Pol. J. Environ. Stud. Vol. 21, No. 2 (2012), 499-508

Original Research

Determination of Dyestuffs Remaining in Dyeing Processes of Vegetable-Tanned Leathers and Their Removal Using Shavings

Gokhan Zengin[1], Hasan Ozgunay[1], Ebru Mavioglu Ayan[2], Mehmet Mete Mutlu[1]*

[1]Faculty of Engineering, Department of Leather Engineering, Ege University
[2]Chemistry Department, Faculty of Science, Ege University
35100 Bornova-Izmir, Turkey

Received: 3 February 2011
Accepted: 23 June 2011

Abstract

This study investigates amounts of acid and metal complex dyes remaining in baths after the dyeing processes of vegetable tanned leathers and their removal using chromium and vegetable shavings as adsorbents. The results indicated that 97-867 mgL^{-1} of acid dyes and 15-369 mgL^{-1} of metal complex dyes remain at the end of dyeing processes of vegetable-tanned leathers. The adsorption behaviors of chromium and vegetable shavings were investigated toward four acid dyes and four 1:1 metal complex dyes having four different types of metal atoms (Cr, Fe, Cu, Co). Batch adsorption technique was used in adsorption experiments. The effects of time, pH, and adsorbent amount parameters on dye adsorption were investigated. Optimum pH values were pH 2.0 and pH 3.8 for vegetable shavings and chromium shavings, respectively. Adsorption capacities of chromium and vegetable shavings were found to be between 123.5-454.5 $mg\cdot g^{-1}$ and 68.0-154.0 $mg\cdot g^{-1}$ depending on the type of dye. 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

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

The worldwide annual production of dyestuffs is over 700,000 tons [1]. However, all of the dyes produced are not totally consumed in the production of goods; certain amounts remain in effluents. In 1978 it was estimated that of the 450,000 tons of dye produced worldwide, some 9,000 tons (2%) were discharged in aqueous effluents from manufacturing operations and 40,000 tons (9%) from the coloration sector [2].

A number of synthetic dyes that are continuously released into the environment accompanying industrial development have caused great damage to biodiversity, principally due to the release of large volumes of wastewaters containing 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

---

*e-mail: mete.mutlu@ege.edu.tr

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 [5]. It is commonly practiced that these dyes are fixed in high amounts when used in chromium-tanned leathers, unlikely lower amounts in vegetable-tanned leathers [6].

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

Dyes even in very low concentrations affect 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 has 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 solutions. 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 that are already wastes of leather industry can be advised as alternative adsorbents [13-15]. They are generated from the shaving process that is applied to tanned leathers for adjusting them to required thickness. As chromium is the most commonly 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 tons of shavings and trimmings each year, and approximately 10 times this amount is generated worldwide [16, 17]. The production of chromium-containing solid wastes in tanneries has been recognized as a problem for many years. 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. Recently, pressure from environmental authorities has given the problem increasing urgency. As a result, many scientific groups have oriented their research to find a process to recycle and reuse these tanned wastes [18-23].

The aim of our research was to determine the residual amounts of acid and metal complex dyes remaining in dyeing baths of vegetable-tanned leathers and remove them 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 isothermal equilibrium data obtained were processed by employing Langmuir and Freundlich isotherm equations.

Table 1. Types of dyes used in trials.

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

Materials and Methods

Materials

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

Chromium shavings obtained from a local company producing upper leather and vegetable shavings obtained from another local company producing sole leather in Izmir/Turkey were used as adsorbents in trials. As high amounts of vegetable tannins leached from sole leather shavings during preliminary trials, and due to the possibility of absorbance interference in the UV spectrophotometer, they were washed with distilled water 2 times for 1.5 hours to remove the excess tannins, dried at 50ºC, and then ground in the mill. Drying temperature was selected as 50ºC because the shrinkage temperatures of vegetable tanned leathers are between 75-85ºC in wet state. Chromium shavings were also ground without any pretreatment. Because their shrinkage temperatures are over 100ºC in dry state, they were later dried at 102±3ºC.

Methods

The hide was tanned according to the recipe in Table 2, 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 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 Tables 2 and 3.

