Scouring of Domestic Wool in Croatia and its Impacts on the Environment

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Wool and wastewaters from scouring can be a mixed blessing – a useful technological raw material or an environmental problem. If wool is scoured with no control, as the case most often is in Croatia, the wastewater released could endanger the environmental stability of the existing water systems. Since the interest has been growing recently for processing domestic wool, which also presents a considerable hazard of polluting water because of unskilled scouring and uncontrolled wastewater release into the natural water flows, we have organized investigations aimed at determining potentially dangerous ecological loads on the Croatian water systems, caused by scouring domestic wool. The results obtained indicate that improper disposal of the wool and/or uncontrolled release of wastewater from scouring present a considerable environmental hazard. We have concluded that impacts on the environment of scouring domestic wool in Croatia are the same as impacts on the environment obtained by normal functioning of a town of 1700–2000 inhabitants.

Key words: *Ecological load, environmental protection, wool scouring, wastewater, wastewater treatment*

Introduction

According to the Croatian Central Bureau of Statistics, some 724 t of raw wool was obtained by shearing sheep in 2005.[1] The wool shared from domestic sheep is not used generally as an input raw material for the Croatian textile industry. Most often it is, not bothering to consider the limited capacity of the natural environment, disposed of by being simply thrown away at so-called "wild" dumps. Throwing the wool away and unskilled and often irresponsible scouring by some sheepherders, with uncontrolled release of scour effluents, frequently into nearby natural water flows, slowly but steadily corrupts the ecological equilibrium and is bound to present a serious problem in Croatia quite soon.[2]

Sheep fleece obtained by shearing, or skin wool obtained by removing the fibres from the skins of dead or slaughtered animals, contain, apart from wool fibres, numerous ingredients, which can be divided into biological (suint and greases produced by sebaceous glands, faeces), acquired (sand, soil, vegetable impurities) and applied (pesticides, insecticides, sighting dyes etc.). The amount of these ingredients depends upon the breed of the sheep, its age, wool curliness, conditions of breeding and herding, pastureland composition, quality, and conditions of the pasture and weather conditions (Table 1).[3–5]

Scouring raw wool, as one of the first processes in transforming the wool from sheep hair to a finished product, results in a highly polluted effluent (Table 2). The impact of this wastewater on the environment is, according to some authors, equal to the impact of a normal functioning town of some 20 to 30 thousands inhabitants.[6–10]

Table 1 – *Average fleece composition of some sheep breeds*
Tablica 1 – *Prosječni sastav runa nekih pasmina ovaca*

Sheep breed Pasmina	Wool fibre Vuneno vlakno *w*/%	Grease Masnoća *w*/%	Suint Znoj *w*/%	Impurities Nečistoće *w*/%	Water Voda *w*/%
Merino Merino	49	16	6	19	10
Cross-breed Križanci	61	11	8	8	12

Table 2 – *The mass concentration of pollutants in the unprocessed wastewater after wool scouring*
Tablica 2 – *Masena koncentracija polutanata u nepročišćenoj otpadnoj vodi od pranja vune*

COD (chemical oxygen demand) KPK (kemijska potrošnja kisika)	30 000 – 60 000 mg L^{-1}
BOD_5 (biochemical oxygen demand) BPK_5 (biokemijska potrošnja kisika)	2 000 – 40 000 mg L^{-1}
Nitrogen concentration (ammonium, nitrates, nitrites) Koncentracija dušika (amonij, nitrati, nitriti)	1 000 – 1 500 mg L^{-1}
Phosphate mass concentration Masena koncentracija fosfata	20 – 30 mg L^{-1}
Overall pesticide mass concentration Ukupna masena koncentracija pesticida	0.4 – 1.0 mg L^{-1}

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As opposed to the situation in Croatia, the ecological considerations and awareness, as well as legislation concerning processing and wastewaters in developed countries, stipulate water recycling in wool scouring and development of environmentally friendly procedures of wastewater purification, trying to separate all the useful products from the wastewater processes, such as lanoline (as a raw material for the pharmaceutical and cosmetic industry), sludge (for composting) and sand (raw material for building and construction industries).[9, 11]

However, since a systematic analysis of the Croatian sheep population and domestic wool is at the moment still being prepared,[12] and the interest for the processing of domestic wool has been growing, which presents an environmental hazard due to unskilled wool scouring and uncontrolled discharge of wastewaters into natural water flows,[2] these investigations have been designed to determine potential ecological loads on the existing Croatian water systems, caused by scouring domestic wool.

