

Recycled wool-based nonwoven material for sorption of acid dyes

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The possibility of using a nonwoven material based on recycled wool for sorption of acid dyes from wastewater has been studied. To improve its sorption properties, the recycled wool-based nonwoven material was treated with low-temperature air plasma and/or biopolymer chitosan. These treatments introduced new favourable functional groups and increased the active surface area. Sorption capacity, sorption kinetics as well as the influence of electrochemical properties of fibre, initial dye concentration, pH and temperature on the sorption have been studied. It is observed that the nonwoven recycled wool-based material can be used as an efficient sorbent for removal of acid dyes. Chitosan and plasma+chitosan treatments of the material remarkably improved the sorption properties for AR88 and AR27 dyes, likely because of the increase in amino groups originating from chitosan that are the main sites for binding of dye anions. However, no significant positive effect of low-temperature plasma and/or chitosan treatment of material on sorption of AB113 dye was observed.

Keywords: Acid dye, Chitosan, Dye sorption, Low-temperature plasma, Wool

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1 Introduction

Both the increase in public interest and concern for the environment as well as the introduction of strict ecological legislation caused an environmental pressure on industry, particularly in highly developed industrial countries¹⁻³. Nowadays, the textile industry is facing the increasing ecological demands for control and purification of effluents, particularly because it generates a huge amount of wastewater. In addition to the limitation of BOD, COD, metal ion and some organic compounds in industrial effluents, the request for almost complete decolorisation of wastewater was introduced⁴. This regulation showed strong impact on the textile dyehouses that produce very complex effluents containing a wide range of dyes and auxiliaries. Normally, the dyehouse effluent contains about 10-50 mg/L of dyes, colour being noticeable at concentrations above 1 mg/L (ref. 1).

The amount of dye released in effluent through the exhaust and wash baths strongly depends on the type of dye, depth of shade, dyeing method, liquor ratio, etc.¹.

Biological treatment, coagulation/floculation, ion exchange, adsorption, reverse osmosis and ultrafiltration are some of the treatments developed for the decolorisation and removal of dyes from wastewater^{1,5,6}. Many different natural materials have also been used as possible sorbents for dyes^{7,8}. Biopolymer chitosan can be used as an efficient and relatively cheap sorbent that shows high affinity for metal ions and almost all classes of dyes^{6,9,10}. It is well documented that the wool has excellent sorption properties for metal ions and oil¹¹⁻¹³ but there are only limited data available about the sorption properties of wool for dyes¹⁴. This study was aimed at investigating the possibility of using the recycled wool-based nonwoven material as a sorbent for acid dyes. To improve the sorption properties, the material was treated with low-temperature air plasma and/or chitosan, both claimed as environment-friendly treatments.

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2 Materials and Methods

2.1 Materials

The experiments were performed using recycled wool-based nonwoven material (78:22 wool/polyester). Second-hand knitted pullovers of the same quality and characteristics were torn off, washed, decolorised with reducing agent, dried and garneted in industry. To avoid the effect of chemical binders on dye adsorption, the needle-punch process was used to produce the nonwoven material. The material was produced from recycled fibres on Dilo (Germany) needle loom. The physical and mechanical properties of the obtained material are given below:

Weight, g/m ²	: 235
Breaking strength, N (machine direction)	: 19.23
Bursting strength, N	: 21.97
Thickness, mm	: 1.56

Three different acid dyes (AR88, AR27 and AB113) were used for the study (Table 1). AR88 is a rather hydrophobic monosulphonated levelling acid dye of the lowest (400.4) r. m. m. (relative molecular mass). AR27 is a rather hydrophilic three-fold sulphonated monoazo levelling dye of 604.5 r. m. m. AB113 is disulphonated milling acid dye of higher r. m. m. (681), known to show poor migration properties.

Chitosan (Vanson, USA) with viscosity of 16 cps and deacetylation degree of 88.6% was used without further purification.

