Wastewater Treatment After Improved Scourings of Raw Wool

D. Došen-Šver,* E. Pernar, and I. Bujević

Faculty of Textile Technology University of Zagreb,
Prilaz baruna Filipovića 30, 10 000 Zagreb, Croatia

Textile industry processes need high amounts of water for wet treatment of textiles. Therefore, high amounts of wastewater also appear containing different inorganic and organic substances depending on the used materials and processes. Raw wool is contaminated with wool wax, suint, skin flakes, dirt, sand, vegetable matter, urine and various microorganisms. The methods for raw wool scouring and cleaning today often in use are: scouring in the suint, scouring with soaps or tenside in alkaline, extraction by organic solvents and freezing. The different methods for wastewater purification after scouring in use are: settling/floculation, biological treatment, adsorption and catalytic oxidation. In this work, wastewater treatments after improved raw wool scouring with enzymes and EDTA have been investigated. Isothermal adsorption on zeolite A, active carbon and a natural and H^+ type of bentonite for removal of the obtained wastewater impurities was used. The results were determined by means of different physical-chemical test methods.

Key words: *Wool scouring, wastewater, complexing agents, enzymes and EDTA*

Introduction

Water is used very often in the textile industry because the most technical processes work in water medium. The wet processes such as scouring, bleaching, washing, dyeing, printing and finishing of textiles need large amounts of water. Through these processes, many chemicals are discharged into effluents causing major water pollution. The effluents consist of the processing chemicals used and other impurities extracted from the textile materials. Wool is a very important raw material for the textile industry, however, the greasy wool is very dirty, which presents major problems for the environment and the technology, depending on the impurities it contains. Wool scouring is the process of removing the impurities adhering to greasy wool. Thus, the pollutants appearing in the wastewaters after raw wool scouring are various inorganic and organic substances, depending on their origin.

Raw woll contains large amounts of: wool wax, suint, skin flakes, dirt, sand, vegetable matter, urine and various microorganisms. Metallic trace elements present in raw wool are often: iron, calcium, magnesium, potassium, aluminium, copper, zinc, manganese and silicon.[1–4]

The wastewater after wool scouring contains about $w = 10–30 \%$ wool fats, $w = 10 \%$ wool suint and $w = 60–80 \%$ other impurities. Wool fats contain lipids, high fatty acids and their esthers, and ethers, followed by alcohols, steroles (cholesterole) and lanoline (a heterogene mixture of these components). Wool suint contains ammonium salts, urea, various amino acids and K, Mg, Ca, Fe, Cu, Zn, Mn sulphates, oxalates and phosphates. Today, only lanoline has found an important use in the pharmaceutical industry. Wool impurities mechanically removed from wastewater after scouring can be used as "cake" for the technological warming.[4,5] The most used methods for raw wool scouring and cleaning are: scouring in the suint, emulsion scouring with soaps or tenside in alkaline (Na_2CO_3), extraction by organic solvent and freezing at 243 K.[4,6]

The obtained wastewater differs greatly in composition and quantities, as the compositions vary considerably from process to process. No universal method of wastewater purification can be suggested and the water treatment depends on the impurities present. Different methods are used for the purification of wastewaters after refining and finishing of textiles: mechanical, chemical, physical-chemical or biologic, and their combinations.[1,7] In the textile technology, the rationalization and reduction of water quantities include efficient purification of wastewater and its reuse.[7–14] In most cases nowadays, the wool scouring effluent is purified by the use of settling/flocculation, biologic treatment (active sludge, bio-filters, stabilizing ponds etc.), adsorption/ion exchange and catalytic oxidation.[3,7,8] A membrane technology is used today for the treatment and recycling of some textile wastewaters.[14]

Complexing agents are used in textile industry processes to eliminate calcium, magnesium and iron that could impair soil removal, the effectiveness of surfactants, bleaching agents and auxiliaries and the sorption of dyes onto textiles during dyeing processes. The complexing agent EDTA (ethylenediaminetetraacetic acid) used in textile processing forms stable chelates with bivalent and trivalent metallic ions. Through the processes of cleaning and washing of textile materials it is used in detergents to stabilize bleach and to boost primary detergency.[15–19] The low toxicity ($LC_{50} =$

---

* Corresponding author:
Prof. Dubravka Došen-Šver, Ph.D.
e-mail: dubravka.sver@ttf.hr

