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Ekološke alternative v konvencionalnem postopku barvanja z reaktivnimi barvili

Izvirni znanstveni članek

Poslano *september 2007* • Sprejeto *januar 2008*

Ecological alternatives in the conventional process of dyeing with reactive dyes

Original Scientific Paper

Received *September 2007* • Accepted *January 2008*

Abstract

Two dyeing recipes from a textile factory were studied, focusing on the quantity and quality of the added textile auxiliaries. The recipes were modified to replace hazardous chemicals with environmentally-friendly products. The COD values indicated that wastewaters resulting from the wash-off process of cotton dyed with modified recipes have a lower waste water load and simultaneously a higher degradable capacity, with the same fastness properties as textiles dyed with the original recipes.
Additionally, improvement in conventional washing was attained using an innovative rinsing technology, called 'hot-washing', after cotton dyeing using a modified recipe. The temperature was a predominant influence on the removal properties of dyestuff and textile auxiliaries. Application of the 'hot-washing' process after reactive dyeing resulted in water and time savings, and an improvement in the fastness properties.

Keywords: dyeing, reactive dye, cotton, 'hot-washing', ecology

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Izvleček

V raziskavi smo v tekstilni tovarni izbrali dve recepturi za barvanje bombažne tkanine z reaktivnimi barvili ter proučili količino in kakovost tekstilnih pomožnih sredstev. Recepture smo modificirali, da bi nevarne kemikalije nadomestili z ekološko prijaznejšimi produkti. KPK vrednosti so pokazale nižjo obremenitev izpiralnih odpadnih voda po barvanju bombaža z modificirano recepturo, kakor tudi višjo biorazgradljivost v primerjavi z izpiralnimi odpadnimi vodami po barvanju bombaža z nemodificirano recepturo, pri čemer je obstojnost barv ostala nespremenjena.
Razen tega smo izvedli izboljšanje konvencionalnega izpiranja bombaža, barvanega z reaktivnimi barvili, po modificirani recepturi z uporabo inventivne tehnologije, imenovane „vroče pranje". Pri kontroli izpiralnega procesa se je pokazal prevladujoč vpliv temperature na lastnosti izpiranja barvila. Uporaba procesa „vročega pranja" po reaktivnem barvanju pomeni prihranek vode in časa ter izboljšanje barvnih obstojnosti.

Ključne besede: barvanje, reaktivno barvilo, bombaž, „vroče pranje", ekologija

1 Uvod

Tekstilna industrija je eden največjih onesnaževalcev okolja, saj v svojih procesih plemenitenja tekstilij, barvanja in tiskanja, ustvari velikanske količine odpadne vode, ki vsebujejo biološko nerazgradljiva barvila, težke kovine, maščobe in olja, sulfidne komponente, anorganske soli in vlakna.

1 Introduction

The textile industry is one of the greatest producers of pollutants, because the processes of textile finishing, namely dyeing and printing, produce great quantities of wastewater that contains biologically non-degradable dyes, heavy metals, fats and mineral oils, sulphuric components, inorganic salts and fibres.

The greatest challenge of the textile industry is to modify production to use safe, environmentally compatible and cost-effective products, reducing water consumption and treatment costs while at the same time keeping competitive prices.

To dye cellulosic fibres, five main classes of dyes are used: direct, sulphur, azoic, reactive and vat dyes [1]. Since their development, reactive dyes have been an increasingly popular dye class for dyeing of cellulosic fibres, mainly due to the bright shades combined with very good colour fastness properties on such fibres, the stability of the dye-fibre bond and the simplicity of the application procedures [2]. Reactive dyes are soluble anionic dyes that contain one or more reactive groups capable of forming a covalent bond with the hydroxyl groups in the fibre [3]. Although reactive dyes are widely used for exhaustion dyeing of cotton and other cellulose fibres, it is well known that, during their exhaustive application to cellulose fibres, commercial ranges of reactive dyes undergo hydrolysis, resulting in dye wastage and environmental problems [4, 5]. Due to the fact that the reactive dye can not only react with the fibre nucleophile (cellulosate anion), but also with the nucleophiles (commonly hydroxyl ions) present in the dye-bath [5], the efficiency of the dye-fibre reaction (fixation) is substantially reduced. A fixation degree of 60% to 80% is, therefore, common in reactive dyeing processes [6]. For the dyeing process to achieve characteristically high levels of fastness against wet treatments, it is necessary, in most cases, to employ a series of rinsing and 'soaping' stages, collectively known as wash-off, in order to remove either unreacted, unfixed dye or at least a sufficient proportion of the unfixed dye and the hydrolysed dye [5, 7, 8]. The wash-off process is time consuming and requires large amounts of water. In many cases, a much shorter washing

Največji izziv je za tekstilno industrijo modificirati proizvodnjo z uporabo varnih, ekološko kompatibilnih in cenovno ugodnih proizvodov, zmanjšati porabo vode in stroške obdelave, pri tem pa ohraniti konkurenčnost cen.

