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A chemical substitution study for a wet processing textile mill in Turkey

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ABSTRACT

Wet processing textile industry has many different processing stages (dyeing, sizing, de-sizing, scouring, softening, etc.). Many chemicals currently used in the wet processing textile industry affect the amount and the type of waste produced and their influence on the aquatic life of the receiving stream. One of the critical steps in pollution prevention studies is auditing the use of chemicals and making the necessary chemical substitutions. This chemical substitution study was conducted on one of the major textile factories in Turkey with a capacity of 20,000 tons of denim fabric per year. During this study, chemical consumption level, receipts applied, environmentally problematic and alternative chemicals were examined. Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques (BAT) for the Textiles Industry was accepted as main reference document and also related case studies were examined. According to the study, over 70% reduction in sulphide, which is very toxic to aquatic life, was achieved by replacing sulphur dyestuff with low sulphide content. By replacing an alternative complexing agent, the mill not only prevented the 3100 kg/month COD load to the wastewater treatment plant (WWTP), but also obtained more biodegradable wastewater generated during production. On the other hand, some of the chemical substitution options were on progress or dropped.

1. Introduction

In textile processing industry, large amount of water is used during dyeing and finishing processes. While Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques (BAT) for the Textiles Industry indicates that water consumption varies from 70 to 250 l/kg fabric depending on the techniques applied [14,35], many sources from South Africa indicated that the specific water intake for the textile industry varies from 95 to 400 l/kg fabric depending on the type of processes used and water efficiency [2–4]. While 20–230 m^3 of water is needed to produce 1 ton of textile fabric in Turkish factories [5]. The total quantity of chemicals used in textile mills varies from 10% to over 100% of the weight of the cloth [6] and the chemical loads are generated mainly due to the residues from preparation, dyeing, finishing, sizing, and other operations. Therefore, the amount of water discharged and the chemical load of textile effluents are the major environmental concern in the textile industry [7,8].

Textile manufacturing generates solid, hazardous and air pollutant wastes, on the other hand, wastewater, by far, is the largest waste stream. For the textile industry, in general, the effluent is highly-colored, high in BOD and COD, has a high conductivity and is alkaline in nature [3,6,9–14]. These factors combine to present numerous operational problems in municipal wastewater treatment works, which are biological processes and not intended for the breakdown of complex organic molecules. The presence of metals and other dye compounds inhibits microbial activity and in some cases may cause failure of biological treatment systems [13]. Therefore, substitution of chemicals having lower hazard potential for chemicals having higher hazard potential should be a main focus for pollution prevention [7,8].

Chemical (Material) Substitution is defined as "the replacement or reduction of hazardous substances in products and processes by less hazardous or non-hazardous substances, whilst achieving an equivalent functionality via technological or organizational measures" [15–18].

Many studies indicate that material or chemical substitution can bring pollution prevention and increase in cost effectiveness together [19–22]. Admittedly, treatment costs can be reduced by introducing more biodegradable chemicals in production lines [8].

Literature indicates that pollution prevention by replacing sizing agents [6,9,14,23], surfactants [1], urea [24], solvent [25–28], acid [29], and reducing agents [30] with environmentally friendly chemicals can be achieved.

In this study, a wet processing textile mill in Turkey was investigated. The average annual capacity of the mill is 20,000 tons of ring yarn and 40 millions meters of denim fabric. In all wet processes, the ground water is used and the daily average water consumption of the mill is about 3500–5000 tons. The total monthly consumption of the chemicals is about 1000 tons and over 100

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textile chemicals including dyestuffs and auxiliaries are used in the wet processes in the factory. The mill has its own wastewater treatment plant (WWTP). The daily wastewater generation of the mill depends on daily number of processes operated. All washing water, pre-treatment, dyeing, softening and sizing solutions are discharged to the WWTP.

2. Methodology

2.1. Chemical screening

The textile industry uses several thousands of chemicals, each designed to accomplish a specific purpose in processing and finishing operations. The selection and use of these chemicals has a considerable impact on the amount and type of pollutants generated at textile facilities.

For better understanding the environmental impacts of the chemicals and making an effective chemical substitution study, screening of the chemicals used in the production lines is necessary. The chemical screening includes two main parts that are inventory analysis (chemical species, process receipts, chemicals consumption levels) and examining Material Safety Data Sheets (MSDS) of all the chemicals.

According to the inventory analysis, over 100 different chemical species and process receipts were identified in the textile mill investigated. These chemical species include dyestuffs, wetting, scouring agents, size and de-size auxiliaries, complexing agents, dispersants, stabilizers, reducing agents, lubricants, softeners, and alkali. All the relevant data about each chemical species, their consumption levels and receipts applied were provided by the mill. According to the investigation, the total average monthly chemical consumption of the mill was about 1000 tons.

After inventory analysis, the MSDS of all the chemicals were examined. All ecological and toxicological data of the chemicals were evaluated to determine the problematic chemicals. According to the information gathered from the MSDS, the problematic chemicals were identified. There were totally 8 out of 128 chemicals identified as environmentally problematic. These problematic chemicals are dispersant, sulphur dyestuffs, easy-care finishing agent and complexing agents.

2.2. Literature and manufacturer's database research and chemical suggestion of the suppliers

Introductory information about the problematic chemicals and their alternatives were identified by chemical screening and literature research. The next step was finding the alternative chemicals. Alternative chemicals for problematic ones were identified by the help of the chemical suppliers currently working with the textile mill investigated.

On the other hand, unfortunately textile manufacturers' databases research did not give satisfactory results. The reason for this problem was that the manufacturers were not eager to share their products' specialties. Chemical specialties used in processing generally contain secret blends of low-cost commodity chemicals. These blends are sold at specialty prices because of the manufacturer's expertise, not only in the mixture composition but also in applying the products to solve site-specific processing problems. Therefore, manufacturers wish to keep formulations secret to protect commercial interests.