2040 mg dm^{-3}) and the low biodegradability confirm the use to form stable complexing products chelates and eliminates metallic ions from textiles.[15,16,19]

Enzymes are natural proteins that act as bio-catalysts. Most of the enzymes used in textiles are hydrolases, which catalyze cleavage reactions through hydrolysis.[20,21] Studies have been conducted into the effectiveness of proteolytic and lipolytic enzymes in improving wool properties such as shrink resistance, softness and wettability.[22] Enzymes are used in finishing treatments of wool such as anti-felting treatments[21,23] and for washing and bleaching of cotton.[24,25] However, the effectiveness of enzymes as scouring agents for wool fibers in comparison with conventional soap scouring has not been studied.[20] For the first time, the use of enzyme agents for raw wool scouring was successful in combination with tenside[4,5] and also alone.[26] Also, a combination of EDTA and an enzymatic complex gave very good wool scouring results.[27]

This work investigates wastewater treatment after improved greasy wool scouring with enzymes and Na$_2$H$_2$EDTA. An isothetmal adsorption on zeolite A, active carbon and a natural and H$^+$ type of bentonite for removal of the obtained wastewater impurities was used. The results were determined by means of various physical-chemical methods of filtrate investigations such as pH, electrical conductivity, surface tension, COD and BOD$_5$.

Experimental part

Materials

For these investigations, the samples of raw wool from Croatia (cross-breed of pramenka and Israeli awassy ram) were used. Water solutions for wool scouring containing Na$_2$H$_2$EDTA (dinatrium salt ethylenediaminetetraacetic acid), an enzymatic complex (Clariant, CH, Bactosol WO), a nonionic tenside (fatty alcohol ethoxylate, Clariant, CH, Sandoclean PC) and Na$_2$CO$_3$ as alkaline medium (pH ≈ 9–10) were used.

The obtained wastewaters after raw wool scouring were treated through isothermal adsorption/ion exchange with the following adsorbents:
– natural bentonite (Monte Negro)
– H-bentonite (H$^+$ type formed from a natural bentonite by treatment with $c = 0.1$ mol dm^{-3} HCl)
– zeolite A (synthetic form with Na$^+$ and Ca^{2+} ions in the structure pores)
– active carbon (commercial)

Raw wool scouring

The samples of raw wool were first cleaned mechanically and then a mass of $m = 10$ g greasy wool was warmed at $T = 318$ K (± 0.1 K) through $t = 1800$ s in $V = 350$ cm^3 of bath contained:

Bath I: $m = 0.175$ g nonionic tenside Sandoclean PC, $m = 1.05$ g Na$_2$CO$_3$

Bath II: $m = 0.175$ g nonionic tenside Sandoclean PC, $m = 0.6$ g enzymatic complex Bactosol WO ($w = 6$ % of wool mass), m = 1.05 g Na$_2$CO$_3$

Bath III: $m = 0.175$ g nonionic tenside Sandoclean PC, $v = 70$ cm^3 $c = 0.01$ mol dm^3 Na$_2$H$_2$EDTA, $m = 1.05$ g Na$_2$CO$_3$

Bath IV: $m = 0.175$ g nonionic tenside Sandoclean PC, $m = 0.6$ g enzymatic complex Bactosol WO ($w = 6$ % of wool mass), $v = 70$ cm^3 $c = 0.01$ mol dm^3 Na$_2$H$_2$EDTA, $m = 1.05$ g Na$_2$CO$_3$

After filtering and washing with cold distilled water, the wool was dried in conditioned air and the loss of wool mass was determined by gravimetric measurements (Table 1). The loss of wool mass was determined as shown in Table 1.