Za barvanje celuloznih vlaken se lahko uporabijo barvila, ki se ločujejo v pet skupin: direktna, žveplova, azo, reaktivna in redukcijska barvila [1]. Trend reaktivnih barvil za barvanje celuloznih vlaken narašča zlasti zaradi briljantnosti tonov v kombinaciji z dobrimi barvnimi obstojnostmi, stabilnosti vezi barvilo-vlakno in zato, ker je aplikativni proces preprost [2]. Reaktivna barvila so vodotopna anionska barvila, ki vsebujejo eno ali več reaktivnih skupin z zmožnostjo tvorbe kovalentne vezi s hidroksilnimi skupinami vlakna (zaestrenje, zaetrenje) [3]. Največ se uporabljajo za barvanje bombaža in drugih celuloznih vlaken po postopku izčrpavanja. Znano je, da so komercialna reaktivna barvila med barvanjem na celulozna vlakna izpostavljena hidrolizi, kar se odraža v izgubi barvila in posledično ekoloških problemih [4, 5]. Ker reaktivno barvilo lahko reagira z nukleofilom vlakna (celulozatni ion), kot tudi z nukleofili (navadno hidroksilni ioni), prisotnimi v izpiralni kopeli [5], je učinkovitost reakcije barvilo-vlakno (fiksiranje) močno zmanjšana. Zato je pri reaktivnem barvanju povprečna stopnja fiksiranja od 60- do 80-odstotna [6]. Za doseganje dobre barvne obstojnosti na mokro drgnjenje je treba v večini primerov pri pranju uporabiti serijo izpiralnih in milnih procesov, da odstranimo ves ali vsaj zadosten delež nefiksiranega in hidroliziranega barvila [5, 7, 8]. Tekstilije se ponavadi izpirajo tako dolgo, dokler ni odstranjeno vse nefiksirano barvilo. Zato je pranje zamudno in zahteva velike količine vode. V veliko primerih bi zadostovali veliko krajši pralni procesi, zato je pomembno, da je izpiranje čim učinkovitejše ob minimalni porabi vode, kemikalij in detergentov [8]. Temperatura, trajanje in lastnosti procesa pranja so odvisni od različnih dejavnikov, kot so globina barvnega tona, vrsta uporabljenega barvila, vrsta in sestava substrata [8]. Čeprav se proces pranja razlikuje glede na priporočila izdelovalcev barvil, se ponavadi izvaja na konvencionalen način, kar pomeni, da se začne z izpiranjem pri nizki temperaturi, čemur sledi pranje v kopeli pri visoki temperaturi (80–98 °C), in ponavadi zajema eno ali več obdelav z vročo raztopino pralnega sredstva (in/ali aditivov) ali vročo vodo. Alternativno se lahko nekatere vrste reaktivnih barvil pozneje obdelajo z izbranimi kationskimi fiksirnimi sredstvi, če je bila barvana tkanina neučinkovito oprana [9, 5]. Številne študije so pokazale, da alkalne raztopine (npr. natrijevega karbonata, natrijevega hidrogenkarbonata in kalijevega hidroksida) pomenijo okolju prijaznejšo alternativo za vodne raztopine tenzidov pri pranju celuloznih vlaken, barvanih z monokloro- in diklorotriazinskimi reaktivnimi barvili [2, 4, 8, 9]. Knudsen in Wenzel [10] sta v raziskavi proučila pranje po reaktivnem barvanju bombažne tkanine s 25 različnimi reaktivnimi barvili, med katerimi so bila uporabljena azo, antrakinonska, ftalocianinska in formazinska barvila, kakor tudi mono in bireaktivna barvila, od tega 15 z vinilsulfonsko *process would be sufficient. Therefore, it is important that the wash-off process is as effective as possible, using a minimum of water, chemicals and detergents [8]. The temperature, duration and the nature of the wash-off process depend on several factors, such as the depth of the shade applied, the type of dye used, as well as the type and construction of the substrate [8]. Although the wash-off process varies according to each dye producer's recommendations, it is usually performed in a conventional way, beginning with rinsing at low temperature, followed by one or more treatments with hot washing agent solutions (and/or other additives) or hot water (80–98°C). Alternatively, some types of reactive dyes can be further treated with selected cationic fixing agents when the dye has been inefficiently washed-off [9, 5]. Several studies have shown that alkali solutions (e.g. sodium carbonate, sodium bicarbonate and potassium hydroxide) are an environmentally friendly alternative to the aqueous solutions of surfactants in the washing-off of mono- and dichlorotriazinyl reactive dyes on cellulosic fibres [2, 4, 8, 9]. Knudsen and Wenzel [10] studied the washing-off process in the reactive dyeing of cotton with 25 different reactive dyes; among these were azo, anthrachinon, phtalocyanin and formazan dyestuffs, including both monoreactive and bireactive dyes, of which 15 had a vinylsulphone as the reactive group. This research showed that during the wash-off process, it is possible to omit detergent and complex agents with no adverse effect on product quality.*

The purpose of this study was to identify and evaluate potential improvements in the reactive dyeing process, aimed at focusing on the recipe modification and alteration of the wash-off process. The quantity and quality of the textile auxiliaries added in the dyeing recipes were studied and then modified by replacing some chemicals with alternative environmentally-friendly chemical products. For dyeing of cotton with a modified recipe improvement in the conventional wash-off process, aimed at water saving and improvement of fastness properties, was studied, using an alternative wash-off process called 'hot-washing' [11], beginning with rinsing in hot washing baths with a final rinse at low temperatures.

reaktivno skupino. Raziskave so pokazale, da je pri pranju mogoče izpustiti detergente in kompleksirna sredstva, pri čemer ni sprememb v kakovosti izdelka.

