

## Determination of Dyestuffs Remaining in Dyeing Processes of Vegetable Tanned Leathers and Their Removal by Using Shavings<sup>\*</sup>

Gökhan Zengin<sup>1</sup>, Hasan Ozgunay<sup>1</sup>, Ebru Mavioglu Ayan<sup>2</sup>, Mehmet Mete Mutlu<sup>1†</sup>

<sup>1</sup>Ege University Faculty of Engineering Department of Leather Engineering,

<sup>2</sup>Ege University Faculty of Science Chemistry Department

35100 Bornova-Izmir – TURKEY

### Abstract

Present study aimed on investigation of amounts of acid and metal complex dyes remaining in dyeing processes of vegetable tanned leathers and their removal by using chromium and vegetable shavings as adsorbents. The results indicated that 97-867 mgL<sup>-1</sup> of acid dyes and 15-369 mgL<sup>-1</sup> of metal complex dyes remain at the end of dyeing processes of vegetable tanned leathers. Batch adsorption technique was used in adsorption experiments. The effects of time, pH and adsorbent amount parameters on dye adsorption were investigated. From the results it was clearly seen that both chromium and vegetable shavings could be used as adsorbents for acid and metal complex dyes, while chromium shavings performed better. The experimental data of adsorption isotherms of all dyes fit well to the Langmuir model.

**Keywords:** Leather shavings, Metal complex dye, Acid dye, Adsorption Isotherm

### Introduction

Colour is one of the aspects determining the sale success of a product. Dyes are used to meet the colour demands of customers, which are affected by the individual preferences and fashion. For this reason, they are widely used in industries such as textile, leather, plastics, rubber, paper, cosmetics, automotive and other consumer goods.

The worldwide annual production of dyestuffs is over 7x10<sup>5</sup> tons [1]. However, all of the dyes produced are not consumed totally in production of goods; certain amounts remain in effluents. In 1978 it was estimated that of the 450 000 tones of dye produced worldwide, some 9

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<sup>†</sup> Corresponding author: M.M.Mutlu - E-mail : [mete.mutlu@ege.edu.tr](mailto:mete.mutlu@ege.edu.tr)

000 tones (2%) were discharged in aqueous effluents from manufacturing operations and 40 000 tones (9%) from the coloration sector [2].

A number of synthetic dyes that are continuously emitted into the environment accompanying industrial development have caused great damage to biodiversity, principally due to the release of large volumes of wastewaters containing a high content of organic discharge and strong coloration. Unfortunately, these post-industrial residues find their way into river causeways because the traditional processes used to treat wastewater do not remove these compounds efficiently. Many dyes used in leather treatment can biologically transform to toxic species and cause interference in natural photosynthetic processes [3, 4].

The simple acid dyes and metal complex dyes are the most important and widely used dye groups in the leather industry representing approximately 70% of the total dyes used<sup>5</sup>. It is commonly practiced that these dyes are fixed in high amounts when used in chromium tanned leathers, unlikely less amounts in vegetable tanned leathers [6].

Customers' requirements on quality and fastnesses of products have been increased in recent decades. This has enforced dye manufacturers to produce dyes with better quality, stability, fixation and fastness properties.

Dyes even in very low concentrations affect the aquatic life and food chain. Hence, the removal of dye from process or waste effluents becomes environmentally important. Because of the high degree of organics present in these molecules and the stability of modern dyes, conventional physicochemical and biological treatment methods are ineffective for their removal. This led to the study of other effective methods [7-9].

The adsorption process is one of the effective methods used to remove dyes from aqueous solution. Activated carbon is the most widely used adsorbent for dye removal, but it is too expensive. Consequently numerous low-cost alternative adsorbents have been proposed including peat, fly ash, slag, alunite, clay, chitosan, various pith, and sawdust [7-12].