After the mill operators ensured that the new chemicals were suitable for the production, then experimental analyses of defined chemicals were conducted. Experimental analyses were performed to evaluate the environmental performance of the problematic chemicals and their alternatives.

2.3. Selection of experimental methodology

In this chemical substitution study, environmental problems of some chemicals were attributed to their low biodegradability. To measure the biodegradability/bioeliminability potential of the problematic chemicals and their alternatives, Organization for Economic Co-operation and Development (OECD) 302b (Zahn–Wellens) test method was chosen. The Zahn–Wellens procedure is an interesting test to prospect the "behavior" of a chemical in an activated sludge treatment plant, since the experimental conditions are similar to this process [31]. Furthermore, the Zahn–Wellens test method is accepted as the most important of the existing standardized methods for testing inherent biodegradability [32].

This test method was chosen because of two main reasons. The first reason was that the method was the reference biodegradability/bioeliminability test method in the MSDS of the problematic and alternative chemicals. The second reason was that this method was mentioned in the IPPC Reference Document on BAT for the Textiles Industry document as reference test method to measure the biodegradability potential of a chemical [14].

2.4. Experiments

2.4.1. Chemicals tested

There are four chemicals found as environmentally problematic due to their low biodegradability characteristics. To evaluate the environmental performance of these chemicals and their alternatives, biodegradability tests were conducted. Table 1 indicates these chemicals, their alternatives and the production lines they applied. Because of the privacy, exact names of the chemicals were not provided.

2.4.2. Wastewater samples tested

The supplier ensured that the alternative complexing agent C* was suitable for the production. Therefore, the operators of the mill decided to try the alternative chemical C* in the dyeing processes. Therefore, there was a chance to see the effects of this chemical substitution on the wastewater characteristics. To identify these effects, the wastewater samples were collected after and before the substitution and biodegradability tests were conducted on these wastewater samples as well.

2.4.3. Experimental procedure

The necessary activated sludge to be used as seed was obtained from the WWTP in the Middle East Technical University (METU) campus. The nutrient solution was prepared in the laboratory of the Department of Environmental Engineering in METU according to the OECD 302b (Zahn–Wellens) test method [33]. The ingredients of the nutrient solution are illustrated in Table 2. The nutrient solution was prepared by dissolving all ingredients in 1 l of de-ionized water. The synthetic wastewater samples of problematic and alternative chemicals were also prepared in the same laboratory. The chemical concentrations in synthetic wastewaters were arranged according to the COD value of each chemical.

Two and a half liter dark colored bottles were used as test reactors. The reason of using dark colored bottle was to achieve the

Table 1
Environmentally problematic chemicals and alternatives tested and the production lines they applied

Chemical tested	Alternative chemical tested	Production line
Dispersant A	–	Dyeing
Complexing agent A	Complexing agent A*	Finishing
Complexing agent B	Complexing agent B*	Finishing
Complexing agent C	Complexing agent C*	Dyeing

Table 2
The ingredients and their amount in nutrient solution (for 1 l de-ionized water)

Ingredients of nutrient solution	Amount of ingredient (g)
Ammonium Chloride, NH_4Cl,	38.5
Sodium dihydrogenphosphate, $NaH_2PO_4 \cdot 2H_2O$,	33.4
Potassium dihydrogenphosphate, KH_2PO_4,	8.5
Di-potassium mono-hydrogenphosphate, K_2HPO_4,	21.75

diffuse illumination. Dissolved oxygen (DO) demands in the reactors were provided by the aquarium type air pumps (Fig. 1). According to the test procedure, the final Total Suspended Solids' (TSSs) concentration of the activated sludge in the reactors should be between 0.2 and 1 g/l. The TSS concentration of the activated sludge seed gathered from the WWTP was 6.8 g/l. According to this measurement, 150 ml of activated sludge was added to each reactor having final mixture volume of 2 l. Therefore, the TSS concentration of activated sludge in the final mixtures of the reactors was adjusted as 0.5 g/l. Last of all, 5 ml of nutrient solution was added to each reactor. For each chemical, the tests were performed in two parallel reactors and one control (blank) reactor was setup.

The pH, temperature and DO levels of the reactors were adjusted to desirable values as the test procedure indicates. The pH values of the final mixtures in the reactors were measured daily and adjusted between 7 and 8. In addition to this, daily temperature and DO concentration were measured. The biodegradability tests were conducted in summer months (June, July and August); therefore, at daytimes especially at afternoon the ambient air temperature of the laboratory and consequently the reactors' temperature reached up to 30 °C and the test method indicates that the temperature of the reactors should be between 20 and 25 °C. During the critical hours when the reactors' temperature was over 25 °C, the reactors were cooled to below 25 °C by placing icepacks on outside of the reactors. Thus, the temperature of the reactors was kept between 20 and 25 °C. According to the test procedure, the DO concentration of the reactors should be at least 2 mg/l. The daily DO measurements indicated that the air pumps used were efficient to supply essential DO with a concentration of between 5 and 8 mg/l.

The test procedure indicates that there is a need for obtaining homogeneity in mixtures in the reactors. Because of this reason, the use of agitators in test reactors is recommended in the test method. In this study, the homogeneity of mixture in the reactors was obtained from the air bubbles originated from the aquarium type air pumps.