Namen predstavljene študije je bil določiti potencialne izboljšave pri reaktivnem barvanju s poudarkom na modifikaciji recepture in spremembi procesa pranja. Proučeni sta bili kakovost in količina tekstilnih pomožnih sredstev, dodanih pri barvanju, in testirana modificirana receptura, v kateri so bile določene kemikalije zamenjane z okolju prijaznejšimi izdelki. Za vzorce, barvane po modificirani recepturi, je bilo proučeno morebitno izboljšanje konvencionalnega procesa pranja zaradi varčevanja z vodo in izboljšanja barvnih obstojnosti, z uporabo alternativnega procesa pranja, imenovanega „vroče pranje" [11], pri čemer se pere v štirih vročih kopelih (pri 95 °C), čemur sledi hladno izpiranje.

2 Eksperimentalni del

2.1 Materiali

Uporabljena je bila očiščena, beljena in mercerizirana bombažna tkanina (245 g/m^2) domačega izdelovalca. Vsi materiali, kemikalije in barvila, opisani v tabeli 1, so bili dobavljeni v okviru tekstilne tovarne.

2.2 Barvanje in modificiranje recepture za barvanje

Barvanje je potekalo pri 40 °C z impregnacijo v kopeli (Labomat, Mathis) po osnovni recepturi 1 in 2 ter modificirani recepturi 1 in 2 (opisani v tabeli 1). Fiksiranje se je izvajalo z odlaganjem pri sobni temperaturi (12–24 ur). Temu je sledilo pranje (Ahiba Texomat, kopelno razmerje 200 : 1, mehka voda), kot je opisano v tabeli 2, izvedeno konvencionalno z začetnim hladnim izpiranjem in večkratnim pranjem z vročo vodo ter dodatkom pralnega sredstva (0,5 g/L Tanaterge LFN (Sybron/Tanatex, USA): anionski tenzid z dobrimi lastnostmi topljivosti in močno dispergirno zmogljivostjo).

Impregnacijska kopel po osnovni recepturi je vsebovala sekvestirno sredstvo (Securon 540), reaktivno barvilo (osnovni recepturi 1 ali 2), sol in alkalije, čemur smo dodali tudi protipenilno (Alviron VKS-B) in omakalno sredstvo (TC Schnellnetzer DF). Pri barvanju z modificirano recepturo (tabela 1) z enakimi reaktivnimi barvili (po modificirani recepturi 1 ali 2) smo zmanjšali količino sekvestirnega sredstva (Securon 540) iz 4 g/L na 2 g/L. Omakalno sredstvo (Cibaflow PAD) smo uporabili namesto protipenilnega sredstva (Alviron VKS-B) ter omakalnega sredstva (TC schnellnetzer DF). Razen tega smo dodali 100 g/L sečnine, da smo dosegli boljšo topljivost barvila.

2.3 Konvencionalen in modificiran proces pranja

Konvencionalen in modificiran proces pranja, imenovan „vroče pranje" (opisano v tabeli 3) smo testirali po barvanju bombažne

Table 1: Original and modified recipes for dyeing of cotton

Textile auxiliary	Function and chemical composition	Producer	Original recipe (g/L)		Modified recipe (g/L)	
			1	2	1	2
Alviron VKS-B	Antifoaming agent (consists of carbon and fatty alcohol etoxylates)	Textile color, Germany	2		–	
TC schnellnetzer DF	Maceration agent (mixture of fatty alcohol etoxylates)	Textile color, Germany	0.5		–	
Cibaflow PAD	Maceration agent (consists of polycarboxylic acids)	Ciba Speciality Chemicals, Switzerland	–		2	
Securon 540	Sequestering agent	Cognis, Germany	4		2	
Urea		/	–		100	
NaOH 38° Bé		/	27*			
Na_2SO_4		/	13.2			
Dyestuff						
Bezactiv Red V5B	Vinylsulphone reactive group	Bezema, Switzerland	55	–	55	–
Benactiv Orange N3R	Vinylsulphone reactive group	Bezema, Switzerland	35	–	35	–
Remazol Blue BB 133%	Vinylsulphone reactive group	Bezema, Switzerland	3.3	–	3.3	–
Remazol deep Black N 155%	Vinylsulphone reactive group	Bezema, Switzerland	–	70	–	70

** units in mL/L*

2 Experimental part

2.1 Materials

Scoured, bleached and mercerized cotton fabric (245 g/m²) from a local producer was used for dyeing. All materials, reagents and dyes, which are described in Table 1, were supplied from within the industrial textile factory.

2.2 Dyeing process and recipe modification

The dyeing process was performed at 40 °C in an impregnation bath (Labomat, Mathis). Fixation was performed with a cold-dwell process

Table 2: Wash-off process

Washing bath	T (°C)	1. cycle	2. and 3. cycle
1	22 °C	cold rinsing	cold rinsing
2	90 °C	washing, hot water	washing with washing agent
3	90 °C	washing with washing agent	washing with washing agent
4	80 °C	washing with washing agent	washing with washing agent
5	22 °C	cold rinsing	cold rinsing

at room temperature (12–24 hours), and was followed by a wash-off process (Ahiba Texomat, liquor ratio 200:1, soft water), which is described in Table 2. It was performed with cold rinsing and repeated washing with hot water and an additional washing agent (0,5 g/L Tanaterge LFN (Sybron/Tanatex, USA: an anionic surfactant with good solubility and a strong dispersion capacity)).