2.2 Methods

The nonwoven material was immersed in 0.1% chitosan solution (liquor-to-material ratio, 25:1), shaken for 6 h, passed through a laboratory padder and dried at room temperature. The dry material was then treated with 5% ammonium hydroxide solution (liquor-to-material ratio, 25:1) for 10 min at room temperature and dried again. Finally, the samples were rinsed in tap water and dried.

Low-temperature plasma treatment was carried out in a capacitively-coupled, radio-frequency induced (13.56 MHz) air plasma for 5 min using 0.2 mbar pressure with the power supply maintained at a constant level of 100 W.

To assess sorption kinetics, all the samples were shaken in 50 mL of 100 mg/L dye solution at appropriate pH for different sorption times (0.25, 0.5, 1, 2, 3, 4, 24 and 48 h) at 20°C. To investigate the influence of initial dye concentrations (100, 150, 200, 250 and 300 mg/L), the sorption capacity was determined after 48 h at 20°C. The influence of temperature increase (40°C and 60°C) on sorption capacity was determined using 100 mg/L dye solution (1 h, pH 3.0).

Table 1—Characteristics of acid dyes

Dye	Commercial name	Manufacturer	C.I. Name	Relative molecular mass	λ_{max} nm	Molecular structure
AR88	—	Sigma Chem.Co	Acid Red 88	400.4	506.5	
AR27	Amaranth Azorubin S	Aldrich Chem.Co	Acid Red 27	604.5	521.5	
AB113	Erionyl Marine 180	Ciba	Acid Blue 113	681.0	595	

Dye concentration in the solution was measured using UV-160 spectrophotometer (Shimadzu, Japan) at λ_{\max} . Sorption capacity of nonwoven material (dye uptake) was calculated from the difference between initial and final concentrations of dye in solution using the following equation:

$$q = \frac{(C_0 - C_f) \cdot V}{m}$$

where q is the sorption capacity (mg/g); C_0 , the initial conc. of dye in solution (mg/L); C_f , the final conc. of dye in solution (mg/L); V , the solution volume (L); and m , the mass of sorbent material (g).

Electrokinetic measurements were carried out with Electro Kinetic Analyser EKA (Anton PAAR, Austria). ζ -potential of samples was determined in accordance with the Fairbrother and Mustin method by measuring the streaming potential and specific electric conductivity of the electrolyte solution in the capillary system¹⁵. An electrolyte solution of 1.00×10^{-3} M KCl was applied and ζ -potential values were determined in the pH range from 3.0-10.0. To adjust the pH values, 0.100 M HCl and 0.100 M NaOH were used.

3 Results and Discussion

Sorption kinetics of untreated, chitosan-treated (CHT), plasma-treated (LTP) and plasma+chitosan treated (LTP+CHT) materials for acid dyes AR88, AR27 and AB113 are presented in Fig. 1. As expected, the prolongation of sorption time increases dye sorption, but equilibrium does not reach even after 48 h of sorption. Sorption capacities of all the samples for AR88 dye are significantly higher as compared to those for AR27 and AB113 dyes. This is due to much lower r. m. m. and low solubility of AR88 dye.

Plasma-treated and untreated samples show similar behaviour in case of AR88 dye, whereas LTP sample exhibits considerably better sorption properties than untreated sample for AR27 dye. However, for the same dye (AR27) both untreated and LTP samples do not show any sorption during the first hour. Sorption capacities of CHT and LTP+CHT samples for AR88 and AR27 dyes are significantly higher as compared to that of untreated sample, showing much faster sorption. In case of AB113 dye, the sorption kinetics of all the samples are very similar, particularly during the first 4 h of sorption. It is interesting to note that after 1 h of rapid sorption, the sorption capacity rapidly decreases during next 3 h and then increases

