Research Article

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Pollutant footprint analysis for wastewater management in textile dye houses processing different fabrics

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Abstract

BACKGROUND: This study investigated the water and pollution footprints of a dye house, which processed cotton knits, polyester (PES) knits and PES-viscose woven fabrics. Experimental evaluation was carried out for each processing sequence. Variations in wastewater flow and quality were established as a function of the production program in the plant. A model evaluation of wastewater dynamics was performed and defined specifications of an appropriate treatment scheme.

RESULTS: The plant was operated with a capacity of 4300 t year^{-1} of fabric, which generated a wastewater flow of 403 500 m^3 year^{-1} and a COD load of 675 t year^{-1}. The overall wastewater footprint of the plant was computed as 91 m^3 t^{-1} and the COD footprint as 160 kg t^{-1} of fabric. Depending on the fabric type, results indicated expected changes in wastewater flow between 600 and 1750 m^3 day^{-1}; in COD load between 1470 and 2260 kg day^{-1} and in COD concentration between 1290 and 3400 mg L^{-1}.

CONCLUSION: A model simulation structured upon COD fractionation and related process kinetics revealed partial removal of slowly biodegradable COD, coupled with high residual COD, which would by-pass treatment. Resulting biodegradation characteristics necessitated an extended aeration system, which could also enable partial breakdown of residual COD. Effluent COD could be reduced to 220–320 mg L^{-1} with this wastewater management strategy.

Supporting information may be found in the online version of this article.

Keywords: textile dyeing; wastewater footprint; COD footprint; modeling; treatment optimization

NOTATION

b_H endogenous decay rate (d^{-1});
COD chemical oxygen demand (mg L^{-1});
C_T total COD (mg COD L^{-1});
f_{ES} residual soluble metabolic fraction of endogenous biomass;
f_{EX} residual particulate metabolic fraction of endogenous biomass;
k_h maximum hydrolysis rate (d^{-1});
k_{hSI} maximum hydrolysis rate for soluble inert COD (d^{-1});
k_{hXI} maximum hydrolysis rate for particulate inert COD (d^{-1});
K_S half saturation constant for growth (g COD g COD^{-1});
K_{SI} hydrolysis half saturation constant for soluble inert COD (g COD g COD^{-1});
K_X hydrolysis half saturation constant for particulate COD (g COD g COD^{-1});
K_{XI} hydrolysis half saturation constant for particulate inert COD (g COD g COD^{-1});
$\hat{\mu}$ maximum heterotrophic growth rate (d^{-1});
MLSS mixed liquor suspended solids (mg L^{-1});
S_H soluble rapidly hydrolysable COD (mg COD L^{-1});
S_I soluble inert COD (mg COD L^{-1});
S_O dissolved oxygen concentration (mg COD L^{-1});
S_P soluble inert microbial product (mg COD L^{-1});
S_R sum of soluble inert COD and soluble inert microbial product (mg COD L^{-1});
SRT sludge retention time (d);
S_S soluble readily biodegradable COD (mg COD L^{-1});
S_T soluble COD (mg COD L^{-1});

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TKN total Kjeldahl nitrogen (mg L^{-1});
TP total phosphorus (mg L^{-1});
TSS total suspended solids (mg L^{-1});
X_H active heterotrophic biomass (mg COD L^{-1});
X_I particulate inert COD (mg COD L^{-1});
X_P particulate inert microbial product (mg COD L^{-1});
X_S particulate slowly biodegradable COD (mg COD L^{-1});
X_T particulate COD (mg COD L^{-1});
Y_H heterotrophic yield coefficient (mg cell COD mg COD^{-1}).

INTRODUCTION

Textile wastewaters constitute a key component of industrial pollution. Water quality management programs involve industrial activities at two different dimensions: (i) wastewater characterization and (ii) effluent discharge limitations. Consequently, the success of any quality management scheme chiefly depends upon how thoroughly wastewaters are characterized and how effective and sustainable the selected treatment scheme is to comply with the effluent limitations. Textile activities usually generate strong wastewaters in terms of their organic carbon (COD) and color content and they are subject to stringent effluent limitations.[1–5]

Generally, effluent limitations imply appropriate treatment by defining the expected quality of wastewater to be discharged. Therefore, they should be correlated with wastewater characteristics and with the specific treatment scheme to be implemented at source. In a way, a specific effluent limitation should be conceived as a fingerprint of the wastewater quality, improved by appropriate treatment. This is a difficult task especially for textile wastewaters, where appropriate characterization is overlooked in most cases. For this purpose, categories and sub-categories are often utilized for textile activities.[6–9] Experimental surveys indicate however that striking differences may be observed in wastewater quality and quantity from one plant to another within the same sub-category, mainly because of different experiences and habits implemented in the production scheme.[10–12]

The worst approach to characterizing textile wastewaters would be to rely on the 'end of pipe' inspection of the wastewater. The spot image that may be obtained with this exercise may at times be totally useless and even misleading, because wastewater quality is closely related to the production schedule in the plant and it is likely to exhibit significant fluctuations with time.

Recently, water and pollutant footprinting has emerged as an effective approach to assess water use related effects associated with consumption and processing of goods and services. Methods and indexes were developed for more efficient footprint analyses.[13,14] The concept of water footprint was first introduced into the textile industry with only a general and narrow framework.[15,16] Miglietta *et al.*[17] conducted an interesting study exploring the effect of water footprint on the sustainable productivity of Italian wines. In this respect, this study should be regarded as a pioneering effort in combining water and pollutant footprints in the textile industry. These footprints were used to generate a database defining the pollution profile of a textile dye house and describing each production step and related individual wastewater stream in terms of its specific properties. The study further investigated the biodegradation and COD fractionation properties of wastewaters generated from different processes and it combined this information with footprint analyses for effective management of wastewaters.

Table 1. Distribution of the production capacity

Fabric type	Production (kg process^{-1})	Production (kg year^{-1})	Production (%)
Cotton	80	1 438 200	34.0
Polyester (PES)	747	1 298 610	30.7
PES-viscose	160	1 357 830	32.1
Others	NA	135 360	3.2
Total	–	4 230 000	100.0

Biodegradation kinetics requires process modeling. The new concept of modeling relies on the identification of a number of substrate fractions with different biodegradation characteristics; it also differentiates active biomass from other biomass components.[18,19] This outstanding evolution totally changed the structure of the traditional models with only two components -*substrate/biomass*- and two processes -*growth/decay*.[20,21] The first multicomponent activated sludge model was ASM1, accounting for all significant substrate and biomass components.[22] After this pioneering effort, amazing developments were achieved to expand the model framework to cover almost all microbial activities that could be accomplished with different activated sludge configurations, such as biological nitrogen and phosphorus removal, substrate storage, control of different chemicals, etc.[23–27]

Textile dye houses represent a most typical example of quantity and quality fluctuations in the wastewater generated in the plant, since they generally process batches of different fabrics, each associated with specific dyes, chemicals and water requirements. The dynamics in wastewater generation inevitably reflect upon the design and operation of a sustainable treatment system. In this context, the main objective of the study was to generate the pollution footprint of a dye house, which processes mainly cotton knits, polyester (PES) knits and PES-viscose woven fabrics. Emphasis was placed on a detailed evaluation of each processing sequence. Variations in wastewater flow and quality were established as a function of the production program in the plant. A model evaluation of wastewater dynamics and biodegradation kinetics was carried out and correlated with the required specifications of an appropriate treatment scheme.