The amount of degradation attained at the end of the test is reported as percent (%) biodegradation. The biodegradation is calculated by Eq. (1):

$$D_t = \left[1 - \frac{(C_T - C_B)}{(C_A - C_{BA})}\right] \times 100 \quad (1)$$

where D_t = biodegradation (%) at time t, C_A = COD values in the test mixture measured 3 h after the beginning of the test (mg/l), C_T = COD values in the test mixture at the time of sampling (mg/l), C_B = COD value of the blank at the time of sampling (mg/l), C_{BA} = COD value of the blank measured 3 h after the beginning of the test (mg/l).

2.4.4. Analytical methods

2.4.4.1. pH and temperature. The pH values were determined with pH meter (Model 2906, Jenway LTD., UK) and a pH probe (G-05992-55, Cole Parmer Instrument Co., USA). The temperature values were determined with pH-meter and a temperature probe.

2.4.4.2. Total solids (TSs). The TS analysis of activated sludge seed culture was measured using Standard Methods (2540) [34].

2.4.4.3. Dissolved oxygen (DO). The DO measurements were conducted using Hach Sension 378 pH, Conductivity, Dissolved Oxygen meter.

2.4.4.4. Chemical oxygen demand (COD). All COD analyses of mixture taken form the reactors were carried out using the spectroquant analysis system, on a PC Multidirect Autotest photometer (Aqualytic) and Aqualytic PC COD vials for COD 0–15,000 ppm (for High Medium Range-COD values) and COD 0–1500 ppm (for Low Medium Range-COD values) as given in Aqualytic PC MultiDirect Instruction Manual. For digestion and heating of samples for 2 h, a thermoreactor at a temperature of 150 °C was used. The basic principle is that oxidizable substances react with sulphuric acids–potassium dichromate solution in the presence of silver sulphate as catalyst. Chloride is masked with mercury sulphate and the reduction in the yellow coloration is evaluated after digestion.

3. Results and discussion

3.1. Problematic chemicals used in the production and their alternatives

3.1.1. Dispersants

Vat, disperse and sulphur dyes already have a high content of dispersing agents in their formulation, which allows the application of these colorants in the form of aqueous dispersions. Substances commonly used as dispersing agents are condensation

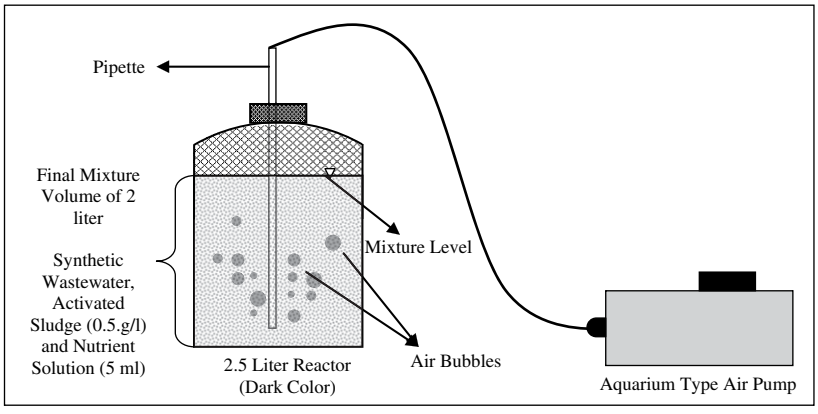

Fig. 1. The experimental setup of biodegradability test.

products of naphthalenesulphonic acid with formaldehyde and lignosulphonates. Anionic and non-ionic surfactants (e.g. ethoxylated alcohols, phosphated alcohols and naphthalene sulphonates) are also applied [14].

3.1.1.1. Environmental problems. The dispersing agents do not have affinity for the fibers and they are therefore found in the final effluent. Due to the significant amounts applied and to their often-low biodegradability/bioeliminability, they contribute to most of the recalcitrant organic load originating from dyeing and printing processes. While these additives are not toxic to aquatic life, they are in general poorly biodegradable and not readily bioeliminable [14].

3.1.1.2. Dispersant used in the production. The Dispersant A is used as dispersant additives in the dyeing processes of the mill investigated. It is available in powder form. The chemical nature of the Dispersant A is naphthalenesulphonic acid with formaldehyde poly-condensate as sodium salt. The average consumption of the chemical is 1500 kg/month. It has a biodegradability of 30–70% stated in its MSDS.

The mill stated that they wanted to be sure of the biodegradability values written on the MSDS of the Dispersant A. To determine the exact level of biodegradability of Dispersant A, the experimental analysis (OECD 302b, Zahn–Wellens) was conducted and the test results of the test are plotted and shown in Fig. 2.

3.1.1.3. Alternative chemical. The supplier of the Dispersant A suggested several alternatives having better biodegradability characteristics. Among the alternatives, Dispersant A* was selected as the best alternative for Dispersant A. This was because of its high biodegradability which was stated as 70–100% in its MSDS.

3.1.1.4. Results of the projected substitution. Although the supplier suggested Dispersant A* as possible substitute for A, the supplier indicated that A* could present quality problem on the final denim products. Therefore, the mill decided that there would be no substitution for Dispersant A.

3.1.2. Sulphur dyes

Sulphur dyes are mainly used for cotton and viscose substrates. Sulphur dyes are made up of high molecular weight compounds, obtained by reaction of sulphur or sulphides with amines and phenols. Sulphur dyes are insoluble in water and they need to be converted to the "leuco-form", which is water-soluble and has a high affinity for the fiber at some stage during the dyeing process [14].

Conventional sulphur dyes are available in powder form. Before dyeing, they have to be reduced with sodium sulphide in alkaline conditions. Other typical sulphur dyes are the "pre-reduced/ready-for-use" dyes. They are supplied in liquid form and already contain the reducing agent in their formulation. The sulphide content of pre-reduced dyes may be higher than 5% [35].