Shavings which are already wastes of leather industry can be advised as alternative adsorbents. They are generated from shaving process which is applied to tanned leathers for adjusting them to required thickness. As chromium is the most common used tanning agent, chromium-containing leather wastes are a major waste product generated during leather-making processes. It was reported that the U.S. leather industry generates more than 50 000 metric tones of shavings and trimmings each year; and approximately 10 times this amount is generated worldwide [13,14]. Although a part of these waste materials are re-utilized in manufacture, the bulk of the waste, at present, is still disposed of through landfill or incineration, which leads to

resource waste and environmental problems. During recent decades, much attention has been given to the methods of converting these materials into useful products [15].

The aim of the research was to determine the residual amounts of acid and metal complex dyes remaining in dyeing baths of vegetable tanned leathers and removal of them by using chromium and vegetable shavings as adsorbents, which are already wastes for leather industry. The effects of time, pH and adsorbent amount parameters on dye adsorption were investigated. The Langmuir isotherms were used to fit the equilibrium data.

## Materials and Methods

### Materials

A lime splitted pickled hide was used for the trials. Four acid dyes and four 1:1 metal complex dyes having four different types of metal atoms (Cr, Fe, Cu, Co) were used for dyeing processes (Table 1).

Table 1. Types of dyes used in trials

Acid Dyes		Metal Complex Dyes & Central Metal Atoms		
<b>Dye 1</b>	Acid Black 210	<b>Dye 5</b>	Acid Black 172	Cr
<b>Dye 2</b>	Acid Brown 165	<b>Dye 6</b>	Acid Brown 373	Fe
<b>Dye 3</b>	Acid Red 88	<b>Dye 7</b>	Direct Blue 199	Cu
<b>Dye 4</b>	Acid Yellow 36	<b>Dye 8</b>	Mixture of Acid Yellow 194 and Acid Brown 451	Co

Chromium shavings obtained from a local company producing upper leather and vegetable shavings obtained from another local company producing sole leather in Izmir/Turkiye were used as adsorbents in trials. As high amounts of vegetable tannins leached from sole leather shavings during preliminary trials, and due to possibility of absorbance interference in UV spectrophotometer, they were washed with distilled water 2 times for 1.5 hours to remove the excess tannins, dried at 50°C and then grinded in the mill. Chromium shavings were also grinded without any pre-treatment. Then all shavings were dried at 102±3°C.

### Methods

The hide was tanned according to the recipe in Table II, with vegetable tannin (tara). Tara was obtained as a commercial product from Silvachimica S.r.l.

The croupon area of the leather was divided into 18 pieces in size of 15x21 cm as experiment samples. 16 pieces were dyed with 8 different types of dyes (Table 1) with two repetitions, and 2

pieces were processed without any dye as blank samples according to the recipes in Table 2 and Table 3.

### Determination of Dyes

Samples were taken from the baths at the end of dyeing processes and filtered before analysis. Amounts of acid dyes remaining in the baths were determined spectrophotometrically by using Shimadzu UV-1601 spectrophotometer at 464, 425, 508, 425 nm for Dye 1, Dye 2, Dye 3 and Dye 4 respectively.

The amounts of metal complex dyes were determined by using UV-Vis spectrophotometer and Perkin Elmer Optima 2100 DV ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry). Spectrophotometric measurements were done at 572 nm for Dye 5, at 402 nm for Dye 6, at 610 nm for Dye 7 and at 449 nm for Dye 8. The parameters of ICP-OES were axial view, echelle optical system, 1.5 ml/min pump rate, 17 L/min plasma gas, 0.2 L/min. auxiliary gas, 0.8 L/min. nebulizer and 1450 W RF power. Wavelengths used for metal ions were 238.2 nm for Fe, 267.7 nm for Cr, 228.6 nm for Co and 327.4 nm for Cu.