Determination of Dyes

Samples were taken from the baths at the end of dyeing processes and filtered (Whatman No. 1) before analysis. Amounts of acid dyes remaining in the baths were determined using a Shimadzu UV-1601 model UV-Visible spectrophotometer at 464, 425, 508, and 425 nm for Dye 1, Dye 2, Dye 3, and Dye 4, respectively. The amounts of metal complex dyes remaining in the baths were deter-

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

Process	%	Product	Temp. (ºC)	Time (min)	pH
Depickle	200	Water	25		
	7	Salt		5	
Pelts added	1.5	Sodium formate		90	4.2-4.5
Drain and 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.

Process	%	Product	Temp. (ºC)	Time (min)	pH
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					

mined by using Perkin Elmer Optima 2100 DV model ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry). 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.

UV-Vis Spectroscopy which gives easier, rapid, and economic measurement opportunity was used in the batch adsorption experiments where a large number of measurements would be carried out. 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.

Adsorbent Characterization

For characterization of the adsorbent, 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 [24, 25]. (IUC: The official methods

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

of the International Leather Chemists' Societies for chemical leather analysis).

The surface areas of the adsorbents were determined using the standard nitrogen adsorption porosimetric technique employing the BET method in a Quantachrome NOVA automated gas sorption system [14].

The electrophoresis method was used to determine the zeta potential of the adsorbents using a Zeta-Meter 3.0+ (with Zeiss DR microscope, GT-2 type quartz cell, molybdenum cylinder anode, and platinum rod cathode) [26]. 0.025 g dry adsorbent was shaken in 50 mL bidistile water (<2.0 µS/cm) for 24 hours at room temperature, in order to obtain suspended particles in the solution. 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 the addition of electrolytes in bidistile water.

Batch Adsorption Procedure

Batch experiments were designed to analyze the influence of contact time, pH and dye concentration on the adsorption process. Dyes given in Table 1, 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 using a UV-Vis spectrophotometer. Whatman No. 1 filter was used for filtration. As the dye could be adsorbed by the filter, the first 30-40 mL of the filtrate was discarded and the rest of the solution was used in measurements.

Various dye concentrations were studied in dye adsorption experiments by Wang et al., Oliveira et al., and Zhang and Shi as 100-500 mgL^{-1}, 25-1000 mgL^{-1}, and 50-2000 mgL^{-1}, respectively [18, 27, 28]. In order to obtain the adsorption isotherms, 100 mL of the test solutions of various dye concentrations (80-250 mgL^{-1}) were added to 0.1 g of adsorbent in volumetric flasks and the suspensions obtained were shaken for an experimentally predetermined time to establish equilibrium (after adjustment of pH). All the experiments were carried out with two repetitions, and their mean values were used if the difference between the results was less than 5%.

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 5. Amounts of dyes remaining in process baths after dyeing (mgL^{-1}).

	Element	Min.	Max.	SD	Mean
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

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^{-1} of metal complex dyes and 97-867 mgL^{-1} of acid dyes remain in the process baths. Aravindhan et al. have found 200-500 ppm of acid dyes and 190-970 ppm metal complex dyes in effluent of a commercial tannery in India [29].

Adsorbent Characterization Results

Chromium shavings amount to more than 30% of the raw skin based on dry weight and contain about 90% protein and 4-6% Cr_2O_3 [30]. 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 [16]. Vegetable shavings amount to 8-11% of vegetable tanned sole leather on sammed weight. For the other types of vegetable-tanned leathers, this ratio is expected to be higher. This amount varies depending on the splitting thickness and type of the product. The properties of chromium and vegetable shavings used in the study are stated in Table 6.

Although both samples were shavings, they exhibited different characteristics. The reason for that is the hides were

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
Specific surface area (m^2/g)	2.070	5.941

tanned with different tanning materials and the tanning materials determine predominantly the characteristics of leathers. While the combined tanning agent amount of vegetable shavings was 21.6%, the Cr_2O_3 content of chromium shavings was 4.0%. This is due to their different percentage of use in tanning over the pelt weight (min. 20% tannin for vegetable tannage, min. 2.5% Cr_2O_3 for chromium tannage). Hide substances of vegetable shavings were found lower because of a higher amount of tanning materials combined to leather. Also, the ash contents of shavings were different as chromium is an inorganic tanning material, whereas vegetable tannins are organic. We have determined the specific surface areas of chromium and vegetable shavings as 2.070 m^2/g and 5.941 m^2/g. Sreeram et al. have determined specific surface area and average pore radius of chromium shaving dusts as 3.6786 m^2/g and 32.8 Å [14]. Depending on the type of tanning materials and tanning parameters used, the pH values were different for both shavings. However, isoelectric points of materials are more important on adsorption properties.