MATERIALS AND METHODS

Dye house characteristics

The textile plant, where the study was conducted, was located at Cerkezkoy, Istanbul. The activity in the plant mainly consisted of fabric dyeing and finishing, amounting to a yearly production capacity of 4230 t of fabric. As shown in Table 1, this capacity was distributed among cotton and cotton based fabrics (34%); polyester (PES) and polyester based fabrics (30.7%) and PES-viscose and viscose based fabrics (32.1%). The production scheme involved jet-type batch reactors with capacities varying over the range 25–1000 kg of fabric batch^{-1}. These reactors were adjusted to work with a liquor ratio of 1/6 and utilized reactive, dispersed, acid and pigment dyes depending on the type of fabric processed. The average time of operation of each batch was 10 h. Chemicals used in the dyeing processes are listed in Table 2.

Experimental approach

The experimental program was designed to allow a footprint approach for the evaluation of wastewater and pollutants profiles.

Table 2. Different chemicals used in the dyeing process

Function	Associated chemicals	Chemical composition
Wetting agent	Haswet IR3	Oil alcohol ethoxylate
Ion keeping agent	Has 45	Polycarbon acid-polycarbonate
Non-ionic wetting agent	Belsoft 200	Two ethanol amine
Buffer	Has ABS	Organic acids
Cationic wetting agent	Hassoft-Set.KAT	Cationic softeners
Dispersing agent	Has DFT	Alkyl benzene sulfonate
Grease remover	Serawash M-TE	Ethoxylate alcohol
Acidic reducing agent	DNG Clean PN	Fluorescent bleaching material
Egalizer	Seragal C-FTC	Alkyl benzene
Soap	Haswash RYS	Soap

For this purpose, each step in the processing sequence for main fabric types were individually assessed for wastewater generation and pollution loads. COD and color content in each wastewater stream were selected as major indicators of pollution loads associated with the plant activity. Therefore, a fingerprint could be determined for the processing of each fabric category. The experimental data were then jointly evaluated for the computation of footprints determining the basis for the design and expected performance of the appropriate treatment system.

Analytical procedures

The wastewater analyses for characterization were conducted on samples taken from both process steps and plant effluent. The sampling program included three separate surveys of the processing sequence of each different fabric and triplicate analyses for each parameter in the survey. COD measurements were performed according to procedures defined in ISO 6060 (1989).[28] Wastewater samples were filtered through membrane filters with a 0.45 μm pore size for soluble COD measurements. pH, conductivity, total suspended solids (TSS), total Kjeldahl nitrogen (TKN) and total phosphorus (TP) parameters were measured according to Standard Methods (2017).[29] Color of the samples was determined by measuring the absorbance values at the three wavelengths 436, 525 and 620 nm according to ISO 7887 (2011).[30]

Modeling

The model adopted in this study included the basic structure of ASM1 modified for direct endogenous respiration.[22,26] This model was successfully tested and calibrated in a number of studies involving organic carbon removal.[31–35]

At this point, a clarification is needed on the choice of the appropriate parameter between BOD_5 and COD for model evaluation. BOD_5 has been the traditional substrate parameter selected for evaluating the performance of activated sludge systems.[21] However, it could not cope with the achievements of modeling efforts, which were structured based on substrate and biomass fractionation. BOD_5 merely indicates an arbitrary point in the course of biochemical reactions taking place during the test. It does not yield the true amount of organic matter in the wastewater or the dissolved oxygen consumption to oxidize the available substrate. Therefore, it cannot be used in the mass balance equations of the activated sludge process, without arbitrary/unreliable coefficients. As such, BOD values can hardly serve as model parameters in the kinetics of activated systems.

In fact, all multi-component activated sludge models suggested since 1986 use COD as the sole parameter for substrate and biomass fractions.[18,22,27] The biodegradable COD sets an electron equivalence between substrate used, biomass generated and oxygen consumed.[22,27] Experimental methods have been proposed and widely implemented for the assessment of soluble and particulate inert COD.[31,36,37] In this context, the model structure implemented in the study used COD as substrate and biomass components. Furthermore, COD limitations in the effluent standards defined for industrial effluents are far more stringent than the corresponding BOD_5 levels.

The model template was adjusted to include components defining the COD fractionation of the selected organic substrate and related biochemical processes. Accordingly, it included readily biodegradable COD, S_S; readily and slowly hydrolysable COD fractions, S_H and X_S; active heterotrophic biomass, X_H and dissolved oxygen, S_O.

The adopted model defined the stoichiometry and process kinetics for direct microbial growth on S_S; a dual mechanism for the hydrolysis of S_H and X_S at different rates, where applicable and endogenous respiration of X_H. Generation of soluble (S_P) and particulate (X_P) microbial products were also included as part of endogenous respiration with the simplifying assumption of decay-associated processes. A matrix representation of the model structure is given in Table 3. Model structure was implemented in a Sumo® process simulator for the evaluation of effluent quality.[36] Process simulations were performed using an aerobic conventional activated sludge system with three reactors in series followed by final clarifier. Simulations were carried out by assuming the following stoichiometric and kinetic coefficients: heterotrophic yield coefficient, $Y_H = 0.64$ g cell COD g COD^{-1}, endogenous decay rate, $b_H = 0.14\ day^{-1}$, residual soluble metabolic fraction of endogenous biomass, $f_{ES} = 0.15$ and residual particulate metabolic fraction of endogenous biomass, $f_{EX} = 0.05$.[31] The clarification process was activated as point settler to separate activated sludge from the treated stream. MLSS concentration in the reactor was set to 3 g L^{-1} by adjusting sludge wastage from the return activated sludge (RAS) line.

EXPERIMENTAL RESULTS

The experimental survey was conducted on representative dyeing recipes associated with the three types of fabrics processed in the plant. It included each step of the respective process profiles in terms of wastewater quantity and quality. Therefore, the collected data enabled calculation of the volume of wastewater generation and the pollution load per unit weight of fabric processes; total COD, soluble COD, color, pH and conductivity were selected as the main parameters to characterize wastewater quality that would be considered for the design and performance of the appropriate treatment system. Batch reactors of different volumes were assigned for each process; reactors were started when they were initially full with water. However, they were mostly operated below their capacity due to the small order packages of the customers. The discharge standards allocated to the textile industry are summarized in the Supplementary information (Table S1).