The impregnation bath using the original recipes contains a sequestering agent (Securon 540), reactive dye (original recipe 1 and 2), salt and alkali, as well as an antifoaming agent (Alviron VKS-B) and a maceration agent (TC Schnellnetzer DF). Dyeing with the modified recipes was performed using the same reactive dyes (modified recipe 1 and 2), but with a reduction of the amount of the sequestration agent (Securon 540) from 4 g/L to 2 g/L. A maceration agent (Cibaflow PAD) was used instead of an antifoaming agent (Alviron VKS) and a quick maceration agent (TC schnellnetzer). In addition, 100 g/L of urea was added to attain better dye solubility.

2.3 Conventional and modified wash-off process

The conventional and modified ('hot-washing') wash-off process, described in Table 3, were performed after dyeing with modified recipe 2, as described in Table 1. In both cases, the wash-off was performed with soft water and without the addition of a washing agent. The conventional process, performed in 3 cycles, was carried out with an initial cold rinsing, followed by hot

tkanine z modificirano recepturo 2, opisano v tabeli 1. V obeh primerih smo prali z mehko vodo, brez pralnega sredstva. Konvencionalen proces, ki je potekal v treh ciklih, se je izvajal z začetnim hladnim izpiranjem, čemur je sledilo pranje v kopeli pri visoki temperaturi (95 °C) in končno hladno izpiranje. „Vroče pranje", ki je potekalo v dveh ciklih s prelivanjem kopeli 1 čez kopel 5, se je izvajalo v štirih vročih kopelih (95 °C) s končnim hladnim izpiranjem.

Table 3: Conventional wash-off process and 'hot-washing' technique

Bath	Conventional washing			'Hot washing', consequent counter current	
	1. cycle	2. cycle	3. cycle	1. cycle	2. cycle
1	25 °C	60 °C	60 °C	95 °C, spilling over bath 5	95 °C, spilling over bath 5
2	95 °C	95 °C	95 °C	95 °C	95 °C
3	95 °C	95 °C	95 °C	95 °C	95 °C
4	95 °C	95 °C	95 °C	95 °C	95 °C
5	25 °C	25 °C	25 °C	50 °C/25 °C	50 °C/25 °C

2.4 Analitične metode

Obremenitev odpadnih voda iz vsake kopeli za vsak cikel izpiranja/pranja je bila določena s kemijsko potrebo po kisiku (KPK) in biokemijsko potrebo po kisiku (BPK_5). KPK vzorcev je bil določen z metodo oksidacije s K-dikromatom glede na standard SIST ISO 6060 in BPK_5 glede na SIST ISO 5815 [12, 13]. Obarvanost odpadnih voda, izražena kot spektralni absorpcijski koeficient SAK (pri valovnih dolžinah λ = 436 nm, 525 nm in 620 nm), je bila določena s spektrofotometrom (Perkin-Elmer Cary 1E) po standardu SIST EN ISO 7887/3 [14]. Kakovost barvane tkanine je bila ovrednotena z barvnimi obstojnostmi na drgnjenje (mokro in suho), pranje pri 60 °C in znoj po standardih ISO 105-X12, ISO 105-C03 in ISO 105-E04 [15, 16, 17].

3 Rezultati in razprava

3.1 Modifikacija receptur za barvanje z reaktivnimi barvili

Osnovna receptura za barvanje, prikazana v tabeli 1, je bila modificirana (tabela 1), da bi uporabili ekološko prijaznejše alternativne kemikalije, pri čemer smo primerjali ekološke parametre odpadnih voda iz pralnih kopeli, potek izpiralnega procesa barvila in morebitne spremembe v barvnih obstojnostih bombažnih tekstilij po barvanju. Rezultati KPK vrednosti odpadnih voda iz vsake pralne kopeli (B1 ... B5) za vsak cikel izpiranja (C1 … C3, slika 1 in 2) kažejo, da so odpadne vode po pranju bombažne tkanine, barvane po modificirani recepturi, manj obremenjene, saj imajo nižje KPK vrednosti. Biorazgradljivost odpadnih voda, ki se *washing baths (95 °C) and final cold rinsing. 'Hot-washing' was performed in 2 cycles using four hot baths (at 95 °C) and a final cold rinsing, with bath 1 spilling over into bath 5.*

2.4 Analytical methods

The burden of the wastewater samples, taken from each washing bath for each washing cycle, was determined using chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5). The COD of the samples was measured using the potassium dichromate method according to SIST ISO 6060, and BOD_5 was measured according to SIST ISO 5815 [12, 13]. Colouration in terms of the spectral absorption coefficient, SAC (at the wavelengths λ = 436 nm, 525 nm and 620 nm), of the wastewater from the washing baths was determined using a spectrophotometer (Perkin-Elmer Cary 1E) according to SIST EN ISO 7887/3 [14]. The fabric quality was estimated using colour fastnesses properties, such as fastness to rubbing, to washing and to perspiration, in accordance with ISO 105-X12, ISO 105-C03 and ISO 105-E04, respectively [15, 16, 17].

3 Results and discussion

3.1 Modification of recipes for dyeing with reactive dyes

The actual recipes for dyeing were modified (Table 1) with the aim of finding an ecologically friendly alternative. Ecological parameters of the wastewaters from washing baths, the course of the rinsing process and the eventual changes in fastness properties of dyed textiles were compared. The COD values for wastewaters from each washing bath (B1 … B5) for each washing cycle (C1 … C3, Figure 1 and 2) show that the wastewater load after washing the cotton dyed with the modified recipe was reduced. Biodegradability, expressed as BOD_5/COD, showed that when using modified recipes, wastewaters from the washing process have a higher capacity for degradability, with an average increase of biodegradability of 15%.