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. Fig. 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 between pH 2.0 and 3.8 that should be favorable to the attraction between active sites and negative charges of dyes, resulting in an electrostatic interaction. Their isoelectrical points were found to be pH 6.4 and 3.2 for chromium and vegetable shavings, respectively. The isoelectric points of inorganic chromed hide powder and mimosa tanned hide powder were found to be pH 6.3 and 3.4 by Heidemann [31].

Dye Adsorption

pH and contact time are the most important factors in the adsorption of dyes. 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. In leather processing, dyeing processes are finalized between pH 3.5-4.0, generally about 3.8 for fixation of anionic dyes. This pH was chosen with the aim to investigate the adsorption of dyes remaining in dyeing baths without any pH adjustment. After the pre-trials it was seen that adsorption at this pH was not so high, especially with vegetable shavings. While chromium reacts with $-COO^-$ groups in chromium-tanned leathers, vegetable tannins mainly react with amino groups; so fewer groups remain to react with dyes in vegetable shavings. For this reason, to bring the pH below the isoelectric point in order to charge more $-NH_2$ groups and to make them available for reaction with dyes, pH 2 was also studied in the research (especially for vegetable shavings). Also, the effect of adsorbent amount was investigated.

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

It can be seen that between 1 and 3 h, there was an approximate 1-6% variation in removal percentage. 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.

Removal percentages for chromium shavings were approximately 10% higher for 3 dyes at pH 2.0 (Table 7). However, the removal percentages were equal or higher for the remaining 5 dyes at pH 3.8. Considering the majority of dyes and advantage of possible direct treatment of dyeing bath without pH adjustment, pH 3.8 was chosen as the optimum pH value for the chromium shavings.

pH has strongly affected the removal percentages of vegetable shavings and the uptake of the dyes was better at pH 2.0 than pH 3.8. So, pH 2.0 was chosen as the optimum pH value for the vegetable shavings (Table 7).

These were expected pH values for both adsorbents because a pH value below the isoelectric point (IEP) of

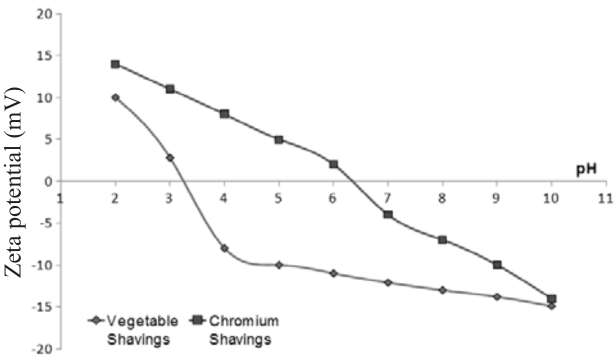

Fig. 1. Relationship between zeta potential of vegetable and chromium shavings and pH of buffer solutions.