Cotton and cotton based fabrics

The selected operation scheme for cotton and cotton based fabrics involved a 100 kg fabric loading capacity and a corresponding

Table 3. Matrix representation of the selected model

Component → Process ↓	S_S	S_H	S_P	X_S	X_H	X_P	S_O	Rate
Growth	$-\frac{1}{Y_H}$				1		$-\frac{1-Y_H}{Y_H}$	$\hat{\mu}_H \frac{S_S}{K_S+S_S} X_H$
Hydrolysis of S_H	1	−1						$k_h \frac{S_H/X_H}{K_X+S_H/X_H} X_H$
Hydrolysis of X_S	1			−1				$k_h \frac{X_S/X_H}{K_X+X_S/X_H} X_H$
Decay			f_{ES}		−1	f_{EX}	$1-f_{ES}-f_{EX}$	$b_H \times X_H$

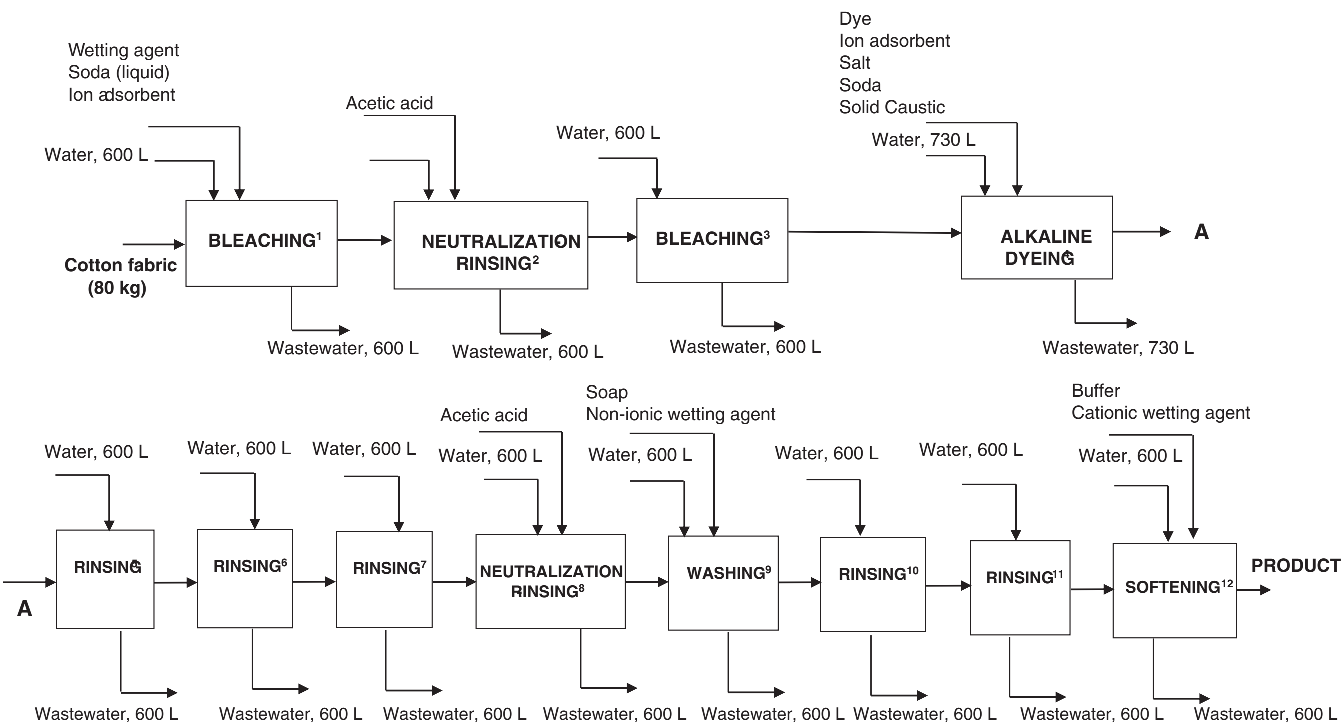

Figure 1. Schematic process scheme for cotton and cotton based fabrics.

initial water supply of 600 L, based on the liquor ratio of 1/6. It should be remembered that the liquid ratio is a textile jargon defining the mass ratio between fabric processed and water used in the reactor. During the survey, the process operation was started with 80 kg of fabric, which lowered the effective liquor ratio to 1/7.5. It involved a sequence of bleaching, neutralizing, dying, washing and softening, all coupled with rinsing steps as schematically illustrated in Fig. 1. As shown in this figure, the wastewater generation in this operation was 7.33 m^3, corresponding to a unit wastewater volume of 91 L kg^{-1} fabric.

Figure 2 reflects the measured COD and color fingerprints for the process cycle: as expected, the COD level peaked at bleaching and dyeing steps with 4250 and 5160 mg L^{-1} respectively, gradually decreasing in the following rinsing steps. Total COD remained at 1015 mg L^{-1} in neutralization/rinsing with acetic acid (step 8) and 747 mg L^{-1} in the following washing step (Fig. 2(a)). It should also be noted that the COD profile exhibited an almost totally soluble character. The COD measurements in each step indicated the total COD load as 10.1 kg cycle^{-1}. This load corresponds to a unit COD load of around 0.13 kg COD kg^{-1} fabric, yielding an average total COD concentration of 1380 mg L^{-1}.

The color profile basically started with the dying step and surprisingly, it reached a peak with the neutralization/rinsing step, especially at 436 nm (Fig. 2(b)). The pH and conductivity levels were 10.0 and 3440 µS cm^{-1} respectively, due to caustic soda addition at the initial bleaching step, gradually decreasing to 7.0 and 476 µS cm^{-1} in the effluent of the final softening step.

Polyester and polyester based fabrics

A similar experimental survey was carried out with the selected processing cycle for polyester and polyester based fabrics. The batch reactor studied during the survey had a water holding capacity of 5400 L and operated with 747 kg of fabric, which yielded a liquor ratio of 1/7.2. The cycle mainly included bleaching, dyeing and reductive rinsing using hydrosulfite, with corresponding rinsing steps (Fig. 3). The process generated a total wastewater volume of 38.65 m^3, yielding a unit wastewater flow of 51.7 L kg^{-1} fabric. It should be noted that this unit flow rate is a little higher than half the level computed for cotton fabrics.