Looking at Figure 3 and Figure 4, it is evident that the maximum colouration, expressed as SAC (at wavelength λ = 436 nm and 525 nm), is observed in the second bath in cycles 1 and 2.

izraža kot razmerje BPK_5/KPK, je pokazala da so odpadne vode iz procesa izpiranja po uporabi modificiranih receptur biološko bolj razgradljive, saj se njihova biorazgradljivost v povprečju poveča za 15 %.

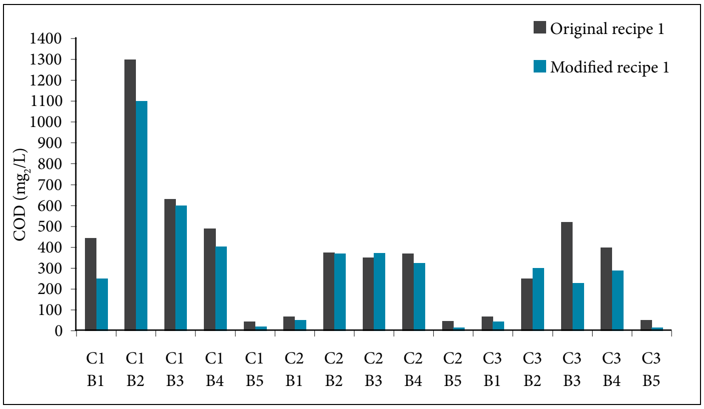

Figure 1: Biodegradability of the wastewaters from each washing bath (B1 … B5) for each cycle (C1 … C3) during washing-off of cotton dyed with the original recipe and modified recipe 1.

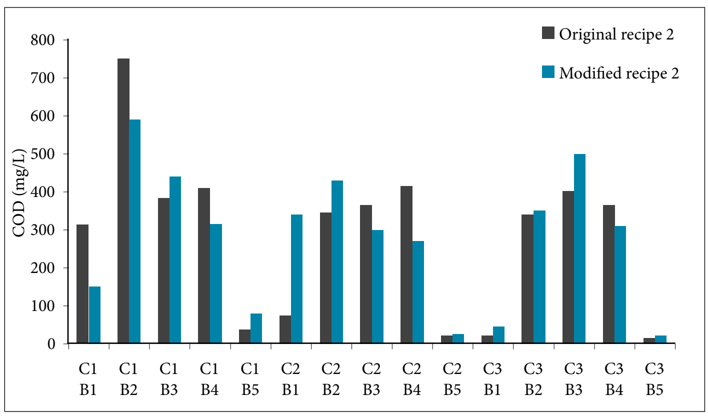

Figure 2: Biodegradability of the wastewaters from each washing bath (B1 … B5) for each cycle (C1 … C3) during washing-off of cotton dyed with the original recipe and modified recipe 2.

Iz slik 3 in 4 je razvidno, da je maksimalna obarvanost odpadnih voda, izražena kot SAK (pri valovnih dolžinah λ = 436 nm in 525 nm), v drugi kopeli v ciklu 1 in 2, kajti izpiranje tukaj poteka pri 90 °C (glej tabelo 2) in se pri tem odstrani največ barvila. Pri primerjavi vrednosti SAK v prvem ciklu pranja smo opazili manjša odstopanja med modificirano in osnovno recepturo (prva in druga kopel), namreč pri modificirani recepturi je v prvi kopeli izpiranje učinkovitejše, zato pa se manj barvila odstrani v drugi kopeli. V drugem in tretjem ciklu nismo opazili bistvenih razlik v vrednostih SAK, kar dokazuje, da sprememba recepture ne vpliva na celoten potek izpiralnega procesa barvila.

In the second bath, rinsing is performed at 90 °C, and therefore, most of the dye is removed. When comparing the values of SAC in the first wash-off cycle (between the first and second baths) between the modified and the original recipes, slight deviations are noted; namely, when using the modified recipe, the rinsing in the first bath is more effective, and therefore less dye is washed off in the second bath. In the second and third washing cycle, no significant differences are noted in the SAC values, indicating that the recipe modification does not influence the wash-off course of the dyestuff.

Colour fastness properties were determined to establish the quality of the dyed fabrics. The efficiency of rinsing, determined with colour fastness to rubbing, is shown in Table 4. The results show only slight differences between the original and modified dyeing recipes, while the results of colour fastnesses to washing at 60 °C and to perspiration (Table 5) show no differentiation in the fastness level.

3.2. Modification of the wash-off process after dyeing with reactive dyes

Modification of the wash-off process was tested after dyeing cotton with reactive dyes using modified recipe 2 (Table 1). For the conventional wash-off process, the sampling of wastewaters was performed during cycle 1 (after 2 min, 6.5 min and at the end) and at the end of cycle 2. When using the modified process ('hot-washing'), samples were taken only during cycle 1 (after 2 min, 6.5 min and at the end). The effectiveness of rinsing the dyed textiles, especially the removal of textile auxiliaries and dye, was ex-

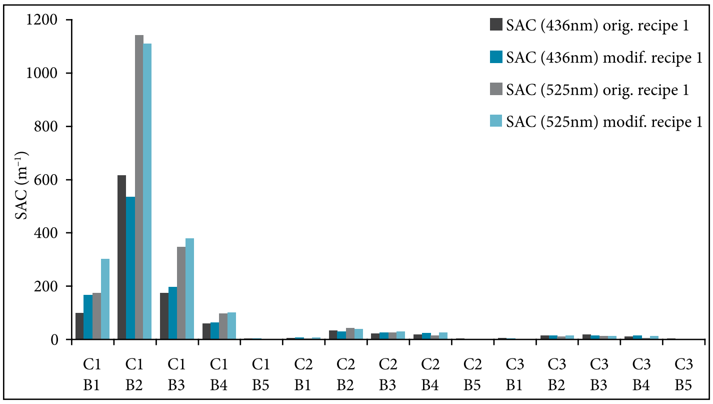

Figure 3: Colouration of the wastewaters in terms of SAC (at λ = 436 nm and 525 nm) after each washing bath (B1 … B5) for each cycle (C1 … C3) in washing-off of cotton dyed with the original recipe and modified recipe 1.

