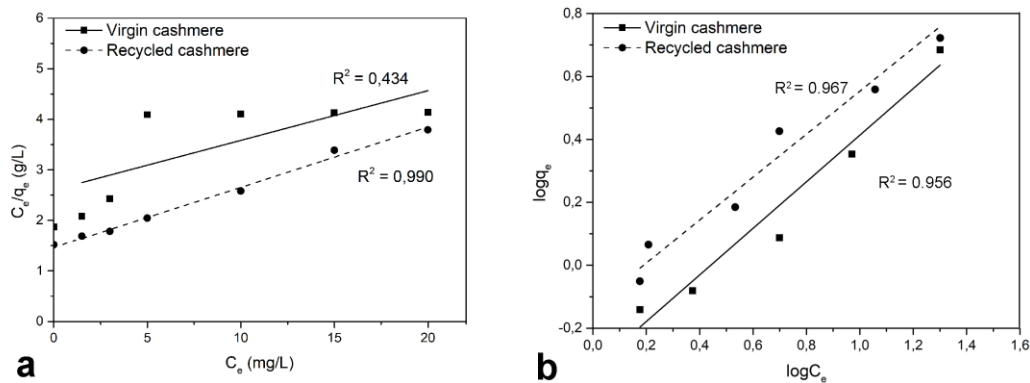


Figure 7: a) Langmuir and b) Freundlich isotherm plot for adsorption of Direct Red 7 onto virgin (solid line) recycled (dotted line) cashmere

The equilibrium data for Direct red 7 adsorption on recycled cashmere fit with the Langmuir equation whereas for virgin cashmere is not applicable as it can be seen from the coefficient of determination (R^2) reported in Figure 7a. These results indicate that the adsorption for virgin and recycled cashmere follows different routes. For recycled cashmere, Direct red 7 molecules are adsorbed in particular on well-defined localized sites, presumably in the damaged sites of the fibers. The saturation coverage corresponds to the complete occupancy of this sites and there is no interaction between adjacent adsorbed molecules. Once the equilibrium is reached, the number of Direct red 7 molecules being adsorbed is equal to the number of molecules leaving the adsorbed

state. Therefore, the rate of adsorption is equal to the rate of desorption. Thus, the Langmuir constants q_m and K_L can be evaluated for the recycled cashmere. The Langmuir monolayer adsorption capacity for recycled cashmere was estimated as 8.48 mg/g. The K_L value is 8.35×10^{-2} and indicates there is a strong interaction between adsorbate and adsorbent.

The equilibrium data for virgin and recycled cashmere fit with Freundlich equation, as shown in Figure 7b. This model suggests that the adsorption energy exponentially decreases on completion of the available centers of virgin and recycled cashmere. The Freundlich constants K_F , related with the multilayer adsorption capacity, and n , correlated with the intensity of adsorption, indicates the heterogeneity of the adsorbent. A $n \ll 1$ reveals that adsorption intensity is suitable over the entire range of concentrations studied, while $n > 1$ means that adsorption intensity is better at high concentrations. The K_F was found out to be -0.327 for the virgin sample. In the adsorption system, the n value is 1.35 which indicates that higher concentration slightly favorites the adsorption. For the recycled cashmere the value of K_F and n are -0.129 and 1.46, respectively. The value of n obtained for virgin and recycled cashmere also suggests that the adsorption of Direct red 7 onto the surface of the samples is mainly a physical process.

In order to study the mechanism of adsorption processes, pseudo-first-order and pseudo-second-order were applied.