**Table 2.** Preparation of leather samples prior to dyeing process

<i>Process</i>	<i>%</i>	<i>Product</i>	<i>Temp. (°C)</i>	<i>Time (min)</i>	<i>pH</i>
Depickle	200	Water	25		
	7	Salt		5	
Pelts added	1.5	Sodium formate		90	4.2 – 4.5
Drain & Wash					
Tanning	100	Water	25		
	7	Tara		20	
	1.5	Sulphited natural and synthetic fatliquor		45	
	8	Tara		60	
	10	Tara		20	
	0.75	Sulphited natural and synthetic fatliquor			
	0.75	Synthetic fatliquor		360	
	X	HCOOH		60	3.5 – 3.7
Washing	250	Water	25	5	
Horse-up					

**Table 3.** Dyeing process of leather samples

<i>Process</i>	<i>%</i>	<i>Product</i>	<i>Temp. (°C)</i>	<i>Time (min)</i>	<i>pH</i>
Neutralization	200	Water	35		
	2.5	Neutral syntan		30	
	1.5	Sulphited natural and synthetic fatliquor		60	
Washing	250	Water	30	15	
Dyeing	100	Water	35		
	3	Dye		45	
	5	Sulphited natural and synthetic fatliquor	45	60	
	X	HCOOH		30	
	X	HCOOH		30	3.7 – 3.8
Washing	250	Water	25	10	
Horse-up					
Drying					

### Adsorbent Characterization

For characterization of the adsorbents; volatile matter, pH, hide substance, fats and other solubles in dichloromethane, water soluble matter, ash content, chromic oxide content and combined tanning agents and degree of tannage analysis were done according to IUC 5, IUC 11, IUC 10, IUC 4, IUC 6, IUC 7, IUC 8 and D 6020 methods respectively [16,17].

The electrophoresis method was used to determine the zeta potential of the adsorbents, by using Zeta-Meter 3.0+ (with Zeiss DR microscope, GT-2 type quartz cell, molybdenum cylinder anode, and platinum rod cathode) [18]. In order to obtain suspended particles in the solution of 0.025 g/50 mL of dry adsorbent were shaken in bidistilled water (<2.0  $\mu$ S/cm) for 24 hours at room temperature. The pH of dispersions was adjusted by adding either HCl or NaOH solutions. Then, the zeta potential of the particles was measured as a function of pH between 2 and 10 without addition of electrolytes in bidistilled water.

### Batch Adsorption Procedure

In this study, batch experiments were designed to analyze the influence of contact time, pH and dye concentration on the adsorption process. Dyes given in Table I, were used as model compounds. For the adsorption tests, 0.1 g of the adsorbent (particle size below 0.2 mm) was added to 100 mL of the test solutions at pH 2.0 and 3.8. The pH values of the solutions were adjusted by using dilute HCl and NaOH solutions. The suspensions were shaken in a rotary shaker at 150 rpm for a predetermined optimum time. At the end of each experiment the suspensions were filtered to completely remove solid particles and filtrates were analyzed for determining the dye concentration by using a UV-Vis spectrophotometer.

In order to obtain the adsorption isotherm 100 mL of the test solutions of various dye concentrations (80-250 mgL<sup>-1</sup>) were added to 0.1 g of adsorbent in volumetric flasks and the suspensions obtained were shaken for an experimentally predetermined time to establish the equilibrium, after adjustment of pH. The experimentally predetermined optimum pH and equilibrium time values are listed in Table 4. Langmuir and Freundlich isotherms were used to describe adsorption equilibrium data.

**Table 4.** Optimum pH and equilibrium time for the dyes in adsorption isotherms

	Vegetable Shavings		Chromium Shavings	
	pH	Equilibrium Time (Hour)	pH	Equilibrium Time (Hour)
Dye 1	2.0	2	3.8	2
Dye 2	2.0	2	3.8	2
Dye 3	2.0	2	3.8	2
Dye 4	2.0	2	3.8	2
Dye 5	2.0	2	3.8	2
Dye 6	2.0	2	3.8	2
Dye 7	2.0	2	3.8	2
Dye 8	2.0	2	3.8	2

## Results and Discussion

### Amounts of Dyestuff Remaining in Dyeing Baths

From Table 5 it is seen that at the end of the dyeing processes 15-369 mgL<sup>-1</sup> of metal complex dyes, 97-867 mgL<sup>-1</sup> of acid dyes remain in the process baths. Aravindhan et.al. have found that 200-500 ppm of acid dyes and 190-970 ppm metal complex dyes found in effluent of a commercial tannery in India [19].