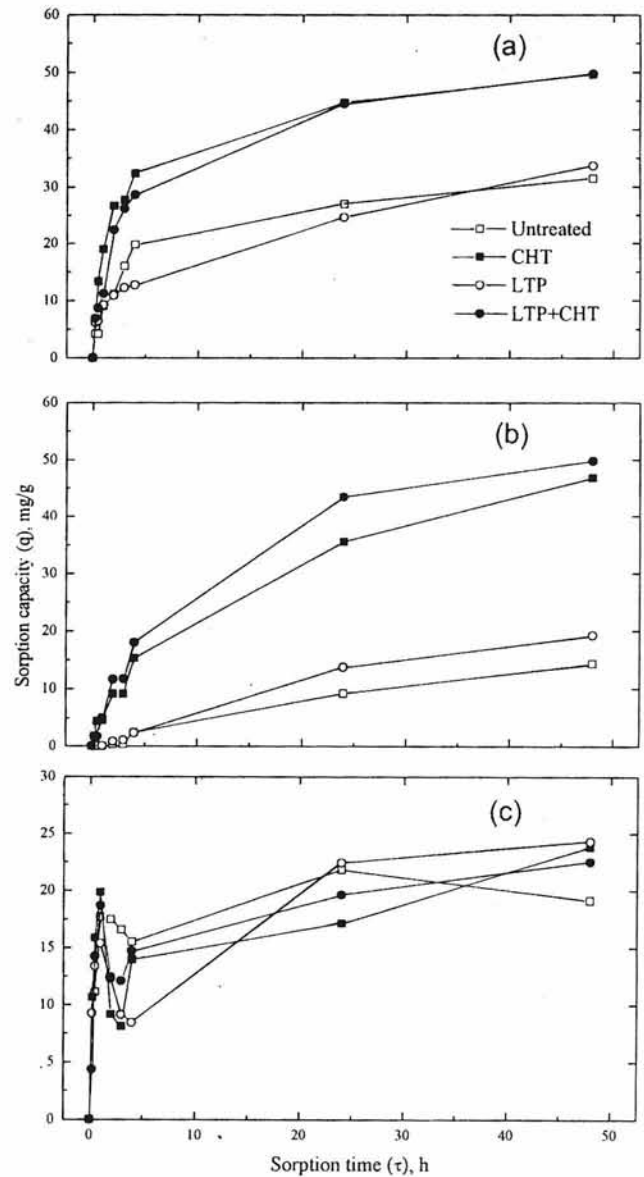


Fig. 1—Sorption kinetics of acid dyes (a) AR88, (b) AR27 and (c) AB113 (Initial dye conc., 100 mg/L; temperature, 20 °C; and pH, 3.0)

and needs about 20 h to reach and exceed the values obtained after the first hour of sorption (Fig. 1c).

The influence of initial concentrations of AR88 and AR27 dyes on sorption capacity of untreated, CHT, LTP and LTP+CHT samples is shown in Fig. 2. Obviously, an increase in initial dye concentration results in insignificant change in sorption capacity, except for the sorption of AR88 dye on CHT and LTP+CHT samples where the sorption capacity significantly increases (Fig. 2a).

Sorption capacities of untreated, CHT, LTP and LTP+CHT samples for AR88, AR27 and AB113 dyes