3.1.2.1. Environmental problems. Wastewater from sulphur dyeing contains sulphides used in the process as reducing agents. In some cases, the sulphide is already contained in the dye formulation and in some other cases, it is added to the dye bath before dyeing. In the end, however, the excess sulphide ends up in the wastewater. The excess sulphide (from the dyestuff and reducing agent) is responsible for aquatic toxicity. In addition, sulphide anions are converted into hydrogen sulphide under acidic conditions, thereby giving rise to problems of odor and corrosivity [14].

Sulphide, as used in the form of sodium sulphide in the dye formulation, is used as reducing agent [14] and stated as hazardous ingredient, which is very toxic to aquatic organisms (effective concentration on Daphnia Magna: 2.1 mg/l; very toxic) [36,37] and microorganisms (toxicity threshold concentration on Pseudomonas Putida: 1.6 mg/l; highly toxic) [38].

3.1.2.2. Sulphur dyes used in the production. There are three sulphur dyestuffs used in the production lines. All these three dyestuffs have high sulphide content. The code names of the dyestuffs and their sulphide contents in their formulations are summarized in Table 3.

In the production, after each dyeing process, the whole dye baths for these dyes are poured into the sewer that discharges into the WWTP. That is, a significant amount of dyestuffs and auxiliaries is wasted after each dyeing operation. The monthly dyestuffs wasted (1000 kg/month) and also corresponding sulphide wasted from the dyeing operations are presented in Table 4.

In addition to the amount of sulphide wasted directly from dye baths as indicated in Table 4, there is also a sulphide load to the WWTP, originating from the unfixed sulphur dyestuffs from dyeing operations. The literature indicates that sulphur dyes have fixation rate of 60–90% [14].

The post-washing process is applied to remove the unfixed dye and auxiliaries form the yarn. That is, by post-washing, 10–40% of sulphur dyestuffs are discharged to the WWTP. This means that significant amount of sulphide again is released by post-washing process to the WWTP. Table 5 presents the monthly average consumption amount of sulphur dyestuff used in the production and possible amount of unfixed sulphur dyestuffs and unfixed sulphide discharged to the WWTP.

The total amount of sulphur dyestuffs and sulphide discharged to the WWTP is the summation of wasted and unfixed amount of the sulphur dyestuffs and sulphide. That is, the total monthly amount of sulphur dyestuffs discharged to the WWTP is 5350–18,000 kg. Consequently, the total monthly amount of sulphide discharged to the WWTP is 310–1900 kg.

3.1.2.3. Alternative chemicals. The mill ordered new dyestuff for sulphur dyestuff A. The substitute dyestuff A* has a sulphide

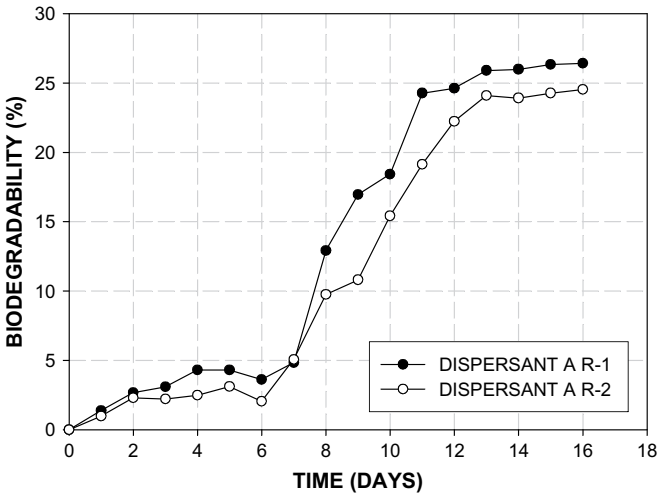

Fig. 2. The biodegradability test results of the Dispersant A(R-1 and R-2 in the legend refer to the parallel reactors 1 and 2 operated, respectively).

Table 3
Sulphur dyestuffs in the production and their sulphide contents

Sulphur dyestuff	Sulphide content (%)
A	5–10
B	12–15
C	12–15

Table 4
The amount of wasted sulphur dyestuffs with high sulphide content used in the mill

Sulphur dyestuff	Amount of sulphur dyestuff wasted (kg/month)	Sulphide wasted[a] (kg/month)
A	1000	50–100
B	22	2.6–3.3
C	110	13.2–16.5
TOTAL	1132	65.8–119.8

[a] Calculated on the basis of sulphide content of the sulphur dyestuffs.

content of 1–3% in its formulation. The mill also decided to quit the use of sulphur dyestuff B. However, there is no color alternative for dyestuff C, the mill has to use dyestuff C in dyeing process.

The supplier ensured that the dyestuff A* was suitable for the production (i.e. there were no detrimental effects on product quality due to the use of this new dyestuff), and the operators of the mill decided to try the alternative dyestuff A* in the dyeing processes. The suppliers also indicated that using the new dyestuff A* in the process could not bring additional cost to the company, because the price of the new chemical was same as the previous dyestuff A. Therefore, the mill operators decided to use this new dyestuff in the process, constantly.

3.1.2.4. Results of the substitution. For the sulphur dye substitution case, the environmental gain was evaluated in terms of sulphide load reduction to the WWTP, rather than the improved biodegradability, as the primary concern with these chemicals was their sulphide content. Table 6 indicates the total sulphide wasted after substitution.

As mentioned before, there is also a sulphide load to the WWTP originating from the unfixed sulphur dyestuffs from dyeing operations. Table 7 represents the current situation of monthly amount of unfixed sulphur dyes and unfixed sulphide discharging to the WWTP, and the reduction in the unfixed sulphide as a result of chemical substitution.