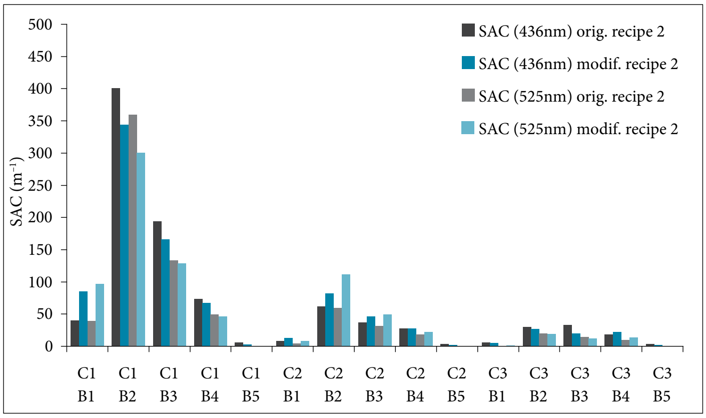

Figure 4: Colouration of the wastewaters in terms of SAC (at λ = 436 nm and 525 nm) after each washing bath (B1 … B5) for each cycle (C1 … C3) in washing-off of cotton dyed with the original recipe and modified recipe 2.

Table 4: Colour fastness to dry and wet rubbing

	Dry rubbing				Wet rubbing			
	warp		weft		warp		weft	
	sample	cotton	sample	cotton	sample	cotton	sample	cotton
Original recipe 1	4–5	4–5	5	4–5	5	2	4–5	2
Modified recipe 1	4–5	4–5	5	5	5	3–4	5	3–4
Original recipe 2	5	4	4–5	4	5	1–2	5	1–2
Modified recipe 2	4–5	4–5	5	5	5	2	5	2

Table 5: Colour fastness to washing 60 °C and to perspiration

	Colour fastness to washing 60 °C			Colour fastness to perspiration		
	sample	cotton	wool	sample	cotton	wool
Original recipe 1	5	3–4	4–5	5	4	4
Modified recipe 1	5	3–4	4–5	5	3–4	3–4
Original recipe 2	5	4–5	4–5	5	4–5	4–5
Modified recipe 2	5	4–5	4–5	5	4–5	4–5

pressed in terms of COD (Figures 5 and 6). The influence of temperature on the removal properties of the hydrolyzed and unfixed dye and textile auxiliaries (Figures 5 and 6) shows that the equilibrium of the wash-off process is dependent upon the time of rinsing and is achieved sooner at higher temperatures, which indicates that the 'hot-washing' technique is an appropriate wash-off process after dyeing with reactive dyes.

For colour fastness to wet rubbing (Table 6), samples were taken after each rinsing cycle, namely after conventional washing (taken after the first, second and third cycles) and after the 'hot-washing' procedure (taken after both washing cycles), and the results indicate somewhat better fastnesses properties with the 'hot-washing' procedure after only the first rinsing cycle.

The measurements of colouration in terms of SAC (at wavelength λ = 620 nm) show that, in conventional wash-off (Figure 7), the first washing bath is nearly colourless, whereas the second bath (hot) removes a vast quantity of removable dyestuff. Due to a poor washing effect in the first bath, the downstream washing baths (3 to 4) have to remove more unfixed dyestuff. In order to guarantee adequate fastness properties, this washing procedure had to be repeated twice. The 'hot-washing' technique (Figure 8) provides much better washing effects, even after only the first washing bath, which shortens the washing process to two cycles with the same colour fastness (to rubbing) (Table 6). With the 'hot-washing' technique, better rinsing characteristics are achieved, and two washing cycles are sufficient to achieve the same washing characteristics. Therefore, fresh water consumption (counter current system) as well as rinsing time is reduced.

Testi barvne obstojnosti so bili izvedeni za določitev kakovosti obarvanih tekstilij. V tabeli 4 je prikazana učinkovitost pranja z barvnimi obstojnostmi na drgnjenje. Rezultati so pokazali le majhne razlike med tkaninami, obarvanimi z osnovno in modificirano recepturo, medtem ko rezultati obstojnosti na pranje pri 60 °C in obstojnosti na znoj (tabela 5) niso pokazali nikakršnih razlik.