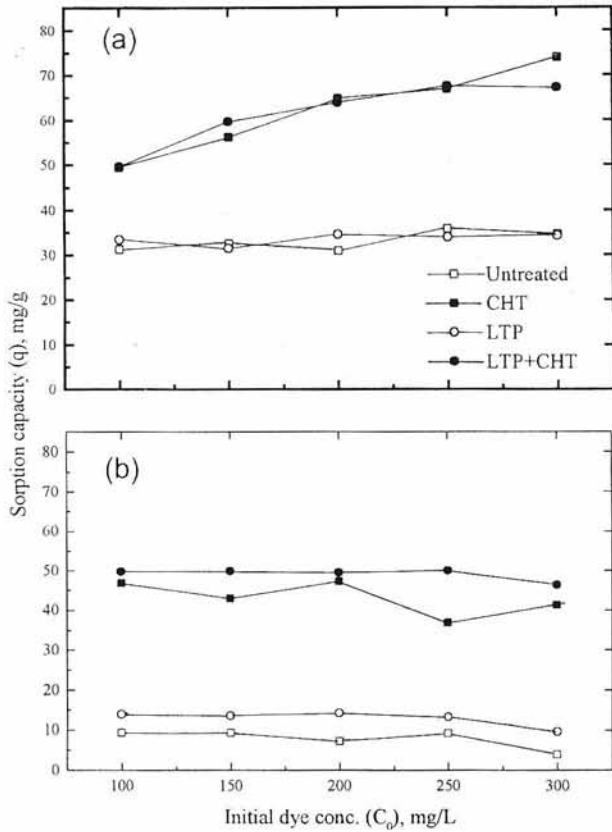


Fig. 2—Influence of initial concentration of (a) AR88 and (b) AR27 dyes on the sorption capacity (Sorption time, 48 h; temperature, 20 °C; and pH, 3.0)

at different temperatures are shown in Fig. 3. Temperature has strong influence on sorption of AR88 and AR27 dyes, whereas in case of AB113 dye, the temperature slightly affects the sorption behaviour of all investigated samples. The influence of temperature is particularly pronounced in case of AR88 dye sorption on untreated and LTP samples, whereas at 60°C the sorption capacities increase five times compared to the values at 20°C. At 60°C, all the samples after 1 h show almost the maximum possible sorption capacity (50 mg/g) for applied initial dye concentration of 100 mg/L (Fig. 3a). These capacities could not be achieved even after 48 h of sorption at 20°C (Fig. 1a) for untreated and LTP samples. CHT and LTP+CHT samples show the sorption capacity of 50 mg/g after 48 h of sorption at 20°C.

Although the temperature increase results in improved sorption of AR27 dye, the sorption capacities do not reach maximum possible value (Fig. 3b). However, after 1 h of sorption at 60°C, the untreated and LTP samples show sorption capacity 3-4 times higher than that observed after 48 h of