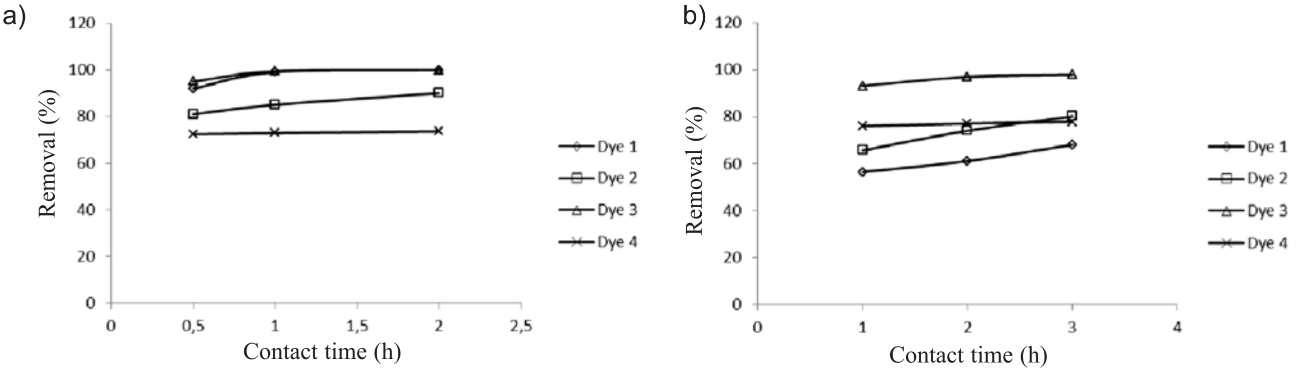

Fig. 2. Acid dye adsorption capacity of (a) chromium (at pH 3.8) and (b) vegetable shavings (at pH 2.0) as a function of contact time.

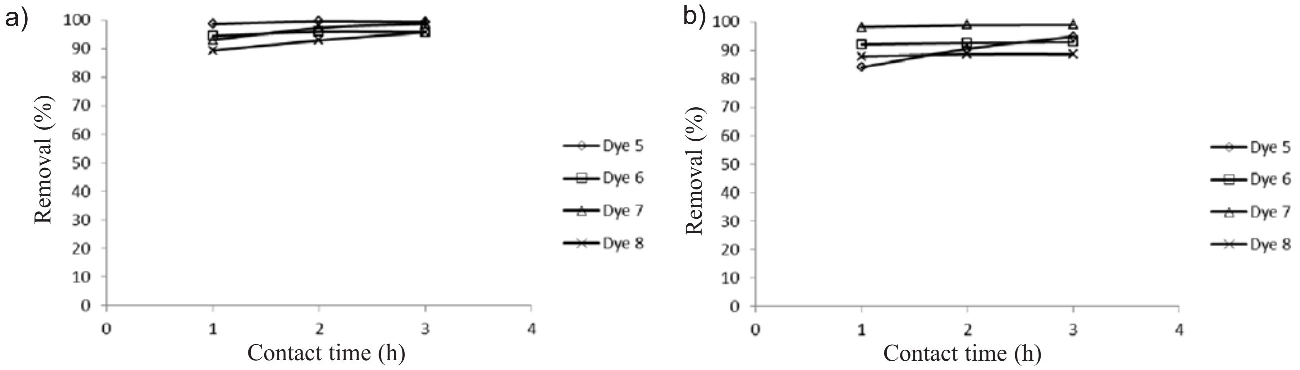

Fig. 3. Acid dye adsorption of (a) chromium (at pH 3.8) and (b) vegetable (at pH 2.0) shavings as a function of contact time.

leather is required for fixation of acid dyes. Considering Zeta Potentials of two adsorbents (Fig. 1), the selected optimum pH values are below their IEPs. Adsorption of acid and metal complex dyes is favorable at acidic pH due to the presence of excess H^+ ions that caused electrostatic attraction.

To investigate the effect of adsorbent amount on the adsorption of dye on vegetable and chromium shavings, batch experiments were carried out with 0.1, 0.25, and 0.5 g for a 100 mL·100 mgL^{-1} concentration of dye solution. There was an approximately 2-10% variation in removal percentages between 0.1 and 0.5 g adsorbent amounts (Removal percentages for Acid Black 210 were 87.4 for 0.1 g, 89.7 for 0.25 g, and 91.5 for 0.5 g. Removal percentages for Acid Red 88 were 99.4 for 0.1 g, 99.5 for 0.25 g, and 100 for 0.5 g). Therefore, the optimum adsorbent amount has been chosen as 0.1 gram.

Table 7. The pH effect of 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

Adsorption Isotherms

Langmuir and Freundlich isotherms that are commonly used for adsorption experiments have been tested for vegetable and chromium shavings. To further understand the adsorption mechanism of adsorbents to dyes, the isotherm equilibrium data were analyzed by the Langmuir model (1) and the Freundlich model (2).

The Langmuir model is expressed as:

$$C_e/q_e = 1/K_L S_M + C_e/S_M \tag{1}$$

...where: S_M ($mg \cdot g^{-1}$) is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface, q_e is the amount of dye absorbed ($mg \cdot g^{-1}$) at equilibrium, K_L (mg^{-1}) is the Langmuir constant, and C_e is the equilibrium liquid phase concentration of dye solutions.