### Adsorbent Characterization Results

The properties of chromium and vegetable shavings are stated in Table 6.

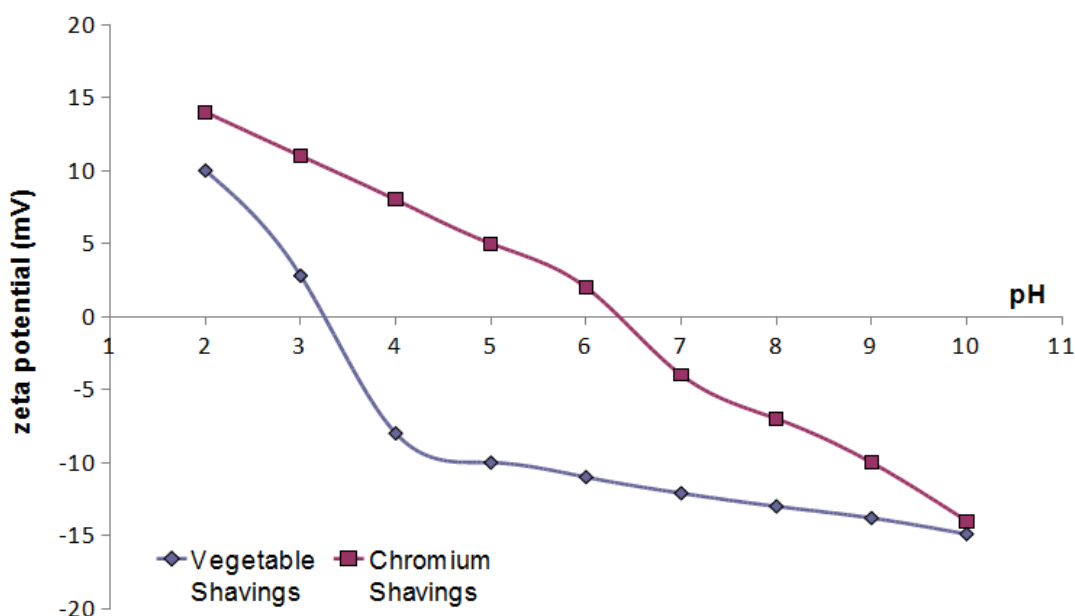
**Table 5.** Amounts of dyes remaining in process baths after dyeing (mgL<sup>-1</sup>)

	<i>Element</i>	<i>Min.</i>	<i>Max.</i>	<i>SD</i>	<i>Mean</i>
Dye 1	-	245.4	260.6	10.7	253.0
Dye 2	-	92.9	100.4	5.3	96.7
Dye 3	-	551.0	592.9	29.6	572.0
Dye 4	-	806.5	928.2	86.1	867.4
Dye 5	Cr	66.4	96.9	21.6	81.7
Dye 6	Fe	357.0	381.2	17.1	369.1
Dye 7	Cu	5.0	24.2	13.6	14.6
Dye 8	Co	171.3	195.8	17.3	183.6

**Table 6.** Properties of chromium and vegetable shavings

	Chromium Shavings	Vegetable Shavings
Volatile Matter (%)	15.8	11.0
pH	3.6	5.2
Hide Substance (%)	82.1	58.7
Fats and Other Solubles in Dichloromethane (%)	0.4	3.9
Water Soluble Matter (%)	4.1	3.2
Ash Content (%)	8.1	1.6
Chromic Oxide (%)	4.0	-
Combined Tanning Agents and Degree of Tannage (%)	-	21.6

Chromium shavings amount to more than 30% of the raw skin based on dry weight and contain about 90% protein and 4-6%  $\text{Cr}_2\text{O}_3$  [20]. Brown et.al. have reported composition of chrome shavings has 12.6% ash, 4.2% chromic oxide, 79.3% protein, 1.1% fat on dry weight basis and 52.8% moisture [13].