T a b l e 1   – *The loss of raw wool mass after scouring*
T a b l i c a 1 – *Gubitak mase sirove vune nakon pranja*

Sample Uzorak	Loss of wool mass, x_i / % Gubitak mase vune	x / %	σ / %	cv / %
Bath I/Kupelj I				
1	24.88			
2	25.83	27.21	2.65	9.74
3	30.92			
Bath II/Kupelj II				
1	29.49			
2	32.20	30.75	1.242	4.039
3	30.56			
Bath III/Kupelj III				
1	33.50			
2	34.04	33.84	0.242	0.715
3	33.98			
Bath IV/Kupelj IV				
1	34.87			
2	33.63	34.20	0.51	1.49
3	34.10			

Isothermal adsorption

Dissolute wastewater 1:10 was left in aliquot parts of $V = 50$ cm^3 by stirring for two hours at $T = 298$ K (± 0.1 K) in contact with $m = 0.1, 0.3, 0.5, 0.75$ and 1.00 g of adsorbent mass. Before adsorption, the used adsorbents were crumbled, passed through a sieve of pore size $d = 0.063$ mm, and dried at $T = 393$ K (bentonite, active carbon) or $T = 633$ K (zeolite A) for two hours. After the adsorption/ion exchange and filtration, the remainder on the filter paper was dried and weighed. The results of isothermal adsorption/ion exchange tests were monitored by measurements of pH, electrical conductivity and surface tension of filtrates after the process, and gravimetric determinations of adsorbed substance onto used adsorbents. The purification of obtained wastewaters was detected by COD and BOD$_5$ investigations. The test results are presented in the diagrams and tables.

Results

The results of these investigations have been monitored by different physical-chemical methods of determination which have been done in figures and tables as follows:

Fig. 1 shows the results of wastewater pollution adsorption on used adsorbents as a gravimetric measurement of adsorbed substance mass in relation to $m = 0.1, 0.3, 0.5, 0.75$ and 1.00 g of adsorbent mass after scouring of greasy wool by bath I and bath II.
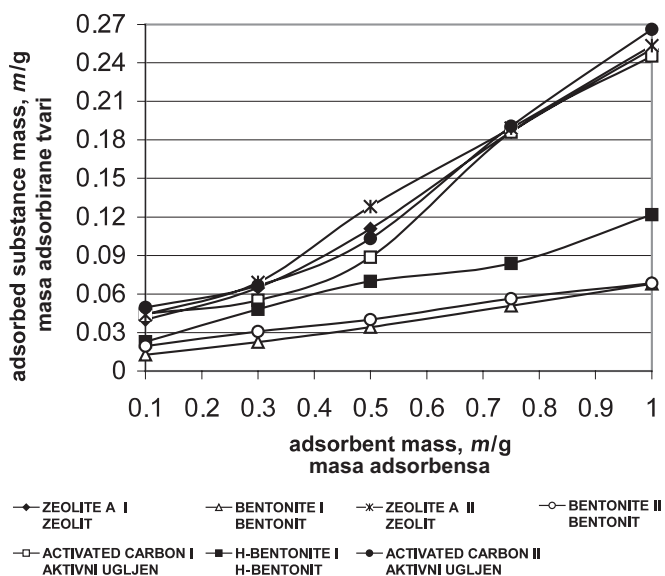
Fig. 2 gives the same results of the adsorption on used adsorbents after wool scouring by bath III and bath IV.

The results of pH measurements of filtrates after a isothermal pollution adsorption have been done in Fig. 3 and Fig. 4 as pH in relation to increased adsorbent mass. Fig. 3 is after wool scouring by bath I and bath II and Fig. 4 after wool scouring by bath III and bath IV.

Fig. 5 and Fig. 6 show the results of electrical conductivity investigations of filtrates during the pollution adsorption on increased adsorbent mass. The same results of surface tension measurements of filtrates in relation to used adsorbent amounts gives Fig. 7 and Fig. 8. Fig. 5 and Fig. 7 are after wool scouring by bath I and bath II and Fig. 6 and Fig. 8 after wool scouring by bath III and bath IV.

F i g. 1 – *Isothermal adsorption of wastewater impurities from bath I and bath II on used adsorbents*