The Freundlich model is given as:

$$q_e = K_F \, C_e^{1/n} \tag{2}$$

...where: K_F is the maximum amount of adsorption and is an indicator of the adsorption capacity. Where C_e and q_e are the equilibrium concentrations and the amount of dye absorbed (mg·g^{-1}) at equilibrium, respectively. n is the Freundlich constant.

Langmuir and Freundlich constants are related to the strength of adsorption. S_M and K_L in the Langmuir model and $1/n$ and K_F in the Freundlich model can be obtained by plotting C_e/q_e *vs*. C_e and log q_e *vs*. log C_e, respectively.

The adsorption isotherms of chromium and vegetable shavings are given in Figs. 4a, 4b, 5a, and 5b. From the figures, it was clearly seen that the experimental data fit well to the Langmuir model ($R^2 \geq 0.95$). This implies that the dyes are adsorbed on the surface of adsorbent in monolayer coverage.

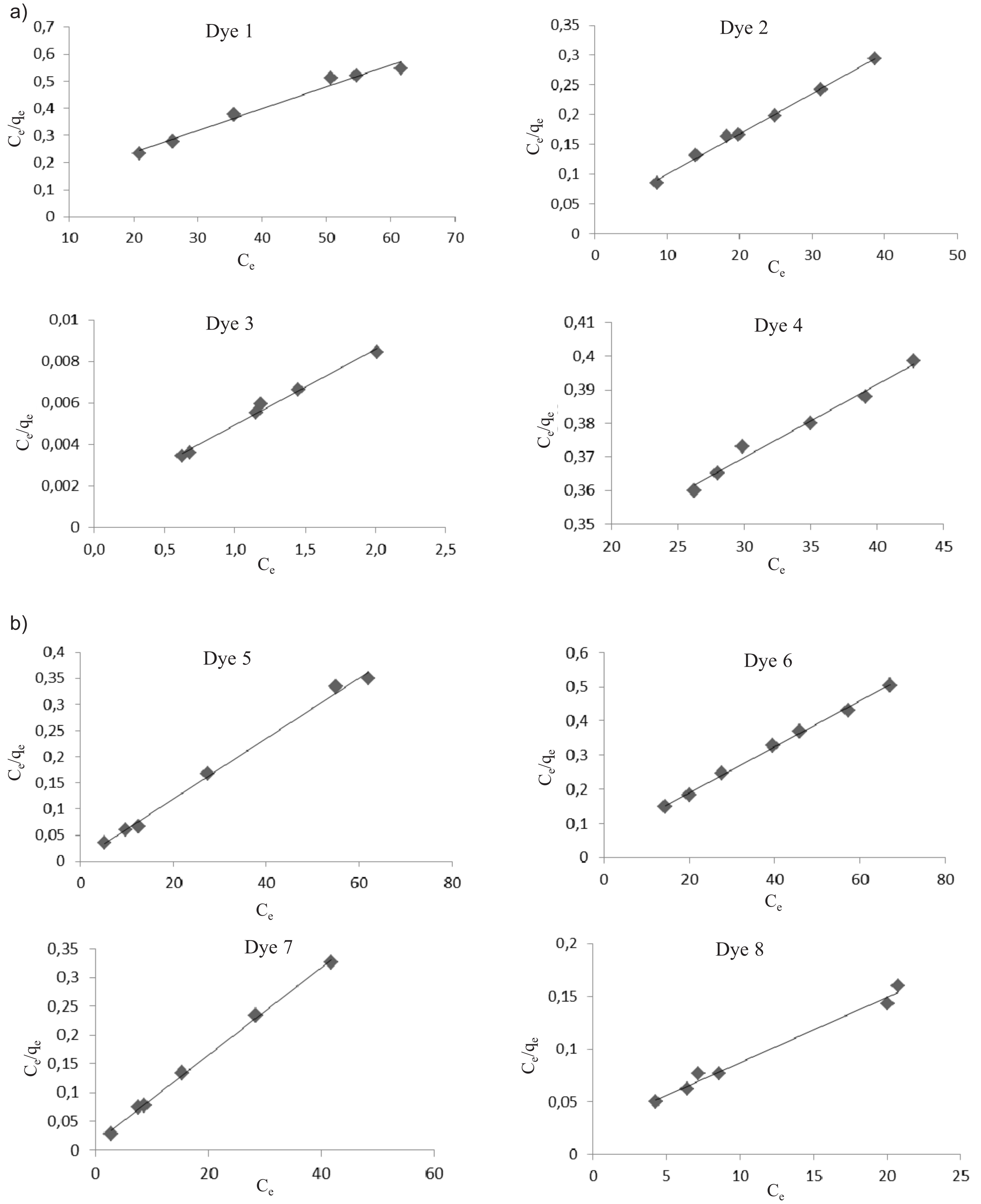

Fig. 4. Adsorption isotherms at 25ºC for a) acid dyes on chromium shavings, b) metal complex dyes on chromium shavings.