Experimental

There are only a few flocks of pure breeds in Croatia, while most of them are cross-bred and mixed breeds. Thus, we have selected, for the purpose of this investigation, the wool belonging to the most numerous domestic sheep breed (approx. 60 %[12]) in Croatia, the so-called pramenka has been selected (Fig. 1; Table 3).

F i g. 1 – *Pramenka breed*
S l i k a 1 – *Pramenka*

T a b l e 3 – *Objective measuring of wool quality*
T a b l i c a 3 – *Objektivno vrednovanje kvalitete vune*

Sample Uzorak	d/μm	M/%	dM/%	kM/%	KF/%	l/cm	l<5 cm %	$Y–Z$
N	1000	1000	1000	1000	1000	1000	1000	3
x_s	32.7	17.9	34.4	67.6	1.1	5.1	46.9	11.5
s	2.1	6.2	5.6	2.0	1.4	1.0	5.9	0.8

where: d – fibre diameter; M – medullation; dM – discontinuous medulla; kM – continuous medulla; KF – kemp fibres e.g. fibres that have medulla width more than 60 % of fibre diameter; l – average fibre length; $Y–Z$ – colour of wool; N – number of measurements; x_s – *average value*; s – standard deviation

gdje je: d – debljina vlakana; M – medulacija; dM – udjel vlakana s diskontinuiranom medulom; kM – udjel vlakana s kontinuiranom medulom; KF – osjasta vlakna tj, vlakna kod kojh je debljina medule veća od 60 % širine vlakna; l – prosječna duljina vlakana; $Y–Z$ – boja vune; N – broj mjerenja; x_s – srednja vrijednost; s – standardna devijacija

The raw (greasy) pramenka wool was conventionally scoured in a laboratory simulation of the industrial scouring conditions (Table 4).

The following equipment and procedures were used in analyzing the wastewater:

– COD reactor – Measuring chemical oxygen demand (COD) was done colorimetrically, using a UV-VIS spectrophotometer, model DR/4000U manufactured by HACH, USA. After heating the prepared sample in a digester (COD reactor) to the temperature of ϑ = 150 °C, for a period of t = 2 hours, and cooling it down to room temperature, the equivalent amount of oxygen necessary to oxidize the organic matter is determined colorimetrically at λ = 350 nm.

– Oximeter – model HACH 330i for determination of BOD_5 – sample in Winkler bottles for 5 days at ϑ = 20 °C in the dark

– DR/2500 HACH spectrophotometer – P and N mass concentrations (P–PO_4^{3-}, N–NO_3^-, N–NO_2^-, N–NH_4^+) spectrophotometrically

– pH meter – model 540 GLP, with the probe SenTix 41, 0–80 °C, by WTW, Germany

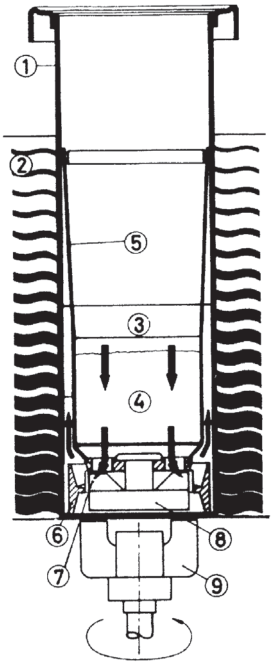
– conductometer – model LF-92, by WTW, Germany

– filtration membranes of cellulose acetate, with pore diameter of d = 0.45 μm, by SARTORIUS, Germany

– UV-VIS Absorbance in a quartz civet of 1 cm – model 8430, by HEWLETT PACKARD, USA

T a b l e 4 – *Wool scouring procedure*[13]
T a b l i c a 4 – *Postupak pranja vune*[13]