For the current situation, the total monthly amount of sulphur dyestuffs discharged to the WWTP is 5330–17,990 kg. Consequently, the total monthly amount of sulphide discharged to the WWTP is 74–731 kg. This value was 310–1900 kg/month before the chemical substitution. Therefore, the result of the substitution shows that a reduction in the amount of sulphide (due to the use of sulphur dye) discharged to the WWTP up to 76% can be achieved.

3.1.3. Easy-care finishing agent

Easy-care finishing agents are the chemical finishers, which are applied to woven and knitted fabrics composed of cotton, other cellulosic fibers and their blends with synthetic fibers. Their function is to reduce the propensity of cellulose-containing fabrics for wrinkling when treated under wet and dry conditions and to stabilize them against progressive shrinkage during laundering. The cross-linking agents play an essential role in this finishing treatment. From a chemical point of view, there are three distinct groups, which are cross-linking agents based on melamine and formaldehyde, cross-linking agents based on urea and formaldehyde, heterocyclic linking agents based on urea, formaldehyde and various other substances such as diamines and, in particular, glyoxal [14].

Table 6
The amount of wasted sulphur dyestuffs and sulphide after the chemical substitution

Sulphur dyestuff	Amount of sulphur dyestuff wasted (kg/month)	Sulphide content (%)	Sulphide wasted[a] (kg/month)
A*	1000	1–3	10–30
B (No Use)	–	–	–
C (No Substitute)	110	12–15	13.2–16.5
TOTAL after Substitution	1110		23.2–46.5

[a] Calculated on the basis of Sulphide content of the sulphur dyestuffs.

3.1.3.1. Environmental problems. All these products may potentially produce emissions of free formaldehyde and methanol. In particular, formaldehyde is suspected of carcinogenity and its presence in these finishing agents represents a potential risk not only for wastewater and exhausted air, but also for the workplace and the final user of the textile good [14,39]. While free formaldehyde is thought to be carcinogenic and is a threat to the workforce, it can also be released, for example, during cutting operations [14].

3.1.3.2. Easy-care finishing agent used in the production. Formaldehyde based chemical Easy-Care Agent A is used for easy-care finishing chemical for the finishing processes in the mill. The monthly average consumption of the chemical in the finishing processes is 840 kg. Easy-Care Agent A contains 0.1–1% formaldehyde on weight base.

3.1.3.3. Alternative chemicals. Low-formaldehyde or even formaldehyde-free products are alternatives [14]. The factory contacted the supplier to identify the low-formaldehyde or formaldehyde-free chemicals for a substitute. The supplier suggested an alternative easy-care finishing agent, which is a formaldehyde-free product.

3.1.3.4. Results of the projected substitution. The supplier of Easy-Care Agent A suggested an alternative formaldehyde-free easy-care finishing agent. However, the supplier indicated that this new chemical is 3–4 times more expensive than Easy-Care Agent A. Therefore, the textile mill has not decided yet to replace the new chemical for the current easy-care finishing agent.

Because the mill is an international company and exports their denim fabric to other countries, they have to comply with the limit on the formaldehyde content of the final denim product. (The formaldehyde content of the product contact with the skin has to be less than 30 ppm.) In addition, the mill declares that the

Table 5
Monthly average consumption of sulphur dyestuffs and amount of unfixed sulphur dyestuffs and unfixed sulphide discharged to WWTP

Sulphur dyestuff	Consumption amount (kg/month)	Sulphide content (%)	Amount of unfixed dyestuff[a] (kg/month)	Amount of unfixed sulphide[b] (kg/month)
A	37500	5–10	3750–15000	188–1500
B	800	12–15	80–320	10–48
C	3900	12–15	390–1560	47–234
TOTAL	42200		4220–16,880	245–1782

[a] Calculated on the basis of sulphur dyestuff fixation rate.
[b] Calculated on the basis of sulphide content of the sulphur dyestuffs.

Table 7
The amount of unfixed sulphur dyestuffs and sulphide, and the reduction in the unfixed sulphide after the chemical substitutions

Sulphur Dyestuff	Consumption Amount (kg/month)	Sulphide content (%)	Amount of Unfixed Dyestuff[a] (kg/month)	Amount of Unfixed Sulphide[b] (kg/month)
A*	37500	1–3	3750–15000	4–450
B (No Use)	–	–	–	–
C (No Substitute)	3900	12–15	390–1560	47–234
TOTAL after Subs.	41400		4140–16,560	51–684

[a] Calculated on the basis of sulphur dyestuff fixation rate.
[b] Calculated on the basis of sulphide content of the sulphur dyestuffs.

Table 8
COD values of the complexing agents A and A* in their formulations, concentrations of the chemicals and the corresponding COD values in the reactors

Chemical	COD value of chemical (mg/ml)	Conc.	Concentration of chemical in the reactor (ml/l)	Corresponding COD value in the reactor (mg/l)
A	350	LOW	1.3	455
		HIGH	2	700
A*	270	LOW	1.5	405
		HIGH	2.9	783

Table 9
COD value of the complexing agents B and B* in their formulations, concentrations of the chemicals in the reactors and the corresponding COD values in the reactors

Chemical	COD value of chemical (mg/ml)	Concentration of chemical in the reactor (ml/l)	Corresponding COD value in the reactor (mg/l)
B	100	8.75	875
B*	110	7.1	781

formaldehyde contents of the final denim products are less than 25 ppm. Therefore, there is not a potential risk for consumer. Since, especially during cutting operation, free formaldehyde can be released and threat the workers' health, so there is a potential risk for the workplace in terms of formaldehyde content.

If the mill starts the use of formaldehyde-free easy-care finishing agent, the potential risk for workplace will be prevented. Since the Easy-Care Agent A is still being used in the process, the use of protecting equipments (like gloves, eyewears and other protecting cloths) by workers is recommended during cutting operation.