S l i k a 1 – *Izotermalna adsorpcija nečistoća iz kupelji I i II na upotrebljenim adsorbensima*
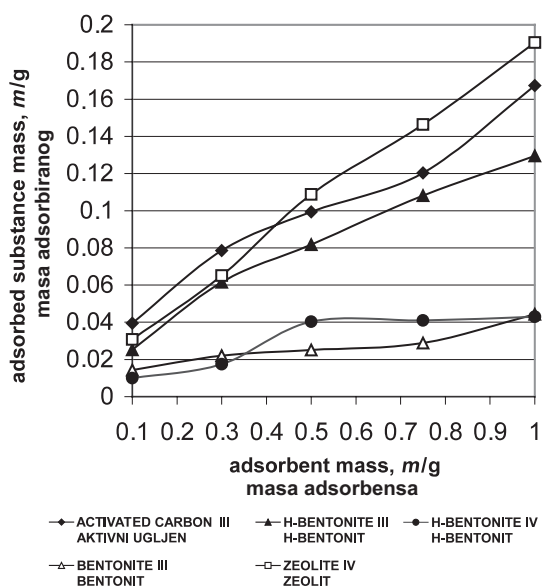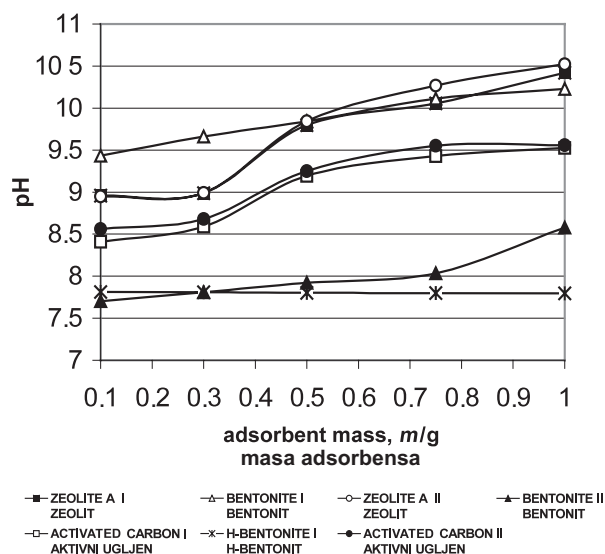

F i g. 3 – *pH of filtrates after adsorption of wastewater impurities from bath I and bath II on used adsorbents*

S l i k a 3 – *pH filtrata nakon adsorpcije nečistoća iz kupelji I i II na upotrebljenim adsorbensima*
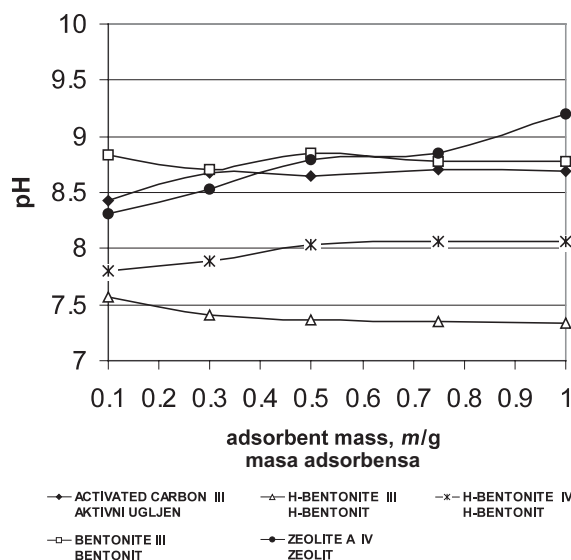

F i g. 2 – *Isothermal adsorption of wastewater impurities from bath III and bath IV on used adsorbents*

S l i k a 2 – *Izotermalna adsorpcija nečistoća iz kupelji III i IV na upotrebljenim adsorbensima*

F i g. 4 – *pH of filtrates after adsorption of wastewater impurities from bath III and bath IV on used adsorbents*

S l i k a 4 – *pH filtrata nakon adsorpcije nečistoća iz kupelji III i IV na upotrebljenim adsorbensima*
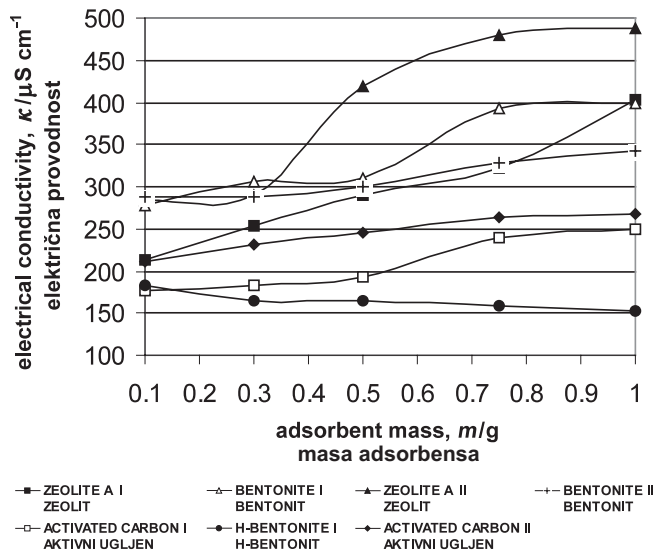
F i g. 5 – *Electrical conductivity of filtrates after adsorption of wastewater impurities from bath I and bath II on used adsorbents*