Zhang and Shi have also studied adsorption behaviors of chromium-containing leather waste toward 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 that acid pH values favored 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 [18].

Adsorption parameters of chromium and vegetable shavings obtained for Langmuir isotherms are given in Table 8.

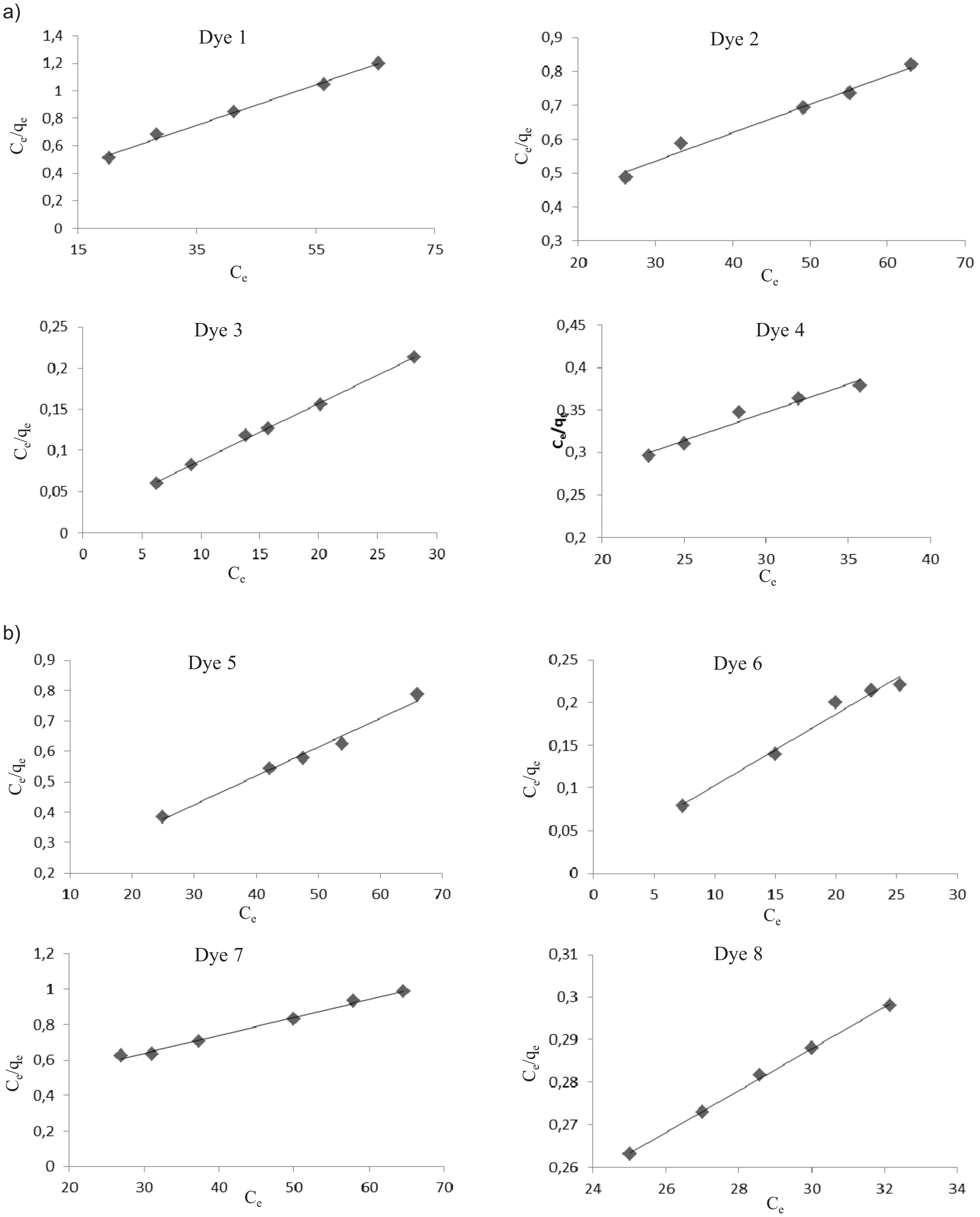

Fig. 5. Adsorption isotherms at 25ºC for a) acid dyes on vegetable shavings, b) metal complex dyes on vegetable shavings.