Apparatus Uređaj	Ahiba Turbomat (Fig. 2); the scouring bath circulates using a drive magnet through a stationary sample, which reduces the danger of felting Ahiba Turbomat (slika 2); Kupelj za pranje cirkulira pomoću pogonskog magneta kroz nepokretan uzorak čime se smanjuje mogućnost pustenja vune
Material Uzorak	raw (greasy) wool from the whole fleece sirovo (masno) runo
Procedure Postupak	batch (scouring/rinsing) diskontinuirani (pranje/ispiranje)
Sample mass m/g Masa uzoraka m/g	100.00
Number of parallel samples Broj paralelnih uzoraka	5
Scouring agent Sredstvo za pranje	Nonionik SVN, γ = 2 g l^{-1}
Bath ratio Omjer kupelji	1:10
Scouring bath pH ϑ/°C Kupelj za pranje t/min	9.5 60 60
Rinsing bath pH Ispiranje ϑ/°C	7.0 22



F i g. 2 – *Working principles of the cell in the AHIBA turbomat: 1 – vessel for the sample, 2 – warming bath, 3 – scouring bath, 4 – treatment area, 5 – basket for fibres, 6 – pump housing, 7 – pump, 8 – magnet*

S l i k a 2 – *Princip rada ćelije turbomata AHIBA: 1 – ćelija, 2 – kupelj za zagrijavanje, 3 – kupelj za pranje, 4 – radni dio, 5 – košarica, 6 – kućište crpke, 7 – crpka, 8 – magnet*

Results and discussion

Table 5 shows the content of particular components in the scoured wool, i.e. offers an analysis of the absolute dry raw-greasy Pramenka wool, while Fig. 3 shows the average values of the loss of wool mass in scouring. Processors and wool producers are much more interested in the data on the amount of clean wool after scouring, since the process of industrial scouring removes from the raw (greasy) wool not only the suint, greases and dirt (vegetable impurities, soil, sand, etc.), but also the short fibres, which means different levels of utilisation can be achieved (i.e. the amount of absolutely dry clean wool) when it is determined by extraction in an organic solvent or in scouring.

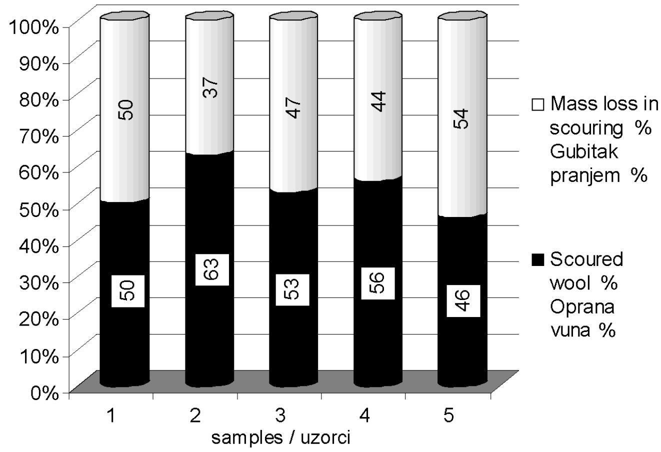
T a b l e 5 – *Pramenka wool composition*

T a b l i c a 5 – *Sastav pramenkinog runa*

Sample Uzorak	Absolutely dry clean wool fibre/% Apsolutno suho čisto vuneno vlakno/%	Absolutely dry extracted grease/% Apsolutno suhe ekstrahirane masnoće/%	Absolutely dry dirt/% Apsolutno suhe nečistoće/%
N	5	5	5
x_s	75.2	11.6	13.2
s	1.9	1.9	3.5

where: N – number of measurements; x_s – average value; s – standard deviation

gdje je: N – broj mjerenja; x_s – srednja vrijednost; s – standardna devijacija



F i g. 3 – *Loss of raw wool mass in scouring*

S l i k a 3 – *Gubitak mase sirove vune pranjem*

The parameters in Table 5, assuming the rest of the raw domestic wool is of similar composition, indicate that the starting mass of the raw wool in Croatia (approx. 724 t) yields 84 t of wool grease annually and around 96 t of solid wastes (vegetable matter, soil, sand).