S l i k a 5 – *Električna provodnost filtrata nakon adsorpcije nečistoća iz kupelji I i II na upotrebljenim adsorbensima*

F i g. 7 – *Surface tension of filtrates after adsorption of wastewater impurities from bath I and bath II on used adsorbents*

S l i k a 7 – *Napetost površine filtrata nakon adsorpcije nečistoća iz kupelji I i II na upotrebljenim adsorbensima*

F i g. 6 – *Electrical conductivity of filtrates after adsorption of wastewater impurities from bath III and bath IV on used adsorbents*

S l i k a 6 – *Električna provodnost filtrata nakon adsorpcije nečistoća iz kupelji III i IV na upotrebljenim adsorbensima*
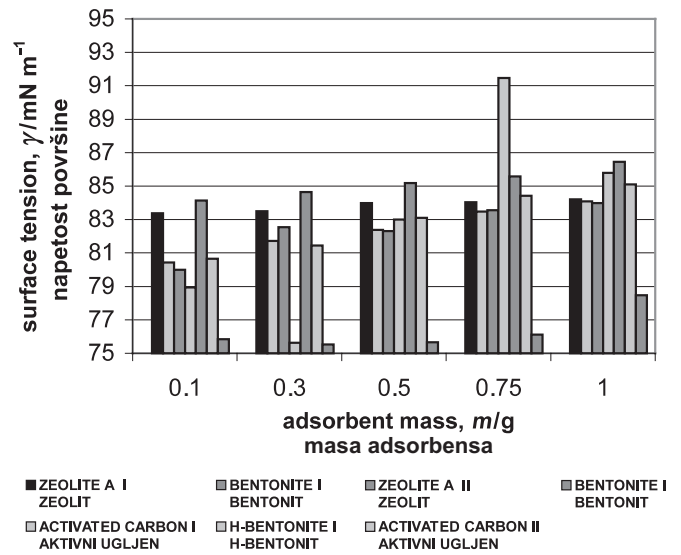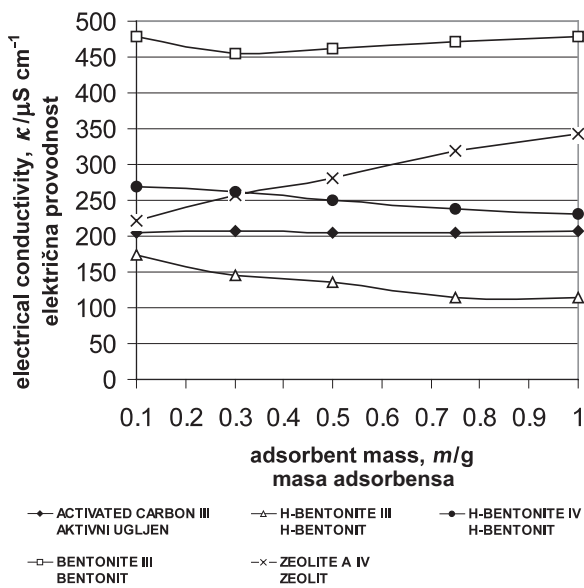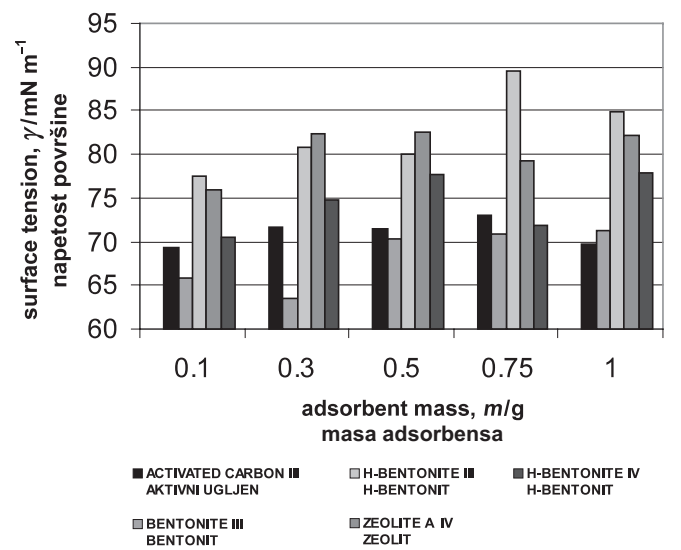