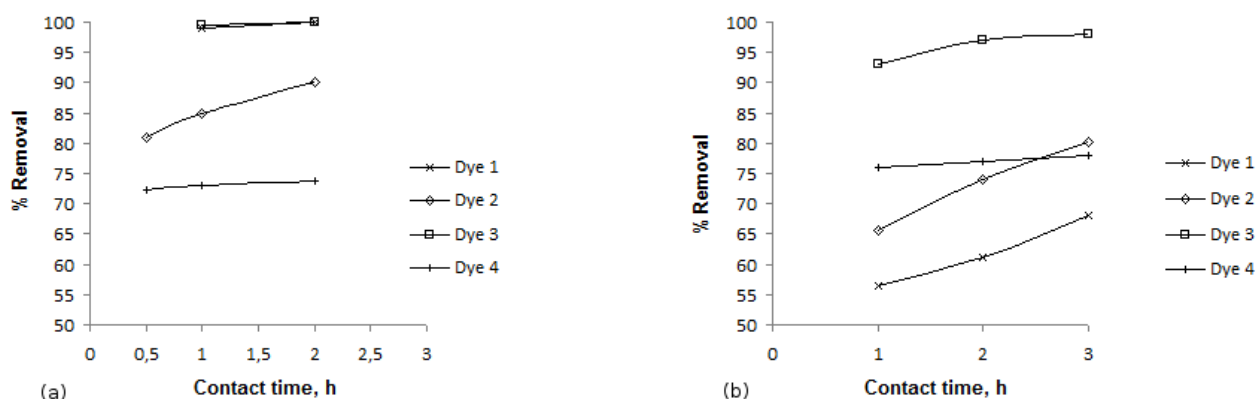
**Fig. 1.** Relationship between zeta potential of vegetable and chromium shavings and pH of buffer solutions.

The surface charges of adsorbents were investigated measuring zeta potential, which can be determined by the measurement of the velocity of particles in the electric field. The zeta-potentials of chromium and vegetable shavings in a pH range of 2.0 to 10.0 were measured. Figure 1 shows the variation of zeta potential of adsorbents as a function of pH. The surface of all adsorbents exhibited an increasing negativity as the pH of the solution increased slightly from 2.0 to 10.0. Chromium and vegetable shavings indicated positive charge values that should be favourable to the attraction between active sites and negative charges of dyes, resulting in an electrostatic interaction.

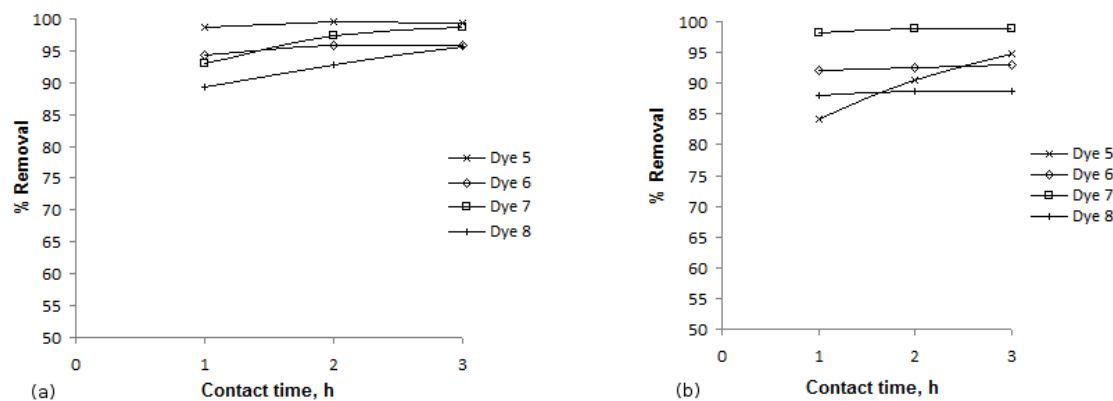
## Dye adsorption

The pH and contact time are the most important factors in the adsorption of dye. The influence of pH on the removal of acid and metal complex dyes was studied at different contact times at pH 2.0 and 3.8. Also, the effect of adsorbent amount was investigated.