3.1.4. Complexing agents

Complexing agents are applied to mask hardening alkaline-earth cations and transition-metal ions in aqueous solutions in order to eliminate their damaging effect, especially in pre-treatment processes (e.g. catalytic destruction of hydrogen peroxide) and during dyeing operations. Commonly used complexing agents are ethylenediamine tetraacetate (EDTA), nitrilotriacetate (NTA), diethylenetriaminepentaacetate (DTPA), phosphonic acid and gluconic acid derivatives. Also, stabilizers are considered as complexing agents [14].

3.1.4.1. Environmental problems. Complexing agents are not intended to fix on the yarns, fabrics and other textile products. Therefore, these process chemicals are released nearly 100% to the wastewater [40].

The main concerns associated with the use of these substances arise from their nitrogen and phosphorus contents, their often-low biodegradability and their ability to form stable complexes with metals, which may lead to remobilization of heavy metals.

EDTA, NTA and DTPA, in particular, form very stable metal complexes. EDTA and DTPA are also poorly eliminable compounds. Therefore, there is a risk they can pass undegraded through the common WWTP system and then eventually release the metals into the receiving effluent or that they may remobilize heavy metals in aquatic sediments [14].

3.1.4.2. Complexing agents used in the production. The complexing agent A is used in the finishing processes and it is a blend of organic compounds. It is available in liquid form and the role of the complexing agent A is to mask the metal ions during finishing processes. The average monthly consumption of A is about 1100 kg.

The complexing agent B is also used in the finishing line of the mill. It is also available in liquid form and it is a phosphonic acid product. The complexing agent B is used as a stabilizer during finishing processes. The average monthly consumption of B is about 1000 kg.

The last problematic chemical is the complexing agent C. It is available in powder form. It is used to mask the metal ions during dyeing processes and it is an EDTA derivative. The average monthly consumption of C is about 4000 kg.

The environmental problem due to the consumption of these complexing agents is mainly about their low biodegradability

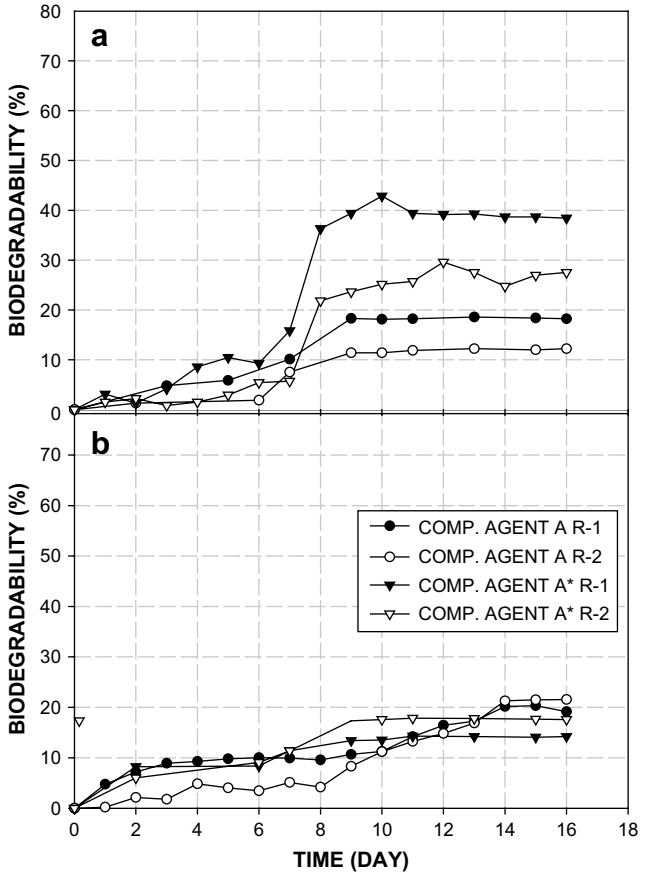

Fig. 3. Biodegradability curves of complexing agents A and A* at (a) low concentration and (b) high concentration (R-1 and R-2 in the legend refer to the parallel reactors 1 and 2 operated, respectively).

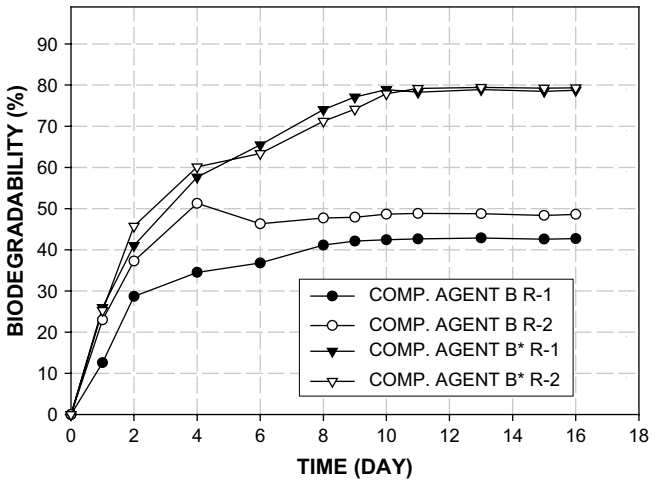

Fig. 4. Biodegradability graphs of complexing agents B and B* (R-1 and R-2 in the legend refer to the parallel reactors 1 and 2 operated, respectively).

Table 10
Summary of the biodegradability tests results of the complexing agents B and B*

Chemical	Biodegradability[a] (%)
B	46 ± 3
B*	79 ± 1

[a] Average of parallel runs, R-1 and R-2.

characteristics. While the MSDS of the complexing agents A and C indicate that the biodegradability of these two chemicals is low, the biodegradability of the complexing agent B is stated as 20–70%.