The COD fingerprint of the process cycle as given in Fig. 4(a), defines a much stronger wastewater character with a peak of

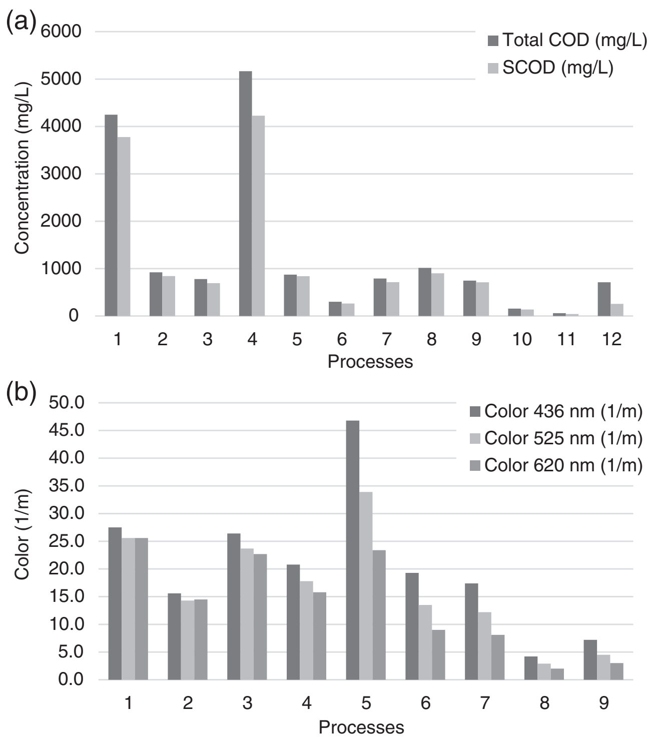

Figure 2. Pollution profile for cotton and cotton based fabrics: (a) COD profile; (b) color profile.

11 700 mg L^{-1} in the dyeing phase and 5300 mg L^{-1} in the following reductive rinsing phase. The average total COD concentration of the wastewater in this process cycle was calculated as 3400 mg L^{-1}. It corresponded to a total COD load of 131.5 kg, yielding a unit COD load of 0.176 kg COD kg^{-1} fabric. The color profile plotted in Fig. 4(b), showed the reductive rinsing phase as the major color contributor to the wastewater after the dyeing step. The measured color levels in the two steps were 50 and 26 m^{-1} absorbance at 436 nm, respectively. The pH level reflected a dual fluctuation from 10.7 at the bleaching phase down to 3.82 at the acidic dyeing phase, then from 9.18 at the reductive rinsing to 4.4 at the final neutralization/rinsing step. The conductivity reached a peak level of 10 400 μS cm^{-1} at the reductive rinsing step, but remained in the range 630–3780 μS cm^{-1} in all other processing phases.

Polyester/viscose fabrics

The dyeing and finishing process of polyester/viscose fabrics constituted the last part of the survey of dye house activities. The analytical program was carried out on a reactor adjusted to 1800 L; during the observed operating cycle, it processed 160 kg of fabric, corresponding to a low liquor ratio of 1/11.5, compared with other processes. The cycle included bleaching, carrier dyeing at 125 °C followed by turquoise dying; washing, neutralizing with acetic acid and softening, with the corresponding rinsing steps (Fig. 5). During the whole cycle, a total wastewater volume of 24.1 m^3 was produced, yielding a unit wastewater flow of 150 L kg^{-1} fabric, a high value that resulted from a very low liquor ratio compared with the default level of 1/6.

As depicted on the COD fingerprint of the whole process cycle plotted in Fig. 6(a), carrier dyeing at 125 °C discharged the highest COD concentration of 4490 mg L^{-1}; bleaching, turquoise dyeing and neutralization with acetic acid produced lower COD levels in the range 1560–1980 mg L^{-1}. The total cycle emitted a COD load of 31.13 kg, which corresponded to an overall COD concentration of 1290 mg L^{-1}. The color profile illustrated in Fig. 6(b) indicated a very high absorbance value of 48 m^{-1} at 620 nm starting from the turquoise dyeing (step 6), declining to 25 m^{-1} at the last rinsing step, while colors at other absorbance level always remained very low. pH started at 10.4 at the initial bleaching phase and gradually decreased to 3.23 until it was increased again to 10.76 at the turquoise dyeing step and continued with a similar decreasing trend, which ended at 6.32 in the final softening phase. A similar fluctuation was also observed for conductivity, which peaked to 43 500 μS cm^{-1} with turquoise dyeing.

The auxiliary parameters, such as TKN, TP and TSS were measured at the plant effluent every week for a period of 2 months. TKN varied in the range 12.8–32.4 mg N L^{-1} with an average value of 20.4 mg N L^{-1}. The TP level exhibited a variation between 0.7 and 4.9 mg L^{-1}, with an average value of 2.8 mg L^{-1}, which indicated a P deficiency for biological treatment. Similarly, TSS concentration varied between 34 and 65 mg L^{-1} around the average value of 46 mg L^{-1}, providing support for the soluble character of the wastewater. In fact, soluble COD to total COD ratio (S_T/C_T) was always quite high; it was calculated as 85% for cotton fabrics, 83% for PES fabric and 95% for PES/viscose fabrics.

Related data in the literature were reviewed and compiled in Table 4 to serve for benchmarking with similar data in this study, derived from COD fingerprints associated with the processing of different fabrics. Table 4 includes several studies on wastewater characterization of different plants on cotton knits dyeing and finishing; additionally, it includes a set of similar data on PES dyeing and finishing and also, another set on acrylic finishing, a synthetic material subject to similar processes to the PES/viscose fabric in this study.

First, a good agreement was observed between COD levels of this study and reported values summarized in Table 4, regarding the cotton fabric processing: (i) the average total COD value of around 1400 mg L^{-1} matched well with 1380 mg L^{-1} characterizing this study. (ii) The soluble nature of COD ($S_T/C_T = 0.85$) was confirmed with average S_T/C_T level of 0.80 in the reported results. (iii) The general character of wastewaters was similar with low levels of TKN and TP. (iv) The TSS level of the wastewater in the study remained lower than that observed in other surveys. Although specific COD values were different, there was a general conformity with the composition of PES and acrylic wastewaters with those in the study, in the sense that they were stronger, mostly soluble and with low TSS contents.