Table 3 lists the results of the rate constant studies obtained by the pseudo-first-order and pseudo-second-order models. The coefficient of determination, R^2 for the pseudo-second-order adsorption model has a high value ($> 99\%$) for both the sample. The correlation coefficients for the pseudo-first-order kinetic model for virgin cashmere is lower than for the recycled cashmere, indicating a poor pseudo-first-order fitting of the virgin experimental data. These facts suggest that the pseudo-second-order adsorption mechanism is predominant for both virgin and recycled cashmere. As shown in Table 3, the value of k_2 calculated for recycled cashmere is lower than the k_2 of the virgin sample. Thus, it is possible to suppose that the adsorption of Direct Red 7 on the cashmere samples occurs with two different pathways. For recycled cashmere the adsorption rate of occupied sites is proportional to the number of unoccupied sites and the adsorption capacity is restricted to the stage where the process is controlled by the external mass transfer. For the virgin cashmere, the pseudo-second-order adsorption mechanism is predominant hence that the active surface sites are difficult to be occupied by Direct red 7.

Sample	Pseudo-first-order		Pseudo-second-order		
	R^2	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg min)
Virgin cashmere	0.973	0.0016	0.995	3.39	7.20
Recycled cashmere	0.997	2.8×10^{-3}	0.997	3.63	4.29

Table 3: Kinetic parameters for the adsorption of Direct red 7 on virgin and recycled cashmere

The good thermodynamic and kinetic results suggest that the Direct red 7 can be efficiently used for a fast discrimination of virgin and recycled cashmere through a staining procedure.

A calibration curve for cashmere blends was performed staining fibers with 500 ppm Direct red 7 solutions for 60 s at room temperature in order to quantify cashmere blends and to evaluate the detection limits.

9 different blends (with a content of recycled cashmere ranging from 10% to 90%) of virgin/recycled cashmere fibers were prepared. The obtained calibration curve is reported in Figure 8.

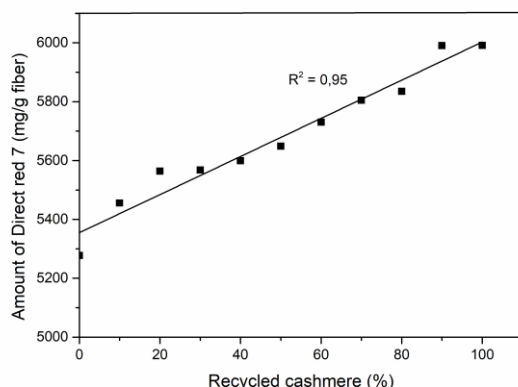


Figure 8: Amount of Direct Red 7 absorbed by different cashmere blends at 60 s staining

Increasing the amount of recycled cashmere, a proportional rising trend of dye adsorption is observed. The optimized staining protocol give rise to a suitable method for quantitative evaluation purposes, including contamination with small amounts of recycled fibers, since even samples with 10% recycled cashmere can be distinguished from virgin cashmere samples.

Conclusion

SEM microscopy turned out to be a useful tool for qualitative identification of virgin and recycled cashmere. In recycled cashmere many ruptures and damages due to the post-consumer treatment are present and clearly visible microscopically. To the contrary, the FT-IR and thermal analyses are ineffective technique to discriminate virgin and recycled cashmere fibers.

The colorimetric analysis developed using Direct red 7 allows to have a quick response in quantitative cashmere discrimination. The study of the kinetic and thermodynamic parameters has shown that two different adsorption pathways are followed by virgin and recycled cashmere. The negative values of ΔH^0 suggest that the process is slightly exothermic and ΔG^0 value indicates the process is feasible and spontaneous, but increasing the temperature, the reaction is less spontaneous for both samples. For recycled cashmere, Direct red 7 molecules are preferably adsorbed on well-defined localized sites, presumably in the damaged sites of the fibers, whereas for the virgin sample, the active surface sites are slightly more difficult to be occupied by Direct red 7. Although, there are no chemical differences between the virgin and recycled cashmere, the results obtained clearly underline how the recycling process can affect the physical characteristic of the material increasing the adsorption ability. The method is rapid and allows the objective identification of recycled cashmere fibers blended with the virgin ones even in small quantity, since even samples with 10% recycled cashmere can be distinguished from virgin cashmere samples.

This approach could provide a system to protect companies and customers against frauds.

Aknowledgement

We thank to Bibiana Dellavalle, Elisa Destro and Alberto Racerro for helping in preliminary experiments and to their teachers for the supervision.

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