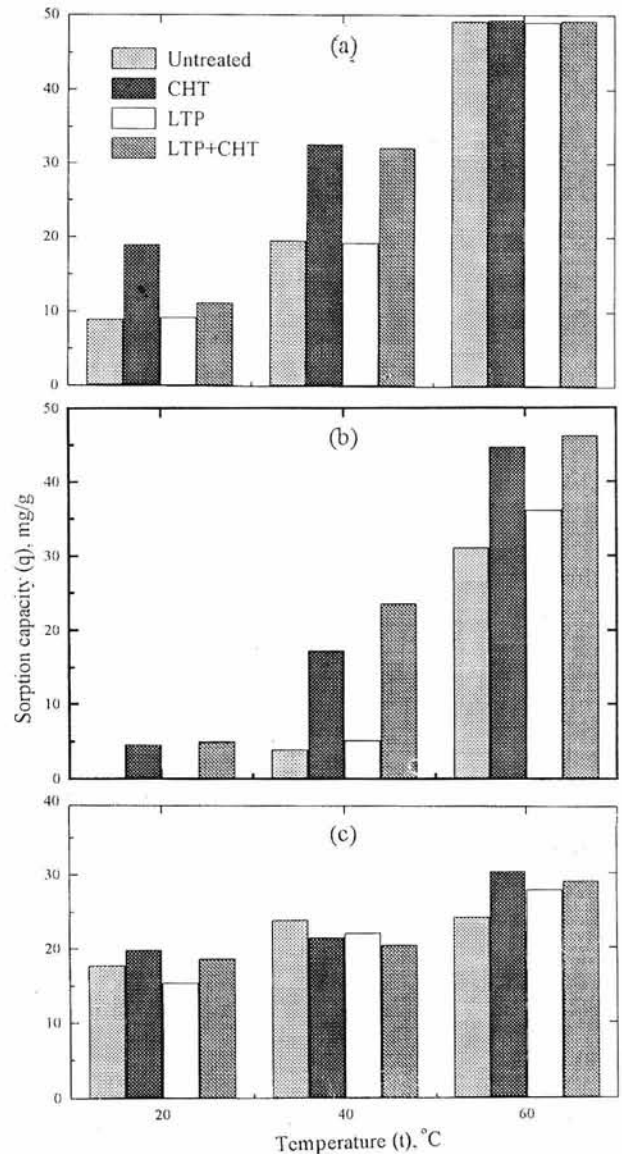


Fig. 3—Influence of temperature on sorption of (a) AR88, (b) AR27 and (c) AB113 dyes (Initial dye conc., 100 mg/L; sorption time, 1 h; and pH, 3.0)

sorption at 20°C. After 1 h of sorption at 60°C, the CHT and LTP+CHT samples show the sorption capacity comparable with that achieved after 48 h of sorption at 20°C.

Raising the initial dye concentration from 100 mg/L to 300 mg/L led to a considerable increase in sorption capacity for AR88 dye after 1 h of sorption at 60°C. However, the same increase of initial concentration of AR27 dye does not affect the sorption properties of untreated and LTP samples, while the sorption capacities of CHT and LTP+CHT samples increase by 37 %. These results are shown in Table 2.

For clear understanding of acid dye sorption, data on the electrochemical properties of all investigated samples are needed. The dependence of ζ -potential on pH is shown in Fig. 4. Negatively charged surface of untreated sample, almost in the whole range of investigated pH, could be the result of easier sorption of anions which are less hydrated than cations on the wool surface¹⁶. The lower the pH, the greater is the decrease in ζ -potential due to the protonation of functional groups on the wool surface. Isoelectric point of untreated sample is around pH 3.6. At higher pH, the LTP sample possesses ζ -potential lower than that of untreated sample, likely because of the hydrophilisation of the fibre surface when the competition between water molecules and anions occurs^{16, 17}. However, below pH 5.5, ζ -potential of LTP sample is higher than that of untreated and isoelectric point is shifted towards the estimated value (pH 3.1), suggesting that the plasma treatment induces the formation of new anionic groups on the fibre surface¹⁸.

Chitosan treatment of the material led to a decrease in negative values of ζ -potential. The isoelectric points of CHT and LTP+CHT samples are found to be around pH 5.6 and 5.9 respectively. A more positively charged surface could be attributed to an increase in amino groups on the wool surface¹⁹. Higher isoelectric point of LTP+CHT sample indicates that the plasma treatment enhances the binding of chitosan to wool via new-formed anionic groups, thereby increasing the content of amino groups originating from chitosan.

The earlier studies have suggested that the sorption of acid dyes on wool and chitosan is governed by similar mechanism (i.e. ion exchange)²⁰. The results of study pointed out that the acid dyes are efficiently sorbed at pH 3.0, likely because of the positively charged surface of the samples (Fig. 4) i.e. due to the protonation of amino groups which become active sites for the interaction with sulphonate groups of dyes. Better sorption properties of CHT and LTP+CHT samples clearly confirm that the amino groups are the main sites for binding of acid dyes. Additionally, van der Waals forces can be formed between aromatic parts of the dye and glucosidic residues of chitosan, and this effect should not be neglected²¹. However, these forces are very much affected by the nature of dye; the higher the r. m. m. and the lower the solubility of the dye, the stronger are the forces²².