EVALUATION OF RESULTS

Wastewater and COD footprints

The effective capacity of the plant was given as 4230 t of fabric $year^{-1}$. The distribution of this capacity among different type of fabrics was provided in Table 1. Then, the corresponding total flow and COD load per year could be derived from the fingerprints of sequential phases in each batch cycle; they are summarized in Table 5 for different type of fabrics processed. As shown in this table, the yearly COD load was around 675 t in an overall wastewater flow of 403 500 m^3, yielding an average COD concentration of approximately 1700 mg L^{-1}. This way, the overall wastewater footprint of the plant was computed as 91 m^3 t^{-1} fabric. Figure 7(a) gives

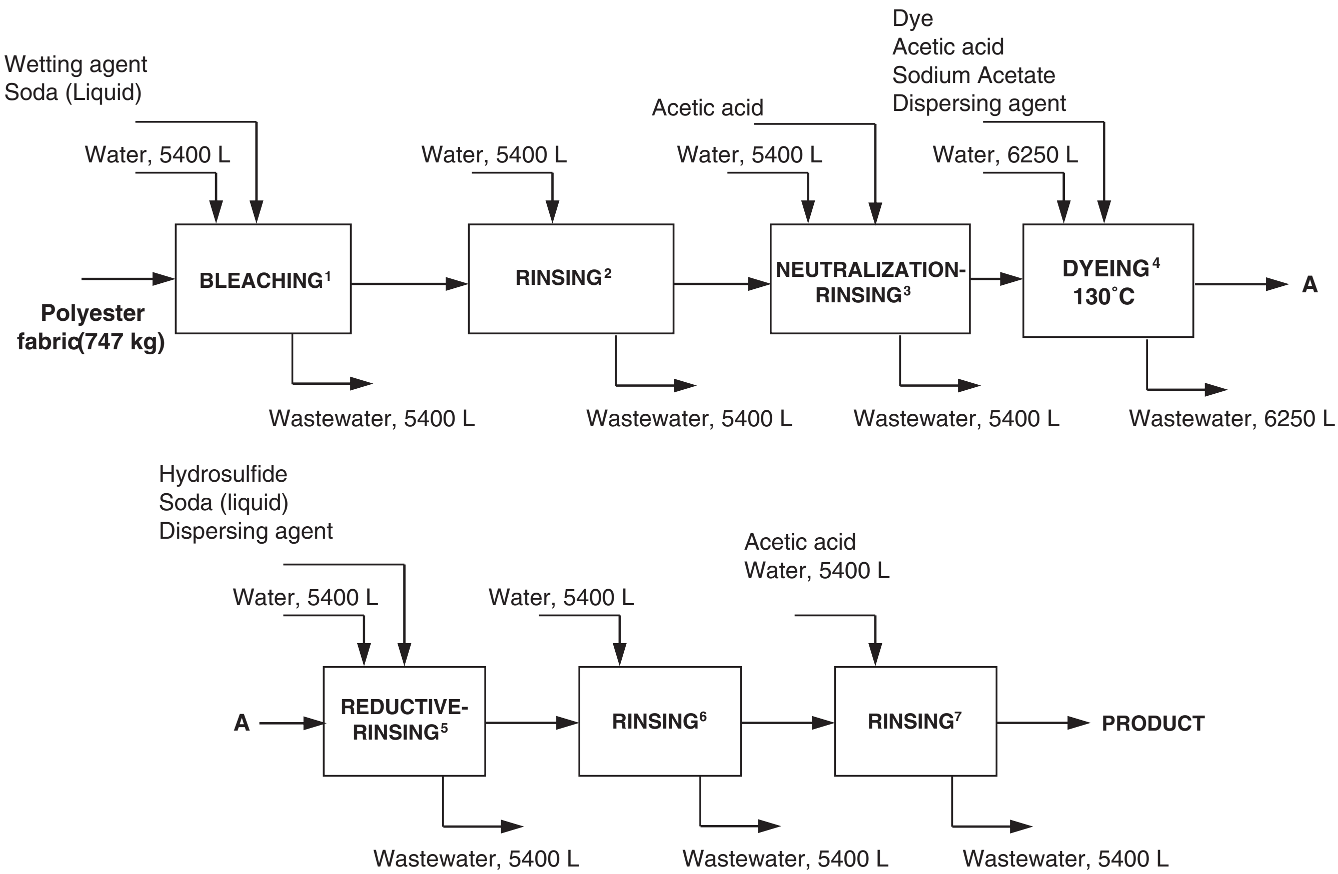

Figure 3. Schematic process scheme for polyester and polyester based fabrics.

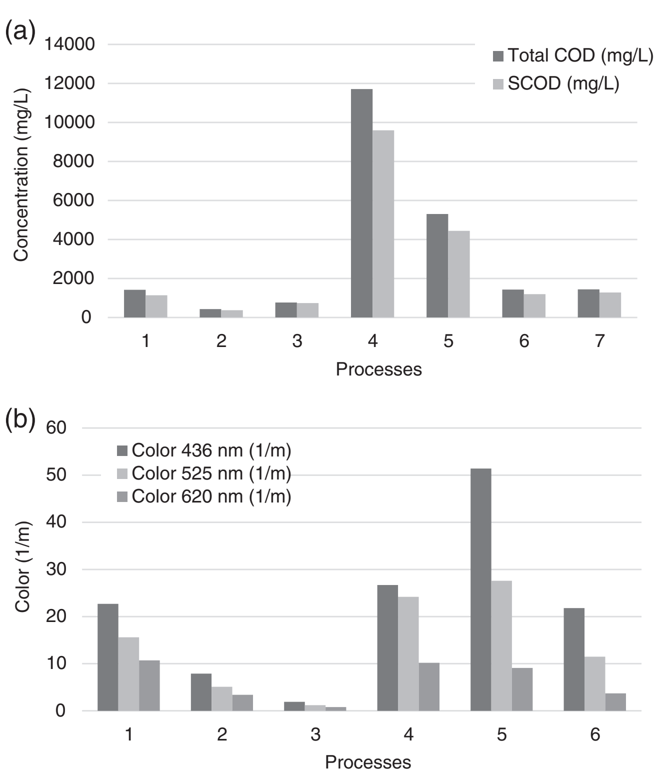

Figure 4. Pollution profile for polyester and polyester based fabrics: (a) COD profile; (b) color profile.

the variation of wastewater footprint as a function of fabric processed.

The data in Table 5, also indicate an overall COD footprint of 160 kg t^{-1} fabric. The specific COD loads discharged in the wastewater were observed as 10.1 kg $cycle^{-1}$ for cotton, 131.5 kg $cycle^{-1}$ for polyester and 31.1 kg $cycle^{-1}$ for PES/viscose, based on the analysis of specific process fingerprints. These values were then extrapolated to yearly production levels for assessing specific footprints for each type of fabric. Figure 7(b) gives the divergence of specific COD footprints from the overall value of 160 kg t^{-1} fabric.

Effluent characteristics

Data in Table 5 indicate significant changes in wastewater flow and COD load as a function of different fabrics. Obviously, these fabrics are processed either alone, or in two-way and three-way combinations during different periods. To determine the extreme conditions in changes of the effluent quality, the specific yearly production rates are hypothetically expressed as periods of days in the same table. Although, these values are fictitious, they certainly apply to certain periods during the year, when single-type production takes place. The table also includes daily specific wastewater flows and COD loads corresponding to these periods. The corresponding data clearly indicate the expected daily extreme values for wastewater flow between 600 and 1750 m^3 day^{-1}; for COD load between 1470 and 2260 kg day^{-1} and for COD concentration between 1290 and 3400 mg L^{-1}; the latter was confirmed by a year-long survey of the plant effluent, where the COD concentration was measured to periodically vary in the range 1150–3250 mg L^{-1}.