F i g. 8 – *Surface tension of filtrates after adsorption of wastewater impurities from bath III and bath IV on used adsorbents*

S l i k a 8 – *Napetost površine filtrata nakon adsorpcije nečistoća iz kupelji III i IV na upotrebljenim adsorbensima*

And finally, the results of physical-chemical, COD and BOD_5 investigations of initial wastewaters (1:10) and filtrates after adsorption/ion exchange processes onto $m = 1$ g of adsorbents have been done at Table 2.

Conclusions

Greasy wool presents many problems in the environment and the technology dependent of its impurity content. There are different methods for raw wool scouring and for wastewater purification to improve environmental protection.

In this work, wastewater treatment after improved greasy wool scouring has been presented. Thus, raw wool has been scoured by means of an enzymatic complex (bath II), then the complexing agent Na_2H_2EDTA (bath III) and also a combination both of agents (bath IV), and has been compared with a conventional scouring only by tenside (bath I).

As shown in Table 1, the loss of wool mass after scouring increased from bath I to bath IV.

The higher loss of wool mass was by the use of EDTA (bath III) probably because the removal of metallic ions from raw

T a b l e 2   – *pH, electrical conductivity, surface tension, COD and BOD$_5$ investigations of initial wastewaters and filtrates after the impurity adsorption on m = 1 g of adsorbents*

T a b l i c a 2 – *pH, električna vodljivost, napetost površine, KPK i BPK$_5$ ispitivanja početne otpadne vode i filtrata nakon adsorpcije nečistoća na m = 1 g adsorbenata*

Wastewater Otpadna voda	pH	$\kappa/\mu S\ cm^{-1}$ el. conductivity el. provodnost	$\gamma/mN\ m^{-1}$ surface tension napetost površine	$\rho_{COD}/mg\ dm^{-3}$ KPK	$\rho_{BOD5}/mg\ dm^{-3}$ BPK$_5$
Bath I	9.556	484.5	82.42	450	35.7
Bath II	9.276	436.8	80.41	280	50.4
Bath III	11.542	1192	76.31	390	46.5
Bath IV	9.401	399.6	85.90	380	58.7
After zeolite A					
Bath I	10.420	402.6	84.20	260	13.1
Bath II	10.523	488.2	86.45	120	12.2
Bath IV	9.192	342.7	82.20	140	19.3
After activated carb.					
Bath I	9.525	248.5	84.09	230	7.6
Bath II	9.559	267.8	85.10	140	19.1
Bath III	8.694	206.2	69.64	120	12.3
After bentonite					
Bath I	10.227	399.0	83.98	280	23.3
Bath II	8.579	342.6	78.47	150	25.8
Bath III	8.774	478.6	71.21	180	32.1
After H-bentonite					
Bath I	7.795	151.9	85.79	240	26.2
Bath III	7.339	114.3	84.94	130	23.5
Bath IV	8.063	231.8	77.80	190	28.8

κ = el. conductivity (*električna provodnost*), γ = surface tension (*napetost površine*), COD = chemical oxygen demand (*kem. potreba kisika*), BOD$_5$ = biologic oxygen demand (*biološka potreba kisika*)

wool occurred, and a combination of enzymatic complex and EDTA (bath IV) increased the wool mass loss because the removal of metallic ions and wool grease was simultaneous. Fig. 1 gives the results of gravimetric investigations of adsorbed substance mass in relation to increased adsorbent mass through the isothermal adsorption of the impurities from wastewaters after wool scouring by bath I and bath II. The best results were obtained with zeolite A as adsorbent, followed then activated carbon. The lowest values were by a natural bentonite and the highest amounts of the adsorbed substance mass gave zeolite A by bath II. Also, zeolite A was the best adsorbent by bath IV as shown in Fig. 2. Activated carbon and H+-bentonite also gave good results by bath III and again the lowest results had a natural bentonite. In all these investigations, the adsorption increased with the increase of adsorbent mass.