Table 2—Sorption of AR88 and AR27 dyes at 60°C
[Sorption time, 1 h; and pH, 3.0]

Dye	Sample	Sorption capacity, mg/g	
		$C_0=100$ mg/L	$C_0=300$ mg/L
AR88	Untreated	49.2	76.8
	CHT	49.4	90.5
	LTP	49.1	74.3
	LTP+CHT	49.3	90.0
AR27	Untreated	31.2	31.6
	CHT	44.7	60.2
	LTP	36.2	39.4
	LTP+CHT	46.2	60.9

C_0 — Initial dye concentration

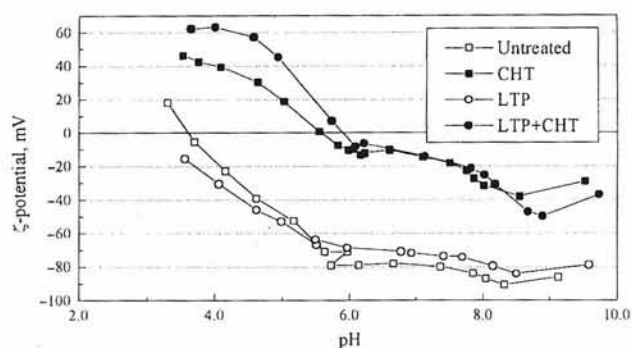


Fig 4— ζ - potential as a function of pH

It is well established that the structure and ionic charge of the dye play an intrinsic role in the sorption of acid dyes on chitosan²³. Several studies demonstrated that a 1:1 stoichiometry between protonated amino groups in chitosan and sulphonate groups of AR88 and AR27 dyes occurs^{23, 24}. Both dyes have similar structure though the former has one and the latter has three sulphonate groups. Thus, the AR27 dye is significantly less sorbed on all investigated samples as a result of higher r. m. m. and better solubility. In other words, the affinity decreases with the increase in degree of sulphonation of the dye and after the first sulphonate group, each additional group has a negative influence on the sorption, facilitating the desorption of dye from the material²⁵. If a 1:1 stoichiometry between amino group of chitosan and anion of the dye is assumed, it is realistic to expect that one sulphonate group of AR27 dye could be bound to chitosan on the material surface while the others two would be oriented towards the solution. This could be confirmed with the results of study on desorption of AR88 and AR27 dyes from the material in 0.100 M NaOH for 30 min. AR88 dye was

desorbed significantly but not completely, whereas AR27 dye was desorbed completely from all investigated samples²⁶.

It is expected that the higher the pH, the worse is the sorption. At pH 6.45, dyes AR88 and AR27 are not sorbed, while AB113 dye is slightly sorbed, suggesting that at this pH the carboxylic groups of wool are present as anions, repulsing the dye from the fibre surface. CHT and LTP+CHT samples do not sorb the dyes since the pK_a of amino groups of chitosan is 6.4, indicating that the only few amino groups of chitosan at 6.45 are dissociated²⁷. Fig. 4 shows that all the samples are negatively charged at pH 6.45.

4 Conclusions

The study indicates that the recycled wool-based nonwoven material can be used as an efficient sorbent for decolorisation of dye solutions. The material shows good sorption properties for all investigated acid dyes (AR88, AR27 and AB113). Chitosan and plasma+chitosan treatments of the material considerably improve the sorption properties for AR88 and AR27 dyes. AB113 dye shows significantly less sorption than AR88 and AR27 dyes and no significant positive effect of low-temperature plasma and/or chitosan treatment of nonwoven material is observed.

Temperature has strong influence on the sorption properties of material for AR88 and AR27 dyes; the effect is particularly pronounced in case of untreated and LTP samples. However, the sorption capacity for AB113 dye is again insignificantly affected by the temperature.

Analysis of electrochemical properties of the material shows that chitosan and plasma+chitosan treatments led to an increase in positive charge on the fibre surface, likely because of the higher content of amino groups originating from chitosan. The increase in amino groups, that are the main sites for binding of dye anions, obviously results in improvement in sorption properties of chitosan and plasma+chitosan treated samples as compared to untreated sample.