3.1.4.3. Alternative chemicals. The suppliers suggested alternative complexing agents A*, B* and C* for the environmentally problematic complexing agents A, B and C, respectively.

3.1.4.4. Results of the substitution

3.1.4.4.1. Results of the projected substitution of complexing agent A for A.* The supplier of the complexing agent A suggested the alternative chemical A*. It is a blend of organic compounds and available in liquid form like the complexing agent A. The biodegradability of the A* is stated as 20–70% in the MSDS. Substances are considered as biodegradable if they have biodegradability of more than 70% according to the OECD 302b test method [14]. Therefore, the biodegradability of A* can be considered as low. This information indicates that there is no significant difference in terms of ecological properties between the complexing agents A and A*.

To identify the biodegradability potential of these two complexing agents, biodegradability tests were conducted. The biodegradability tests were performed as two runs for each chemical. For each run, different concentrations (one high concentration and one low concentration) of the chemicals were tested owing to the range (100–1000 mg/l COD for synthetic test water) given in the OECD 302b (Zahn–Wellens) test method. The concentrations of the chemicals in the reactors were determined by the help of COD values of the chemicals' formulations. In Table 8, COD values of the complexing agents A and A* (the amount of COD in 1 ml of the chemical formulation (mg/ml)), the concentration of the chemicals in the reactors (in terms of ml/l) and the corresponding COD values in the reactors (in terms of mg/l) are exhibited.

The results of the biodegradability test are illustrated in Fig. 3. Fig. 3a represents the biodegradation curve of the chemicals at low concentration and b represents the biodegradation curve of the chemicals at high concentration.

3.1.4.4.2. Results of the projected substitution of complexing agent B for B.* The supplier of the complexing agent B suggested the alternative chemical B*. The chemical nature of the chemical B* is phosphonic acid and it is available in liquid form. The biodegradability of B* is stated as more than 80% in its MSDS. Therefore, the biodegradability of B* is much better than chemical B, since the biodegradability of the complexing agent B is stated as 20–70% in its MSDS. Although it is clearly indicated in their MSDS documents that B* is more biodegradable than B, further biodegradability tests were carried out to verify the biodegradability of these chemicals.

The biodegradability tests were performed as one run for each chemical. The concentrations of the chemicals in the reactors were determined by the help of COD data of the chemicals. Table 9 indicates COD values of the complexing agents B and B* (the amount of COD in 1 ml of the chemical formulation (mg/ml)), the concentration of chemicals in the reactors (in terms of ml/l) and the corresponding COD values in the reactors (in terms of mg/l). The results of the biodegradability test are illustrated in Fig. 4.

Table 11
COD value of the complexing agents C and C* in their formulations, concentrations of the chemicals in the reactors and the corresponding COD values in the reactors

Chemical	COD value of chemical (mg/g)	Concentration of chemical in the reactor (g/l)	Corresponding COD value in the reactor (mg/l)
C	1300	0.5	650
C*	525	1	525

Table 12
Biodegradability test results of chemicals C and C*

Chemical	Biodegradability[a] (%)
C	15 ± 1
C*	87 ± 4

[a] Average of parallel runs, R-1 and R-2.

The biodegradability test results indicate that the complexing agent B* is more biodegradable than the chemical B. While the average biodegradability value of two parallel reactors of the chemical B is 46%, the average biodegradability value of two parallel reactors of the chemical B* is 79% for the studied chemical levels. In other words, on the ecological side, the test result indicates that the chemical B* is more environmentally friendly than chemical B. The summary of the test results is demonstrated in Table 10.

The operators of the mill stated that some modifications in the finishing processes will be necessary, if they switch to use the alternative chemical B* in the production. This means that the implementation of the new chemical needs initial financial supply, and a cost benefit study should be conducted to decide whether to implement the use of the alternative chemical in the production is feasible or not.

3.1.4.4.3. Results of the substitution of complexing agent C for C.* The supplier of the complexing agent C suggested the chemical C* as the alternative chemical. The chemical nature of the chemical C* is NTA and it is available in powder form. On the other hand, the chemical C is an EDTA derivative. As mentioned before, EDTA is poorly eliminable and it cannot be degraded in WWTP. Conversely, NTA is more biodegradable than EDTA [14]. In addition, MSDS of the complexing agents C and C* indicate the biodegradability of these chemicals as low and over 70%, respectively.

Experimental analyses were also conducted on the chemicals C and C* to determine the biodegradability potential. COD values of the complexing agents C and C* (the amount of COD in 1 g of the chemical formulation (mg/g)), the concentration of chemicals in

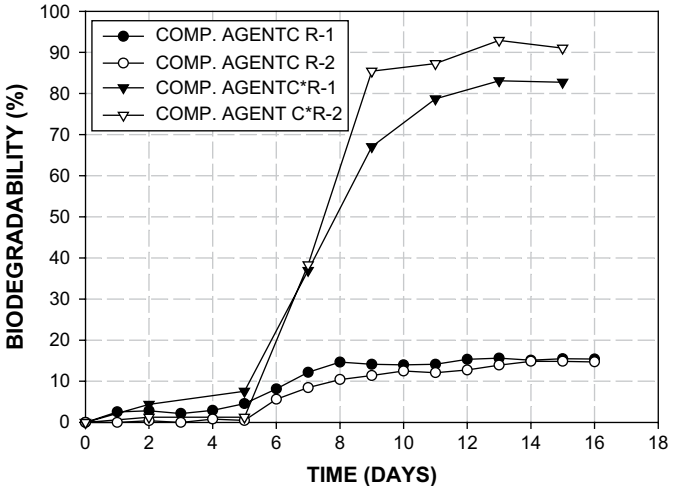

Fig. 5. Biodegradability test results of chemicals C and C* (R-1 and R-2 in the legend refer to the parallel reactors 1 and 2 operated, respectively).