Table 8. Adsorption parameters obtained for Langmuir isotherm.

	Chromium Shavings			Vegetable Shavings		
Dyes	S_M (mg·g^{-1})	K_L(1/mg)	R^2	S_M (mg·g^{-1})	K_L(1/mg)	R^2
Dye 1	123.5	0.11	0.98	68.0	0.003	0.99
Dye 2	166.7	0.19	0.99	119.1	0.03	0.98
Dye 3	333.3	2.31	0.99	144.9	0.36	0.99
Dye 4	454.5	0.007	0.98	154.1	0.41	0.96
Dye 5	172.4	1.28	0.99	111.1	0.066	0.98
Dye 6	166.7	0.11	0.99	125.0	0.33	0.98
Dye 7	142.9	0.53	0.99	100.0	0.03	0.99
Dye 8	166.7	0.24	0.99	133.0	0.01	0.99

Adsorption capacities of chromium and vegetable shavings were found to be between 123.5-454.5 mg·g^{-1} and 68.0-154.0 mg·g^{-1}, depending on type of the dye (Table 8). The functional groups available in leathers for reaction with dyes are mainly the -NH$_2$, -CO-NH-, and -COO$^-$ groups [14]. As leathers are generally dyed with anionic dyes, they react with positively charged -NH$_3^+$ groups. While chromium reacts with -COO$^-$ groups in leathers, vegetable tannins mainly react with -NH$_2$, -CO-NH- groups, fewer groups remain to react with dyes in vegetable shavings. For this reason comparing the adsorption capacities of the adsorbents, chromium shavings generally have shown higher values than vegetable ones. Within the dyes used in experiments, maximum adsorption capacities were observed for Dyes 3 and 4, of which Dye 4 was the maximum for both adsorbents.

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 the 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 the Langmuir model well.

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 tannery effluent. It is probably also worth mentioning that the shavings are abundant and free of charge material for the leather industry.

A question may arise about the evaluation of the dye-enriched shavings. Conventionally, chrome-tanned wastes, splits, trimmings, and shavings have been useful in obtaining glue, gelatin, protein flavor and reconstituted collagen [32]. The adsorbed dye could limit their conventional evaluation. Alternatively, dye-enriched adsorbents can be evaluated in production of composite materials such as leather-board and porous clay brick [16, 33].

Acknowledgements

The authors wish to acknowledge financial support from the Ege University Scientific Research Projects Unit (Project No. 2009-MUH-020) and instrumental support from DPT (Project No. 2007-DPT-001).

References

1. POON C.S., HUANG Q.P., FUNG C. Degradation of Cuprophenyl Yellow RL by UV/H$_2$O$_2$/Ultrasonication (US) process in aqueous solution, Chemosphere, **38**, 1005, **1999**.
2. BROWN D. Effects of colorants in the aquatic environment, Ecotox. Envıron. Safe, **13**, (2), 139, **1987**.
3. BUITRON G., GONZALES A. Characterization of the microorganisms from an acclimated activated sludge degrading phenolic compounds, Water. Sci. Technol., **34**, (5-6), 289, **1996**.
4. MOHN W. W., MARTIN V. J. J. E., YU Z. T. Biochemistry and ecology of resin acid biodegradation in pulp and paper mill effluent treatment systems, Water. Sci. Technol., **40**, (11-12), 273, **1999**.
5. TREMLETT R.J., LEAFE M. K. Leather Technologists Pocket Book, Society of Leather Technologists and Chemists, 101, **1999**.
6. OZGUNAY H., MUTLU M.M., KILICARISLAN C., YUMURTAS A. Dyeing properties of simple acid and metal-complex dyestuffs on the leathers tanned with various tanning materials, Journal of Textile and Apparel, **4**, 292, **2009**.
7. MALIK P.K. Use of activated carbon prepared from sawdust and rice husk for adsorption of acid dyes: a case study of acid yellow 36, Dyes Pigments, **56**, 239, **2003**.
8. CHIOU M.S., LI H.Y. Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, Chemosphere, **50**, (8), 1095, **2003**.