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References

1 Laing I G, *Rev Prog Color*, 21 (1991) 56.

- 2 Profile of the Textile Industry: EPA/310-R-97-009, 1997.
- 3 Tincher W C & Robertson J R, *Text Chem Color*, 14 (1982) 41.
- 4 Hönings R, Peters R, Müller B M, Thomas H & Höcker H, *Proceedings, 9th International Wool Textile Research Conference*, Vol. I (International Wool Secretariat, Biella), 1995, 300.
- 5 Tünay O, Kaldasli I, Eremektar G & Orhon D, *Wat Sci Technol*, 34 (1996) 9.
- 6 Smith B, Koonce T & Hudson S, *Am Dyest Rep*, 82 (1993) 18.
- 7 Meyer V, Carlsson F H H & Oellermann R A, *Wat Sci Technol*, 26 (1992) 1205.
- 8 Sanghi R, Bhattacharya B, *Color Technol*, 118 (2002) 256.
- 9 Muzzarelli R A A, *Chitin*, 1st edn (Pergamon Press, Oxford), 1977.
- 10 Yoshida H, Fukuda S, Okamoto A & Kataoka T, *Wat Sci Technol*, 23 (1991) 1667.
- 11 Maclaren J A & Milligan B, *Wool Science - The Chemical Reactivity of the Wool Fibre* (Science Press, Marickville, Australia), 1981.
- 12 Radetic M, Jovic D, Jovancic P, Rajakovic Lj, Potkonjak B & Petrovic Z Lj, *Proceedings, 1st Autex Conference Technitex 2001 - Technical Textiles: Designing Textiles for Technical Applications*, Vol. I (Williams, Lda, Portugal), 2001, 414.
- 13 Choi H M & Moreau J P, *Microscopy Res Technol*, 25 (1993) 447.
- 14 Weltrowski M, Patry J & Beaudoin B, *Proceedings, 9th International Wool Textile Research Conference*, Vol. IV (International Wool Secretariat, Biella), 1995, 343.
- 15 Severich B, *Characterization of Chemical and Physical Properties of Some Polymer Surfaces and Correlation to Chemical Compatibility*, Ph.D. thesis, RWTH-Aachen, Aachen, Germany, 1994.
- 16 Merten T, *The Application of Low-temperature Plasma for Felt-free Treatment of Wool*, Ph.D. thesis, RWTH-Aachen, Aachen, Germany, 1998.
- 17 Monser V, *Barriere Discharge Treatment of Wool*, Ph.D. thesis, RWTH-Aachen, Aachen, Germany, 2001.
- 18 Denda B, *The Influence of Plasma Induced Functionalisation of Fibre Surface on Wool Dyeability*, Ph.D. thesis, RWTH-Aachen, Aachen, Germany, 1999.
- 19 Radetic M, Jovic D, Jovancic P, Rajakovic Lj, Thomas H & Petrovic Z Lj, *Proceedings, 21st Summer School and International Symposium on the Physics of Ionized Gases* (University of Nis, Nis, Serbia and Montenegro), 2002, 486.
- 20 Giles C H, Hassan A S A, Laidlaw M & Subramanian R, *J Soc Dyers Colour*, 74 (1958) 647.
- 21 Giles C H & Hassan A S A, *J Soc Dyers Colour*, 74 (1958) 846.
- 22 Dzokic D, *Theory and Technology of Textile Material Dyeing* (TMF, Beograd), 1989 (in Serbian).
- 23 Maghami G G & Roberts G A F, *Makromol Chem*, 189 (1988) 2239.
- 24 Gummov B D & Roberts G A A, *Makromol Chem*, 186 (1985) 1239.
- 25 Giles C H, Hassan A S A & Subramanian R, *J Soc Dyers Colour*, 74 (1958) 682.
- 26 Radetic M, *Study of Recycled Wool Based Sorption Material with Multifunctional Properties*, Ph.D. thesis, TMF, Belgrade, Serbia and Montenegro, 2003.
- 27 Jovic D, Vilchez S, Topalovic T, Navarro A, Juliá M R & Erra P, *19th IFATCC Congress* (ACIT, France), 2002, CD-ROM, C20.