Table 13
The COD concentration of the wastewater (WW) samples before and after the substitution, the amount of WW sample added to the reactors and the corresponding COD values in the reactors

WW sample	COD concentration of WW sample (mg/l)	Amount of WW sample added to the reactors (ml)	Corresponding COD value in the reactor (mg/l)
Before Substitution	2000	350	700
After Substitution	840	750	630

the reactors (in terms of g/l) and the corresponding COD values in the reactors (in terms of mg/l) are illustrated in Table 11. The results of the biodegradability test are also exhibited in Table 12 and in Fig. 5.

However, in order to make the results obtained for complexing agents C and C* comparable, initial COD values were adjusted more or less same (about 500–600 mg/l) which could be attained with different concentrations of C and C* (i.e. 0.5 g/l for C, 1 g/l for C*).

The biodegradability test results indicated that the alternative chemical C* is more biodegradable than the chemical C as their MSDS also indicated. The biodegradability potentials of the chemicals C and C* were determined as about 15% and 87%, respectively.

The supplier ensured that the alternative chemical C* was suitable for the production (i.e. there were no detrimental effects on product quality due to the use of this new dyestuff), and the operators of the mill decided to try the alternative chemical C* in the dyeing processes. Therefore, there was an opportunity to observe the effects of this chemical substitution on the wastewater characteristics. To identify these effects, the wastewater samples from the first post-washing tank just after the dye bath were collected after and before the substitution.

The wastewater samples were collected from the first post-washing tank just after the dye bath. The COD concentration of the wastewater sample was 2000 ± 43 mg/l before the substitution. After the substitution, the COD concentration of the wastewater sample was reduced to 840 ± 22 mg/l. This difference is due to the difference of the chemicals' COD value in their formulations. The COD value of the chemical C is 1300 mg/g and the COD value of the chemical C* is 525 mg/g (Table 11). The ecological properties of these chemicals influenced the wastewater characteristics directly. Therefore, this substitution leads to the COD concentration reduction in the wastewater.

As mentioned before, due to their chemical properties, complexing agents are released to nearly 100% to the wastewater [40]. By substituting the alternative chemical C*, the mill achieves 775 mg COD reduction while using 1 g of chemical C* instead of 1 g of chemical C. The operators use the alternative chemical C* as the same amount of C. That is the average monthly consumption of the C* is 4000 kg. Before the substitution, the COD load due to the use of chemical C was 5200 kg/month. After the substitution, this value is reduced to 2100 kg/month. That is, monthly 3100 kg of COD load to the WWTP is prevented.

This substitution influenced the biodegradability of the wastewater sample as well. Table 13 indicates the COD concentration of the wastewater samples, wastewater volume added to the reactors and the corresponding COD values in the reactor.

The biodegradability tests conducted on the wastewater samples before and after the chemical substitution show that there is a biodegradability enhancement by at least 25%. Before substitution, the biodegradability of wastewater sample was about 38%, after substitution this value is increased to over 64%. The test results are summarized in Table 14 and exhibited in Fig. 6.

Table 14
Biodegradability test results of WW samples

WW Sample	Biodegradability[a] (%)
Before Substitution	38 ± 2
After Substitution	64 ± 3

[a] Average of parallel runs, R-1 and R-2.

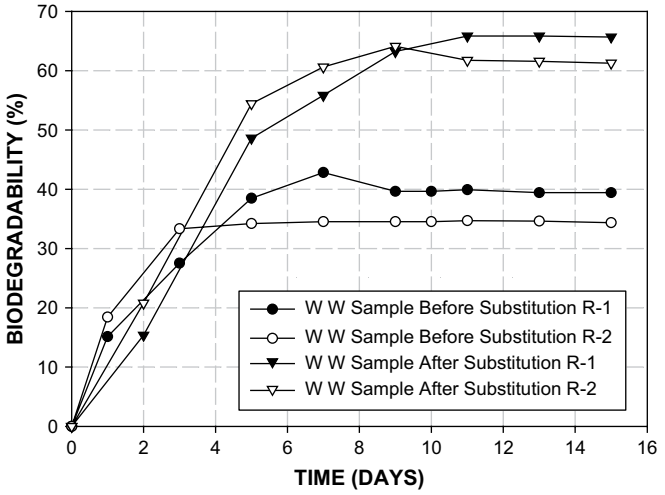

Fig. 6. Biodegradability test results of WW samples before and after the substitution of complexing agent C* for C (R-1 and R-2 in the legend refer to the parallel reactors 1 and 2 operated, respectively).

The suppliers also indicated that using the new chemical C* in the process could not bring additional cost to the company, because the price of the new chemical was same as the previous chemical C. Therefore, the mill operators decided to use this new chemical in the process, constantly.

4. Conclusion

A chemical substitution study for a wet processing textile mill in Turkey has led to the following conclusions:

- There were totally 8 out of 128 chemicals identified as environmentally problematic. The total monthly consumption of these problematic chemicals is about 50 tons. This value represents 5% of the total monthly consumption amount of all chemicals used in the factory.
- By substituting the dyestuff A with a lower sulphide product, up to 76% reduction in the amount of sulphide (due to the use of sulphur dyes) discharged to WWTP is achieved. That is, this substitution decreases the inhibition risk on microorganisms in the WWTP and consequently prevents a possible fail in WWTP system due to use of sulphur dyestuffs.
- Substitution of Complexing Agent C* for C has led to improvement in the biodegradability of wastewater samples collected from the first post-washing tank just after the dye bath by at least 25% (from 38% to 64%). Also, by this substitution, monthly 3100 kg of COD load to the WWTP is prevented.

Acknowledgements

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