3.2 Modifikacija procesa pranja po barvanju z reaktivnimi barvili

Modifikacijo pranja smo testirali po barvanju bombažne tkanine z reaktivnimi barvili po modificirani recepturi 2 (tabela 1). Pri konvencionalnem pranju je bilo vzorčenje odpadnih voda izvedeno med ciklom 1 (po 3 minutah, 6,5 minute in ob koncu pranja) in na koncu cikla 2. Pri modificiranem procesu, imenovanem „vroče pranje", so bili vzorci odvzeti med ciklom 1 (po 3 minutah, 6,5 minute in ob koncu pranja). Učinkovitost izpiranja barvanih tekstilij, zlasti odstranitev tekstilnih pomožnih sredstev in barvila, je bila izražena kot KPK (sliki 5 in 6). Vpliv temperature na lastnosti odstranjevanja hidroliziranega in nefiksiranega barvila ter ostankov tekstilnih pomožnih sredstev (sliki 5 in 6) kaže, da je ravnotežje

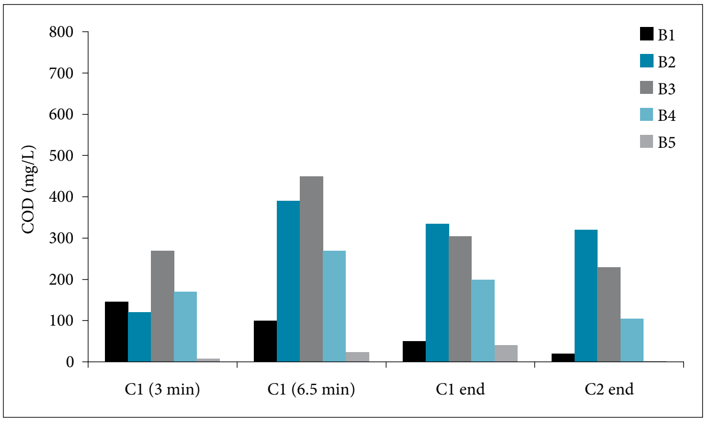

Figure 5: COD values for the wastewater samples from conventional washing for each washing bath (B1 … B5) during cycle 1 (C1) and at the end of cycle 2 (C2).

4 Conclusions

Improvements in the conventional wash-off process were first focused on modification of the original dyeing recipes. Research has shown that the replacement of some chemicals with environmentally-friendly products results in reduced wastewater loads, improved biodegradability of the wastewater and better colour fastness properties. However, recipe modification is dependent upon many factors, such as the process of dyeing and the recommendations of dye producers. Therefore, it is necessary to deal with each case separately.

Another possibility of improving the conventional wash-off process of cotton dyed with a reactive dye (vinylsulphone dye) is the technique of 'hot-washing'. The COD values and colouration of wastewaters, which depend on the removal properties of the hydrolyzed, unfixed dyestuff and textile auxiliaries, showed a significant dependence on the temperature. The washing equilibrium is obviously dependent on the washing time and is achieved more quickly at higher temperatures. The colour fastnesses to wet rubbing was already better in the case of 'hot-washing' after the first washing cycle. The 'hot-washing' technique resulted in a shortened wash-off process with the same fastness level as that achieved with conventional washing. With the consequent counter current (bath 1 spilling over bath 5), more than one third of the water and washing time are saved, considering that less freshwater is required at the beginning of the wash-off process and two cycles are sufficient to guarantee the same washing effects.

Acknowledgements

Financial support for this study provided by EU project No. EVK1-2000-00580: Minimization of Water Consumption in European Textile Dyeing and Printing Industry Using Innovative Washing and Water Recycling Technologies is gratefully acknowledged.

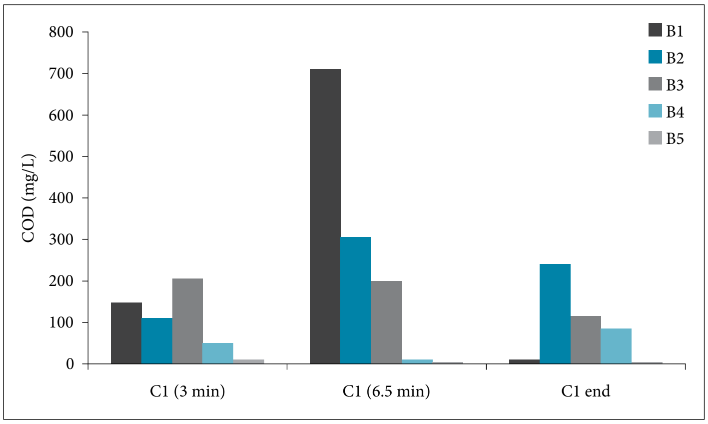

Figure 6: COD values for the wastewater samples from 'hot-washing' for each washing bath (B1 … B5) during cycle 1 (C1).

izpiranja odvisno od časa izpiranja, in ga prej dosežemo z višanjem temperature, kar nakazuje, da je tehnika „vročega pranja" ustrezen način pranja po barvanju z reaktivnimi barvili.

Rezultati barvnih obstojnosti na mokro drgnjenje (tabela 6), odvzetih po vsakem ciklu izpiranja na konvencionalen način (1., 2. in 3. cikel) in z načinom „vročega pranja" (1. in 2. cikel), so pokazali nekoliko boljšo barvno obstojnost po „vročem pranju" že po prvem ciklu izpiranja.

Table 6: Colour fastness to wet rubbing for samples washed-off with conventional and 'hot washing' technique

		warp	weft
		Staining on cotton	
Conventional washing	Cycle 1	3	3
	Cycle 2	2–3	3
	Cycle 3	2	2–3
'Hot washing'	Cycle 1	2–3	2–3
	Cycle 2	2–3	2–3

Meritve obarvanosti v obliki SAK (pri valovni dolžini λ = 620 nm) so pokazale, da je pri konvencionalnem načinu pranja (slika 7) prva kopel skoraj brezbarvna, medtem ko se z drugo (vroča) odstrani večji delež odstranljivega barvila. Zaradi slabe učinkovitosti izpiranja v prvi kopeli morajo naslednje kopeli (od 2. do 5.) odstraniti preostanek nefiksiranega barvila. Da so zagotovljene zahtevane barvne obstojnosti, se mora ta izpiralni proces ponoviti še 2-krat.