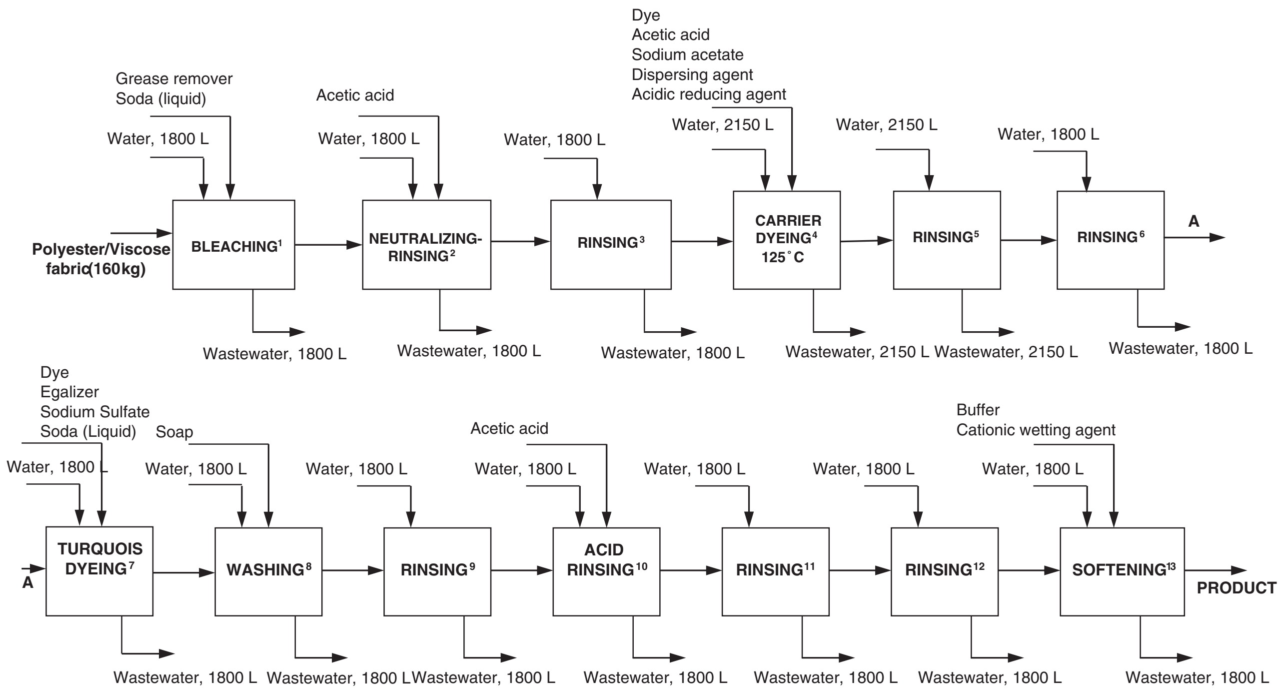

Figure 5. Schematic process scheme for polyester/viscose fabrics.

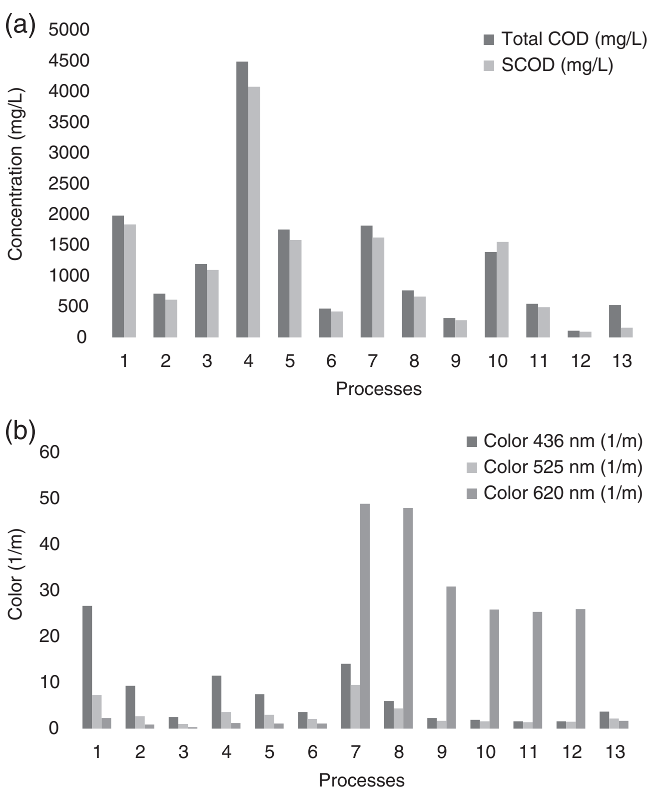

Figure 6. Pollution profile for polyester/viscose fabrics: (a) COD profile; (b) color profile.

Modeling for wastewater management

It is clear that without an in-plant survey carried out in the study, a wastewater management and treatment strategy would be most likely incomplete, and even misleading. This shows the serious shortcomings of most attempts in practice today, solely relying on the 'end of pipe' observations. In this context, a model evaluation was conducted at this stage to explore the impact of extreme conditions in the plant effluent on the expected performance and optimum design of an appropriate biological treatment. For this purpose, model implementation used applicable COD fractionation and kinetic information derived from previous similar studies and summarized in Tables 6 and 7.[31,38]

The model simulation started with a preliminary design of the treatment facility as a conventional activated sludge plant. The system was designed for a daily overall wastewater flow of approximately 1100 m^3 day^{-1}, with 1700 mg COD L^{-1}, adopting a sludge retention time (SRT) of 10 days, which yielded a total suspended solids level of 3000–3500 mg L^{-1} in the reactor. The resulting aeration volume was calculated as 1170 m^3, corresponding to a hydraulic retention time of 1.1 day.

The simulation exercise was conducted at three different SRT values of 6, 10 and 15 days, mainly to visualize the impact of SRT on effluent quality. Maintaining the same TSS level of 3000–3500 mg L^{-1} in the reactor required adjustment of the reactor volume in the range of 810–1500 m^3 as a function of the selected SRT value. Model simulation basically evaluated periods where the plant effluent solely consisted of cotton, polyester or PES/viscose wastewaters. Only soluble COD fractions were considered in the wastewater plant effluent, since current technology is now capable of full retention of particular components.