Table 6 shows the results of determining basic parameters of wastewater from wool scouring. The wastewater sample was analyzed on an UV-VIS spectrophotometer as well, and Fig. 3 offers an UV-VIS spectrum of the water filtrated through the 0.45 μm membrane, as well as for the water diluted 10x, 20x and 500x, so as to point out the regularities present and define the areas that need to be observed in later experiments with wastewater treatment.

Absorbencies of A(254 nm) and A(436 nm)[14] are conventionally used to monitor organic loads in the water, especially in natural springs, where the water already contains higher or lower amounts of natural organic matter, humine and fulvine acids. In the case described here, due to high absorbency in the UV spectrum, it is quite inefficient to monitor the A(254 nm). However, the A(436 nm) is appropriate, especially due to the fact that this range of wavelengths offers a directly proportional monitoring of the content of dissolved organic matter. Water dilutions filtrated through a 0.45 μm membrane 10 and 20 × perfectly reflect the linear correlation of the amount of dissolved organic matter (Table 6; Fig. 3). This proves that the A(436 nm) can be used, even for the dissolved substances in wastewater from wool scouring, as a fact and simple indicator for particular processes of water purification efficiency (e. g. coagulation/flocculation, filtration). Obviously, it is necessary to perform additional analyses of a series of groups (COD, BOD_5, TOC) and individual parameters, apart from the above parameter, to obtain a comprehensive view of the efficiency of a water purification process.

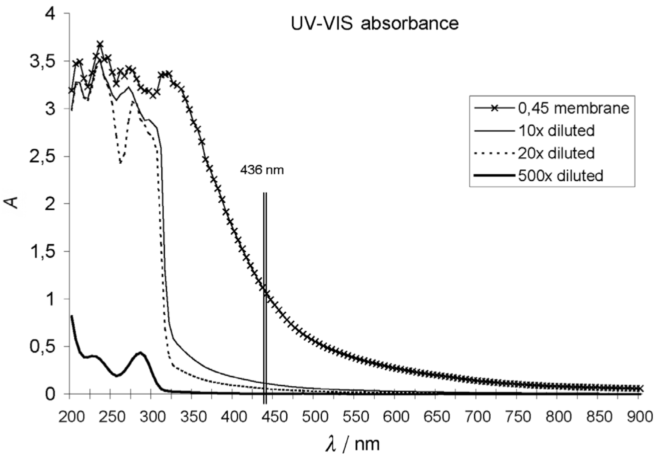
Most of the authors presume an average COD for the wastewater from wool scouring at the specific volume of v = 10 L kg^{-1} of wool, amounting to γ = 45 000 mg L^{-1} O_2.[7,8,10,15] Up to 75 % of the overall COD is attributed to the emulated wax, which can be removed almost entirely by sedimentation in the process of chemical coagulation and flocculation, followed by a biological treatment.[15] However, even

T a b l e 6 – *Basic parameters of wastewater from wool scouring*
T a b l i c a 6 – *Osnovni parametri otpadne vode od pranja vune*

Quantities Veličine	Values, bath ratio Vrijednosti, obujmni omjer kupelji $\Psi = 1:10$
Sedimentation in an Imhoff cone after t = 30 min Sedimentacija u Imhoffovoj posudi nakon t = 30 min	44 ml (49 ml after 2 days) 44 ml (49 ml nakon 2 dana)
pH	7.82
Electrical conductivity, $\kappa/\mu S\ cm^{-1}$ Električna provodnost, $\kappa/\mu S\ cm^{-1}$	3580–3640
COD (after filtration through a 0.45 μm filter), γ/mg L^{-1} KPK (nakon filtracije kroz 0,45 μm filtar), γ/mg L^{-1}	344–540
COD, γ/mg L^{-1} KPK, γ/mg L^{-1}	10 201–10 209
A(436 nm), path l = 1 cm A(436 nm), putanja l = 1 cm	1.10595
A(436 nm), path 1 cm, 10× diluted A(436 nm), putanja 1 cm, 10× razrjeđenje	0.11662
A(436 nm), path 1 cm, 20× diluted A(436 nm), putanja 1 cm, 20× razrjeđenje	0.06057
BOD, γ/mg L^{-1} BPK, γ/mg L^{-1}	576–584
P-PO_4, (after filtration through a 0.45 μm filter) γ/mg L^{-1} P-PO_4, (nakon filtracije kroz 0,45 μm filtar) γ/mg L^{-1}	2.04
N total inorganic, (after filtration through a 0.45 μm filter) γ/mg L^{-1} N ukupni anorganski, (nakon filtracije kroz 0,45 μm filtar) γ/mg L^{-1}	20.27
Suspended solids, γ/mg L^{-1} Suspendirane čestice, γ/mg L^{-1}	2034