Tehnika „vročega pranja" (slika 8) prinaša veliko boljše učinke izpiranja že po prvi kopeli, kar omogoči skrajšanje izpiralnega

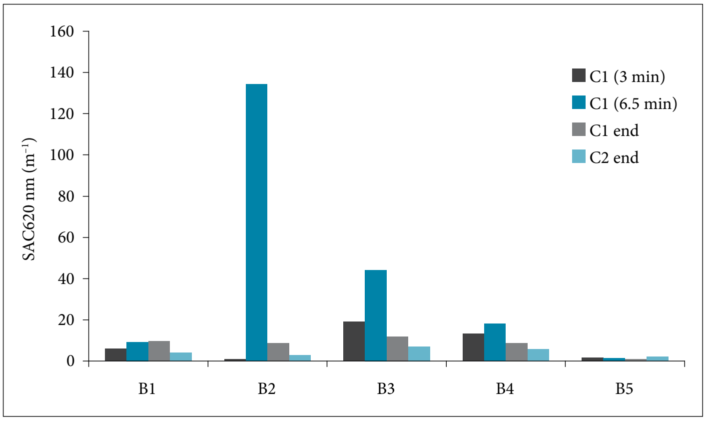

Figure 7: Colouration of the wastewaters in terms of SAC (at λ = 620 nm) from each washing bath (B1 … B5) for cycles 1 and 2 (conventional washing).

procesa (na dva cikla), pri enakih rezultatih barvne obstojnosti na drgnjenje (tabela 6). S tehniko „vročega pranja“ se tako doseže boljše izpiranje, zmanjša se poraba sveže vode in skrajša čas izpiranja, saj za dosego enakih učinkov pranja zadoščata že dva cikla.

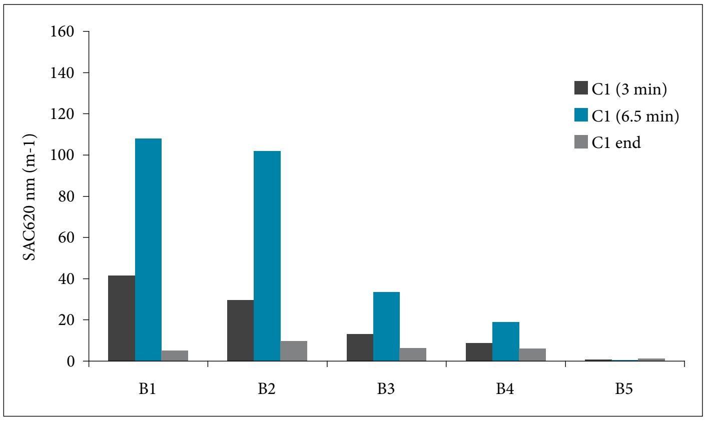

Figure 8: Colouration of the wastewaters in terms of SAC (at λ = 620 nm) from each washing bath (B1 … B5) for cycle 1 ('hot washing').

4 Sklepi

Izboljšanje konvencionalnega načina barvanja bombažne tkanine z reaktivnimi barvili je bilo sprva osredotočeno na modificiranje receptur za barvanje. Rezultati so pokazali, da zamenjava nekaterih kemikalij z ekološko prijaznejšimi izdelki pomeni manjšo obremenitev in izboljšano biorazgradljivost odpadnih voda ter primerljivo barvno obstojnost. Modificiranje receptur je seveda odvisno od številnih dejavnikov, kot npr. od samega barvanja in priporočil izdelovalca barvil, zato je treba obravnavati vsak primer posebej.

Kot alternativna možnost izboljšanja konvencionalnega načina pranja bombažne tkanine po barvanju z reaktivnim barvilom (vinilsulfonskim barvilom) se je pokazala tehnika „vročega pranja“. Iz KPK vrednosti in obarvanosti odpadnih voda je razvidno, da temperatura pomembno vpliva na odstranjevalne lastnosti hidroliziranega, nefiksiranega barvila in tekstilnih pomožnih sredstev. Ravnotežje pranja je očitno odvisno od časa izpiranja in se hitreje doseže pri višjih temperaturah. Rezultati barvnih obstojnosti na mokro drgnjenje so pri uporabi „vročega pranja“ izboljšani že po prvem ciklu izpiranja. Z uporabo tehnike „vročega pranja“ skrajšamo izpiralne procese z dosego enakih barvnih obstojnosti kot pri konvencionalnem načinu pranja. Prav tako se ob sočasni uporabi protitočnega sistema (prelivanje kopeli 1 čez kopel 5) lahko prihrani tretjina vode in skrajša izpiralni čas, če pri tem upoštevamo, da se zmanjša poraba sveže vode že na začetku procesa pranja in da je dovolj uporabiti dva cikla za zagotovitev enakega učinka izpiranja.

Zahvala

Iskreno se zahvaljujemo za finančno podporo k raziskavi v okviru EU projektu št. EVK1-2000-00580: Minimization of Water Consumption in European Textile Dyeing and Printing Industry Using Innovative Washing and Water Recycling Technologies.

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