Figure 2 shows the acid dye and Figure 3 shows the metal complex dye adsorption capacities of chromium and vegetable shavings as a function of contact time with an initial 100 mgL<sup>-1</sup> concentration of dye and an adsorbent amount of 0.1 g for 100 mL of dye solution.



**Fig. 2.** Acid dye adsorption capacity of (a) chromium (at pH 3.8) and (b) vegetable shavings (at pH 2.0) as a function of contact time



**Fig. 3.** Acid dye adsorption of (a) chromium (at pH 3.8) and (b) vegetable (at pH 2.0) shavings as a function of contact time

It can be seen that between 1 and 3 h, there was an approximately 1-6% variation in adsorption capacity. Therefore, it was decided not to extend the investigation to a larger period of time and the optimum contact time has been chosen as 2 hours.



The optimum pH values were 3.8 for the chromium shavings and 2.0 for the vegetable shavings. These were expected pH values; because, a pH value below the isoelectric point (IEP) of leather is required for fixation of acid dyes. Considering Zeta Potentials of two adsorbents (Figure 1), the selected optimum pH values are below their IEPs. Adsorption of acid and metal complex dyes is favourable at acidic pH due to the presence of excess  $H^+$  ions which caused electrostatic attraction.

As seen in Table 7, the adsorption capacities for chromium shavings were approximately equal at pH 2.0 and pH 3.8. So, pH 3.8 which is the general final fixation pH of dyeing process was chosen as the optimum pH value.

The pH has strongly affected the adsorption capacity for vegetable shavings and the maximum uptake of the dyes was observed at pH 2.0. So, pH 2.0 was chosen as the optimum pH value (Table 7).

**Table 7.** The pH effect of the adsorption capacity (removal %) of the acidic and metal complex dyes for vegetable and chromium shavings

	Vegetable Shavings		Chromium Shavings	
	pH 2.0	pH 3.8	pH 2.0	pH 3.8
Dye 1	61.1	34.6	87.4	88.1
Dye 2	74.0	38.0	97.7	88.9
Dye 3	97.0	67.4	99.5	99.4
Dye 4	77.1	25.3	79.6	73.7
Dye 5	90.5	55.9	99.5	98.5
Dye 6	92.7	71.3	95.9	88.4
Dye 7	80.8	43.9	97.3	99.8
Dye 8	88.6	52.1	92.9	96.4

To investigate the effect of adsorbent amount on the adsorption of dye on vegetable and chromium shavings, batch experiments were carried out at 0.1, 0.25 and 0.5 gram for 100mL test solution. There was an approximately 2-10% variation in adsorption capacity between 0.1 and 0.5 gram adsorbent amounts. Therefore the optimum adsorbent amount has been chosen as 0.1 gram.

### Adsorption Isotherms

In the study, Langmuir and Freundlich isotherms which are commonly used for adsorption have been tested for vegetable and chromium shavings. For adsorption capacities obtained for chromium shavings and vegetable shavings (Table 8) Langmuir model was found to fit well to the experimental data for all adsorbents as indicated by the higher correlation coefficients ( $R^2 \geq 0.95$ ).

Zhang and Shi have also studied on adsorption behaviours of chromium-containing leather waste towards Acid Yellow 11 and Direct Red 31 in aqueous solution. They have stated that both the acid dye and direct dye could be significantly adsorbed by this adsorbent and acid pH values favoured the adsorption and the adsorption capacity decreased with the increase of pH, and the experimental data of adsorption isotherms of both the dyes fit well to the Langmuir model rather than the Freundlich model [15].