The following observation may be expressed about the simulation results, which are summarized in Fig. 8: (i) the selected SRT range allows for complete removal of S_S for the three wastewaters; therefore, effluent COD only includes S_H, S_I and soluble residual metabolic products, S_P generated as part of metabolic reactions. (ii) Obviously, the initial S_I value associated with the wastewaters by-passes treatment and it is discharged with the effluent; the effluent residual COD was increased by S_P, which varied in the range 15–25 mg L^{-1} for cotton; 28–53 mg L^{-1} for PES and 10–19 mg L^{-1} for PES/viscose. (iii) Evidently, system operation at

Table 4. Reported wastewater characterization in similar textile plants

Process	TCOD (mg L^{-1})	SCOD (mg L^{-1})	TKN (mg L^{-1})	TP (mg L^{-1})	TSS (mg L^{-1})	VSS (mg L^{-1})	Reference
Cotton knit							
	981	535	40	14	–	–	Orhon *et al.*[36]
	1470	1165	110	4	490	160	Germirli *et al.*[31]
	2310	1900	14	4.5	135	80	Germirli *et al.*[37]
	1180	890	14	13	100	90	Orhon *et al.*[39]
	2100	1558	62	13.6	700	–	Germirli *et al.*[40]
	828	–	22	10	65	32	Orhon *et al.*[41]
Polyester knit	1985	1485	27	9	213	22	Germirli *et al.*[31]
Acrylic knit	1990	1590	7.2	4.2	90	43	Germirli *et al.*[37]

Table 5. Variation of wastewater flow and COD load with the type of fabrics processed

	Flow (m^3 $year^{-1}$)	COD (t $year^{-1}$)	Production (%)	Operation period (days)	Flow (m^3 day^{-1})	COD (kg day^{-1})	COD (mg L^{-1})	SCOD (mg L^{-1})	BOD_5 (mg L^{-1})
Cotton	131 775	182	34	124	1060	1470	1380	1170	325
PES	67 200	228	30.7	112	600	2040	3400	2830	620
PES-viscose	204 525	264	32.1	117	1750	2260	1290	1170	250
Total	403 500	675							

an SRT of 15 days yielded the lowest S_H levels in the effluent; S_H could be lowered to 60 mg L^{-1} for cotton, 194 mg L^{-1} for PES and 152 mg L^{-1} for PES/viscose wastewaters.

The data in Fig. 8, suggest that an activated sludge plant operated at an SRT of 15 days would not be able to reduce the effluent COD below the range 300–530 mg L^{-1} depending on the mixture of fabrics processed. This range remains significantly higher than permissible effluent limitations for textile operations.[42–44] Partial treatment may be associated with (i) the strong character of the wastewater with a high S_I/C_T ratio of 13–20%; it should be noted that the same ratio is usually reported around 5–7% for domestic sewage;[45–47] (ii) significantly lower hydrolysis rates of the slowly biodegradable COD components, compared with domestic sewage and other industrial wastewaters.[9,48]

Based on the above observations, a more sustainable treatment strategy could be envisaged involving an extended aeration configuration of the activated sludge process operated at a higher SRT value of 25 days. Furthermore, it is conceivable that this SRT level may provide a limited/partial biodegradation of inert components, which is accepted to be residual based on laboratory experiments.[49,50] In fact, experiments conducted on sludge stabilization indicated hydrolysis/biodegradation of particulate inert COD at a very slow rate of $k_{hXI} = 0.012$ day^{-1} and $K_{XI} = 0.01$ g COD g^{-1} COD.[51] In this context, model simulation was extended to cover an extended aeration system at SRT of 25 days, also including partial hydrolysis of the S_I fraction using model coefficients of $k_{hSI} = 0.02$ day^{-1} and $K_{SI} = 0.01$ g COD g^{-1} COD. Effluent quality derived by the simulation was (i) $S_R = 175$ mg COD L^{-1} and $S_H = 44$ mg COD L^{-1} for cotton; (ii) $S_R = 290$ mg COD L^{-1} and $S_H = 12$ mg COD L^{-1} for PES and (iii) $S_R = 240$ mg COD L^{-1} and $S_H = 81$ mg COD L^{-1} for PES/ viscose. The simulation results provided a clear indication that the effluent soluble COD could be reduced to the range 220–320 mg COD L^{-1} with this wastewater management strategy.

Conceptual concerns

The experimental results outlined above obviously related to a specific plant. However, it was not an 'end of pipe' survey, where effluent characterization would be likely to reflect serious quantity and quality fluctuations, since they would not relate to the production schedule in the plant; involving different fabrics requiring different chemicals/dyes and different water use. This way, the study strongly underlined the need for abandoning the traditional 'end of pipe' surveys, which basically consider the plant as a 'black box' and focus on the inspection of the plant discharge alone.

On the contrary, the survey was carried out inside the plant, observing the processing schedule of each different fabric, that is, cotton knits, polyester (PES) knits and PES-viscose woven fabrics. The results obtained enabled evaluation of the pollution footprint of the dye house for each different fabric. In this context the results would equally extend to other plants which process the same type of fabrics. Footprint analysis is now a hot topic for assessing water use related environmental effects of all kind of activities and services. The study introduced this novel approach for the first time to the textile industry.

Moreover, the study also established a novel example of supplementing footprint analyses with corresponding biodegradation kinetics, which allowed model evaluation for system optimization. The evaluation was based on the biodegradability characteristics of wastewaters generated in other plants, processing the same type of fabrics, as reported in the literature.

Most important of all, the study advocated a methodology, involving a sequence of footprint analyses inside the plant; prediction of quantity and quality variations of the effluent; modeling, which displays biodegradability analysis and limitations involved and the choice of optimum treatment strategy. It recommended that the proposed evaluation approach be adopted and implemented in all similar plants, regardless of the nature of collected experimental information.

CONCLUSIONS

Detailed evaluation of sequential steps in different process cycles associated with cotton, polyester and polyester/viscose dyeing and finishing revealed highly variable footprints both