after properly performed processes, considerable amount of dissolved organic and inorganic matter remains in the water. The procedures of coagulation/flocculation are generally able to yield the water of COD values of 500 – 3000 mg L^{-1}. The trend in technological processing of such waters is to reduce the COD values to the level below 200 mg L^{-1}, depending on the recipient.[11]

The COD values shown in Table 6 are $\gamma(O_2)$ = 344 mg L^{-1}, referring to the water previously filtrated through the filter pores of d = 0.45 μm, which means that the measured values include only the dissolved matter and are similar to the values from the literature for the residual dissolved organic and inorganic matter in the water after coagulation/flocculation.[10] To remove the dissolved organic matter it is necessary to further degrade the organic matter in the water having in mind ecological considerations as much as possible.



F i g. 4 – *UV-VIS spectrum of the sample filtrated through a 0.45 μm membrane and its dilution 10, 20 and 500 times*
S l i k a 4 – *UV-VIS spektar uzorka otpadne vode filtriranog kroz 0,45 μm membranu i uz razrjeđenje 10, 20 i 500 puta*

Literal data for BOD_5 used in this article (Table 2) originate mostly from the investigations of the wool quality of the sheep breed merino, which is rather different form the quality of the most numerous domestic sheep breed in Croatia, so-called *Pramenka*. So, relatively low values for the measured BOD_5 (γ = 580 mg L^{-1}, Table 6) in comparison to literal values could be connected to specific fleece composition of the Pramenka sheep breed. These differences should be systematically investigated.

If we suppose that all the wool is scoured using water in the above mentioned bath ratio (BR 1:10), some v = 7240 m^3 of wastewater from wool scouring is created in Croatia annually. Regarding the other parameters mentioned in Table 2, around m = 5 kg of pesticides is expected to be released into the environment in Croatia annually, just through scouring domestic raw (greasy) wool. Using the measured data for the COD in untreated wastewater from the scouring, it could be calculated that organic load from this wastewater in Croatia is the same as impact on environment caused by normal functioning of a town of 1700–2000 inhabitants (1 PE = 120 g d^{-1} COD).[16]

Conclusion

Considerable amounts of harmful substances are released into the environment in Croatia annually that are linked, by origin and impact, to sheep wool. The sheared wool in Croatia reaches approximately 724 t a year. Since wool is not used in Croatia as a raw material for the textile industry, it is generally not processed and scoured. In most cases, it is simply dumped at legal or illegal dump grounds, making it possible for the pollutants contained to reach the environment.

The expected pollution by substances in wool in Croatia is around 5 kg of pesticides, as well as 96 t of solid matter and 84 t of extracted dry grease yearly. Although measured

BOD_5 values are rather low, according to measured COD values it can be stated that wool scouring effluent has the same impact on the Croatian environment as caused by a town of 1700–2000 inhabitants (1 PE = 120 g d^{-1} COD).

As the number of sheep in Croatia is expected to grow, these values of environment pollution are expected to rise in the near future.

The first step of a realistic strategy of solving the problem of environmental pollution by substances from wool in Croatia should be preventing pollution through simple technological procedures, in accordance with the accepted ecological principles. However, this implies not exploiting the raw materials contained in the wastewater generated. The second step, after a thorough techno-chemical analysis of the processes and investigation of the market demands, should include developing processes for recycling and separating the usable substances from the wool scouring wastewaters.