**Table 8.** Adsorption capacities for chromium and vegetable shavings

	<b>Chromium Shavings</b>	<b>Vegetable Shavings</b>
	<b>S<sub>M</sub> (mg g<sup>-1</sup>)</b>	<b>S<sub>M</sub> (mg g<sup>-1</sup>)</b>
Dye 1	123.5	68.0
Dye 2	166.7	119.1
Dye 3	333.3	144.9
Dye 4	454.5	154.1
Dye 5	172.4	111.1
Dye 6	166.7	125.0
Dye 7	142.9	100.0
Dye 8	166.7	133.0

## Conclusions

From the evaluation of adsorption capacities of adsorbents it is seen that chromium shavings performed better owing to their more positive surface charge. However, dyes belonging to same group showed different adsorption properties depending on their chemical structure. The greatest adsorption capacities of chromium and vegetable shavings, through the dyes used in the experiments, were for Dye 3 (Acid Red 88) and Dye 4 (Acid Yellow 36). The experimental data of adsorption isotherms of all dyes fit well to the Langmuir model.

The results indicated that both the acid dyes and metal complex dyes could be significantly adsorbed by both adsorbents. As chromium and vegetable shavings are collagenous material they have many functional groups available for reaction with dyes, which makes them valuable adsorbents for removal of dyes from effluents of tanneries. It is probably also worth mentioning that the shavings are abundant and free of charge material for leather industry.

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## References

1. Poon C.S., Huang Q.P., Fung C., 1999, Degradation of cuprophenyl Yellow RL by UV/H<sub>2</sub>O<sub>2</sub>/Ultrasonication (US) process in aqueous solution, *Chemosphere*, 38, 1005–1014p.
2. Brown D., 1987, *Ecotoxicology Environ. Safety*, 13, 139p.
3. Buitron G., Gonzales A., 1996, *Water Sci. Technol.*, 34, 289p.
4. Mohn W. W., Martin V. J. J. E., Yu Z. T., 1999, *Water Sci. Technol.*, 40, 273p.
5. Tremlett R.J., Leafe M. K., 1999, *Leather Technologists Pocket Book*, Society of Leather Technologists and Chemists, 101p.
6. Ozgunay H., Mutlu M.M., Kilicariskan C., Yumurtas A., 2009, *Tekstil ve Konfeksiyon*, 4, 292p.
7. Malik P.K., 2003, *Dyes Pigments*, 56, 239p.
8. Chiou M.S., Li H.Y., 2003, *Chemosphere*, 50, 1095p.
9. Shukla A., Zhang Y.H., Dubey P., Margrave J.L., Shukla S.S., 2002, *J. Hazard. Mater.*, 95, 137p.
10. Garg V.K., Gupta R., Yadav A.B., Kumar R., 2003, *Bioresour. Technol.*, 89, 121p.
11. Ozacar M., Sengil I.A., 2005, *Bioresour. Technol.*, 96, 791p.
12. Ramakrishna K.R., Viraraghavan T., 1997, *Waste Management*, 17 (8), 483p.
13. Brown E.M., Taylor M.M., Marner W.M., 1996, *Journal of the American Leather Chemists Association*, 91(10), 270p.
14. Cabeza L.F., Taylor M.M., Dimaio G.L., Brown E.M., Marmer W.N., Carrio R., Celma P.J., Cot J., 1998, *Waste Management*, 18, 211p.
15. Zhang M., Shi B., 2004, *Journal of the Society of Leather Technologists and Chemists*, 88 (6), 236p.
16. SLTC Official Methods of Analysis, 1996
17. American Society for Testing and Materials (ASTM), 2005
18. Saka E.E., Guler C., 2006, *Clay Minerals*, 41, 853p.
19. Aravindhan R., Fathima N.N., Rao R., Nair U., 2006, *Journal of the American Chemists Association*, 101, 223p.
20. Cot J., Aramon C., 1986, *Journal of the Society of Leather Technologists and Chemists*, 70 (3), 69p.