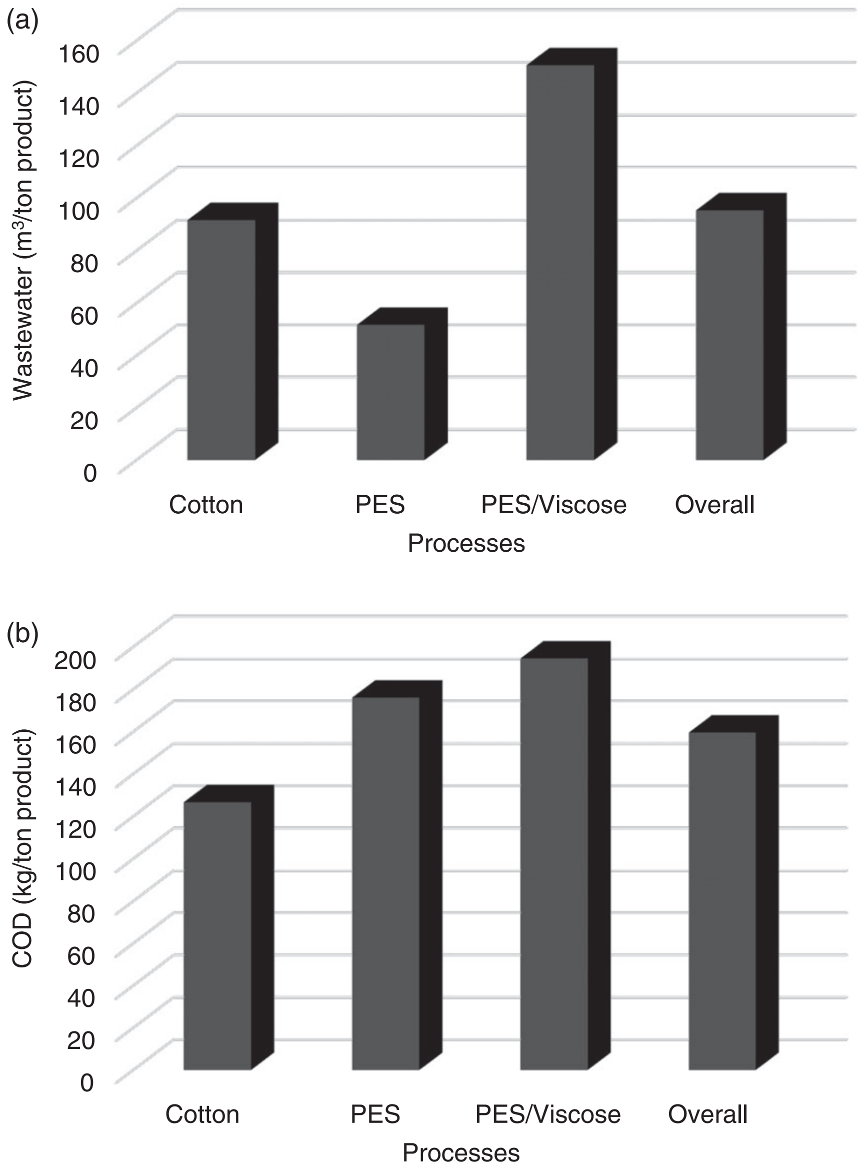

Figure 7. Variation of footprints with the type of fabrics processed: (a) wastewater footprint; (b) COD footprint.

Table 6. COD fractionation used for model implementation

	C_T	S_T	X_T	S_S		$S_H + X_S$	S_H	X_S	S_I		X_I	
Fabric	(mg L^{-1})	(%)	(%)	(mg L^{-1})	(%)	(mg L^{-1})	(%)	(%)	(mg L^{-1})	(%)	(mg L^{-1})	(%)
Cotton knit	1380	85	15	304	22	828	41	13	220	16	28	2
Polyester knit	3400	83	17	544	16	2278	57	16	442	13	136	4
PES/viscose knit	1290	95	5	180	13	924	62	5	276	20	0	–

for wastewater flow and COD: Depending on the type of fabric, wastewater footprint changed over the wide range 52–150 m^3 t^{-1} fabric and the COD (pollutant) footprint between 130 and 195 t COD t^{-1} fabric. These variations would inevitably reflect similar daily fluctuations for the overall wastewater flow between 600 and 1750 m^3 day^{-1}; for COD load between 1470 and 2260 kg day^{-1} and for the resulting COD concentration between 1290 and 3400 mg L^{-1}. This observation clearly underlines the shortcomings of the 'end of pipe' approach for wastewater management, which would only depict certain spots within the dynamics of the plant effluent, and would attempt to build a treatment strategy upon insufficient and sometimes misleading information.

Nowadays, an appropriate treatment strategy requires model evaluation with full information on COD fractionation and applicable model coefficients defining process kinetics. Processing different fabrics also imparted significant dissimilarities between COD fractions and process kinetics, with the following common features: highly soluble residual (inert) COD and soluble hydrolysable

Table 7. Kinetic coefficients used for model implementation

Fabric	C_T (mg L^{-1})	Y_H (mg mg^{-1})	$\hat{\mu}_H$ (day^{-1})	K_S (mg L^{-1})	b_H (day^{-1})	k_h (day^{-1})	K_X (mg mg^{-1})
Cotton knit	1380	0.64	3.6	9	0.14	1.8	0.37
Polyester knit	3400	0.64	5.3	25	0.12	3.8	0.65
PES/viscose knit	1290	0.64	3.9	16	0.17	1.6	0.40

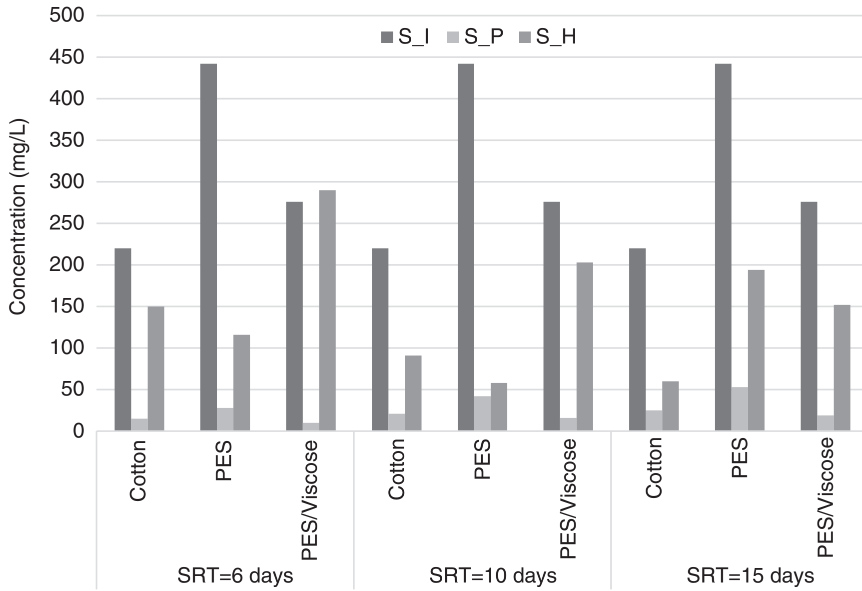

Figure 8. Simulation of COD fractions in the effluent.

COD; slow hydrolysis kinetics. Based on simulation results, these features make it impossible to meet the effluent limitations for COD, using the routine conventional activated sludge scheme operated at SRTs as high as 15 days. This study recommended a more sustainable treatment strategy involving the *extended aeration* configuration of the activated sludge process operated at a higher SRT value of 25 days, which would also enable partial breakdown of residual COD and reduce the effluent COD to the range 220–320 mg COD L^{-1} under all operating conditions in the dye house. It is suggested that further studies be conducted to provide results on the biodegradability trend of soluble residual COD under extended aeration conditions.

The significant conclusive message of the study was the merit of the novel approach based on water and COD footprints for waste management in all similar dye house operations, which generally involve processing batches of different fabrics, replacing the traditional 'end of pipe' inspection of wastewater discharge.

Supporting Information

Supporting information may be found in the online version of this article.

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