References
Literatura

1. …, Statististički ljetopis RH 2005, Državni zavod za statistiku, Zagreb, 2006, str. 267 i str. 272.
2. *E. Vujasinović, I. Soljačić*, u: Zbornik radova savjetovanja Tehnologije zbrinjavanja otpada, (Ed. B. Salopek), Varaždin, HATZ, 2006, 63.
3. *E. V. Truter,* Wool wax, Cleaver Hume Press Ltd., London, 1965.
4. *A. Lutkić, E. Erlač, I. Soljačić,* Tekstil **55** (2005) 596.
5. *E. Erlač, Z. Dragčević, N. Vuljanić*, Tekstil **46** (1997) 255.
6. *J. Pearson, F. Lu, K. Gandhi*, Autex Res. J. **4** (2004) 147.
7. *F. W. Jones, D. J. Westmoreland*, Wat. Res. **33** (1999) 1775.
8. *A. J. Poole, R. Cord-Ruwisch,* Wat. Res. **38** (2004) 1419.
9. …, Utilising Wool Scouring Wastes as a Resource, CSIRO, Geelong, 1998.
10. *A. J. Poole*, Wat. Res. **38** (2004) 3458.
11. …, Integrated Pollution Prevention and Control (IPPC); Reference Document on Best Available Techniques for the Textile Industry, European Commision, EU, 2003.
12. *E. Vujasinović*, Prilog istraživanju kvalitete domaćih vuna – finoća i medulacija, Magistarski rad, Tekstilno-tehnološki fakultet Sveučilišta u Zagrebu, Zagreb, 1996.
13. *E. Vujasinović, D. Raffaelli,* in: Proceedings of the 1st International Textile, Clothing & Design Conference – Magic World of Textiles, (Ed. *Z. Dragčević*), Dubrovnik, University of Zagreb Faculty of Textile Technology, (2002) 136.
14. *F. H. Frimmel, G. Abbt-Braun, G. Baldauf, H.–J. Brauch, A. Grohmann, B. Hambsch, S. Huber, W. Huber, W. Kuehn, D. Maier, U. Rohmann, P. Scherer, S. Schullerer-Jageilla, W. Steuer, I. Wagner, P. Werner, B. Wricke,* Wasserchemie für Ingenieure, DVGW – Oldenbourg Verlag GmbH, München, 1993.
15. *A. J. Poole, R. Cord-Ruwisch, F. W. Jones*, *Wat. Res.* **33** (1999) 1981.
16. *M. Henze, P. Harremoes, J. Cour Jansen, E. Arvin,* Wastewater Treatment, Biological and Chemical Proecesses, Springer, New York, 2002.

List of symbols
Popis simbola

A – absorbance
– apsorbancija

d – fibre diametar, µm
– debljina vlakna, µm

l – fibre length, cm
– duljina vlakna, cm

m – mass, g
– masa, g

N – number of measurements
– broj mjerenja

s – standard deviation
– standardna devijacija

t – time, min
– vrijeme, min

v – specific volume, L kg^{-1}
– specifični obujam, L kg^{-1}

V – volume, L
– obujam, L

w – mass fraction, %
– maseni udjel, %

χ – average value
– srednja vrijednost

γ – mass contentration, mg L^{-1}
– masena koncentracija, mg L^{-1}

ϑ – temperature, °C
– temperatura, °C

κ – conductivity, µS cm^{-1}
– provodnost, µS cm^{-1}

λ – wawe length, nm
– valna duljina, nm

Ψ – volume ratio
– obujmni omjer

SAŽETAK

Pranje domaće vune u Hrvatskoj i utjecaj na okoliš

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Vuna i otpadne vode od pranja vune mogu biti korisna tehnološka sirovina ili su pak ekološki problem. Ukoliko se vuna nekontrolirano pere, kao što je to najčešće slučaj u Hrvatskoj, ispuštene otpadne vode mogu ugroziti prirodnu ekološku stabilnost postojećih vodenih sustava. S obzirom da je u posljednje vrijeme povećano zanimanje za preradu domaće vune, a time i opasnost od onečišćenja voda zbog nestručnog pranja vune i nekontroliranog ispuštanja otpadne vode od pranja vune u prirodne vodotokove svrha ovog rada bila je odrediti potencijalno moguće ekološko opterećenje vodenih sustava Hrvatske uzrokovano pranjem domaće vune. Rezultati istraživanja pokazuju da nekontrolirano odlaganje vune i/ili otpadne vode od pranja domaće vune u Hrvatskoj predstavlja značajnu opasnost za okoliš, koja je ekvivalentna onečišćenju koje nastaje normalnim funkcioniranjem grada s 1700 do 2000 stanovnika.

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