Fig. 3 and Fig. 4 show the results of pH measurements of filtrates after adsorption processes and one can see that the highest values were by zeolite A and by a natural bentonite, and the lowest values were by H+-bentonite in all baths. The highest value of pH by initial bath III (11.542) was the result of alkaline metallic ions removal by the use of EDTA. The high values of pH in filtrates after the adsorption are due to the high amounts of Na_2CO_3 in the initial baths were, also exchanged Na+ ions from the structure of used adsorbents (zeolite A or bentonite) in filtrates appear (Table 2).

The results of electrical conductivity measurements of filtrates after wool scouring by bath I and bath II show the highest values by using of zeolite A and a natural bentonite as asdorbent. Also, activated carbon gives some lower values. The lowest values were given by H+-bentonite with bath I and these values decreased with the increase of the adsorbent mass. All the other values increased with the increase of the adsorbent mass (Fig. 5). Fig. 6 presents the same results after wool scouring with bath III and bath IV, and gives high values with bentonite (bath III) and some lower by zeolite A (bath IV) increased with the increase of adsorbent mass. With other adsorbents the values decreased with the increase of adsorbent mass. The lowest values were by H+-bentonite (bath III). These results are similar as the results of pH investigations of filtrates.

The results of surface tension measurements of filtrates after wool scouring are presented in Fig. 7 and Fig. 8. The values by zeolite A, activated carbon and a natural bentonite (bath I) are similar and almost constant, but H+-bentonite gives some different results. By bath II zeolite A and activated carbon give the high values of surface tension measurements and a natural bentonite gives the lowest values (Fig. 7). The values increased with the increase of adsorbent mass.

Also activated carbon and a natural bentonite give the low values of surface tension by bath III (nearly distilled water

72.0 mN m^{-1}) and zeolite A (bath IV) and H$^+$-bentonite (bath III) give the higher values as shown in Fig. 8.

COD and BOD$_5$ investigations show the lower values after adsorption processes than before them in initial wastewaters (Table 2). Initial wastewaters show the highest value of COD by bath I and the lowest by bath II, and the highest value of BOD$_5$ by bath IV and the lowest by bath I. Through these investigations the use of zeolite A and activated carbon for the adsorption gave the lowest values of COD and BOD$_5$ in filtrates.

On the basis of these investigations one can conclude that the use of an enzymatic complex and also a complexing agent Na$_2$H$_2$EDTA can improve greasy wool scouring and the best results are by using these agents together. Also, the use of aluminosilicates as adsorbents makes the possibility for a good purification of obtained wastewaters. Synthetic zeolite A and activated carbon give very good results for the impurities adsorption from wastewaters after greasy wool scouring.

References
Literatura

1. *E. Menezes*, *B. Desai, K. Kulkarni*, Mell. Int. **9** (2003) 269.
2. *B. O. Bateup,* Text. Res. J. **54** (1984) 299.
3. *D. Došen-Šver, S. Bešenski,* Tekstil **35** (1986) 5, 325.
4. *D. Raffaelli, D. Došen-Šver, E. Vujasinović,* Kem. Ind. **48** (1999) 5, 189.
5. *D. Došen-Šver, Z. Čavlek,* Proceed. of 7th Int. Conf. of Textile Row Materials, Hungary, Budapest May 1999, pp. 197.
6. *D. Došen-Šver*, *Z. Čavlek,* Proceed. of 3rd Int. Meet. of Textile Chemists and Colourists, Hungary, Budapest June 2001, str. 54.
7. *D. Došen- Šver, S. Bešenski*, Tekstil **37** (1988) 4, 193.
8. *A. J. Poole, R. Cord-Ruwisch*, Water Res. **38** (2004) 6,1419.
9. W. *Hohn, Th. Bohme*, Mell. Textilb. **9** (1998) 647.
10. *W. Hohn,* Textilver. **33** (1998) 9/10, 24.
11. *K. H. Gregor, S. A. Solvay*, Mell. Textilb. **9** (1998) 643 .
12. *E. Dopkens, P. Metzen, R. Krull*, Mell. Textilb. **5** (2004) 362.
13. *J. Sarsour, M. Linke, Th. Stegmaier, H. Planck*, Textilver. **1/2** (2005) 12.
14. *D Bottger, C. Meyer*, Textilver. **9/10** (2006) 14.
15. *P. Schoberl, L. Huber*, Tenside Surf. Det. **25** (1988) 2, 99.
16. *Ch. Gousetis, R. Baur, A. Oftring*, Tenside Surf. Det. **27** (1990) 1, 41.
17. *A. Losonczi, E. Csiszar, G. Szakacs, L. Bezur*, Text. Res. J. **75** (2005) 5, 411.
18. *K. Schafer, Th. Neyers, H. Hocker*, Tenside Surf. Det. **37** (2000) 2, 127.
19. *D. Došen-Šver, E. Pernar*, Proceed. of 2nd Int. Textile, Clothing & Design Conf., Croatia, Dubrovnik October 03rd – 06th (2004) 988.
20. *D. Trina, G. N. Ramaswamy*, Text. Res. J. **2** (2006) 1, 126.
21. *P. Jovančić, D. Jocić, J. Dumić*, J. Text. Inst. **89** (1998) 2, 390.
22. *H. Nolle, D. P. Bishop*, J. Text. Inst. **87** (1996) 1, 212.
23. *J. Shen, D. P. Bishop, E. Heine, B. Hollfelder*, J. Text. Inst. **90** (1999) 3, 404.
24. *H. Schacht, W. Kesting, E. Schollmeyer*, Textilver. **30** (1995) 11/12, 237.
25. *M. Marzinkowski, M. Schellentrager, M. Constapel, S. Gab, U. Vogt, B. Koenemund*, Textilver. **9/10** (2006) 4.
26. *D. Došen-Šver, Z. Čavlek*, Proceed. of 1st Int. Textile, Clothing & Design Conf., Croatia, Dubrovnik October 06th – 09th (2002) 677.
27. *D. Došen-Šver*, *I. Bujević*, Proceed. of 3rd Int. Textile, Clothing & Design Conf., Croatia, Dubrovnik October 08th –11th (2006) 971.

List of symbols
Popis simbola

BOD$_5$ – biologic oxygen demand
– biološka potreba kisika

c – (amount) concentration mol dm^{-3}
– (množinska) koncentracija, mol dm^{-3}

COD – chemical oxygen demand
– kemijska potreba kisika

d – diameter, mm
– promjer, mm

m – mass, g
– masa, g

t – time
– vrijeme

T – absolute temperature, K
– apsolutna temperatura, K

V – volume, cm^3
– obujam, cm^3

w – mass fraction, %
– maseni udjel, %

γ – surface tension, mN m^{-1}
– napetost površine, mN m^{-1}

κ – electrical conductivity, mS cm^{-1}
– električna provodnost, mS cm^{-1}

SAŽETAK

Obrada otpadnih voda nakon poboljšanih pranja sirove vune

D. Došen-Šver, E. Pernar i I. Bujević

U tekstilnoj industriji troše se velike količine vode za mokre obrade tekstila. Stoga nastaju i velike količine otpadnih voda, koje sadrže različite anorganske i organske tvari ovisno o uporabljenim materijalima i procesima. Sirova vuna je onečišćena vunenim voskom, znojem, komadićima kože, pijeskom, vegetabilnim tvarima, urinom i različitim mikroorganizmima. Najčešće se primjenjuju metode pranja i čišćenja vune: pranje u znoju, u sapunima ili tenzidima u alkalnoj sredini, ekstrakcija u organskim otapalima i zamrzavanje. Također su poznate različite metode pročišćavanja otpadnih voda poslije pranja vune: taloženje/flokulacija, biološka obrada, adsorpcija i katalitička oksidacija.

U ovom radu je ispitivana obrada otpadnih voda nakon poboljšanih pranja sirove vune s enzimima i EDTA. Za uklanjanje onečišćenja otpadnih voda upotrijebljena je izotermna adsorpcija na zeolitu A, aktivnom ugljenu, prirodnom i H^+ tipu bentonita. Rezultati su određivani upotrebom različitih fizikalno-kemijskih metoda ispitivanja.

Tekstilno-tehnološki fakultet Sveučilišta u Zagrebu
Prilaz baruna Filipovića 30, 10 000 Zagreb, Croatia