9. SHUKLA A., ZHANG Y.H., DUBEY P., MARGRAVE J.L., SHUKLA S.S. J. The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater., **95**, (1-2), 137, **2002**.
10. GARG V.K., GUPTA R., YADAV A.B., KUMAR R. Dye removal from solution by adsorption on treated sawdust, Bioresource Technol., **89**, 121, **2003**.
11. OZACAR M., SENGIL I.A. Adsorption of metal complex dyes from aqueous solutions by pine sawdust, Bioresource Technol., **96**, (7), 791, **2005**.
12. RAMAKRISHNA K.R., VIRARAGHAVAN T. Use of slag for dye removal, Waste Manage., **17**, (8), 483, **1997**.
13. TAHIRI S., MESSAOUDI A., ALBIZANE A., AZZI M., BOUHRIA M., YOUNSSI S.A., BENNAZHA J., MABROUR J. Removal of dyes from aqueous solutions by adsorption on chrome-tanned solid wastes generated in the leather industry, Water Quality Journal of Canada, **38**, (2), 393, **2003**.
14. SREERAM K.J., SARAVANABHAVAN S., RAO J.R., NAIR B.U. Use of chromium-collagen wastes for the removal of tannins from wastewaters, Ind. Eng. Chem. Res., **43**, (17), 5310, **2004**.
15. GAMMOUN A., TAHIRI S., ALBIZANE A., BOUHRIA M., AZZI M., GUARDIA de la M. The Use of Chrome Shavings for the Decontamination of Water Polluted with Dyes and Oils, Water Quality Journal of Canada, **42**, (1), 46, **2007**.
16. BROWN E.M., TAYLOR M.M., MARNER W.M. Production and potential uses of co-products from solid tannery waste, J. Am. Leather Chem. As, **91**, (10), 270, **1996**.
17. CABEZA L.F., TAYLOR M.M., DIMAIO G.L., BROWN E.M., MARMER W.N., CARRIO R., CELMA P.J., COT J. Processing of leather waste: pilot scale studies on chrome shavings. Isolation of potentially valuable protein products and chromium, Waste Manage., **18**, 211, **1998**.
18. ZHANG M., SHI B. Adsorption of dyes from aqueous solution by chromium-containing leather waste, J. Soc. Leath. Tech. Ch., **88**, (6), 236, **2004**.
19. TAHIRI S., AZZI M., ALBIZANE A., MESSAOUDI A., BOUHRIA M., SIBARI A. Processing of chrome tanned solid waste generated in the leather industry: recovery of proteins and synthesis of a pigment for paint. Journal of the American Chemists Association, **96**, 1, **2001**.
20. TAHIRI S., AZZI M., ALBIZANE A., MESSAOUDI A., BOUHRIA M., ALAMI YOUNSSI S., MOURID A., AMGHAR J. Study of quality of a pigment prepared by complexation of chromates recovered from treated chrome shavings and tanned splits, Journal of the American Chemists Association, **96**, 426, **2001**.
21. TAYLOR M.M., CABEZA L.F., DIMAIO G.L., BROWN E.M., MARMER W.N., CARRIO R., CELMA P.J., COT J. Processing of leather waste: pilot scale studies on chrome shavings. Part I. Isolation and characterization of protein products and separation of chrome cake, Journal of the American Chemists Association, **93**, 61, **1998**.
22. CABEZA L.F., TAYLOR M.M., DIMAIO G.L., BROWN E.M., MARMER W.N., CARRIO R., CELMA P.J., COT J. Processing of leather waste: pilot scale studies on chrome shavings. Part II. Purification of chrome cake and tanning trials, Journal of the American Chemists Association, **93**, 83, **1998**.
23. PANSWAD T., CHAVALPARIT O., SUCHARITTHAM Y., CHAROENWISEDSIN S. A benchscale study on chromium recovery from tanning wastewater, Water. Sci. Technol., **31**, 73, **1995**.
24. SLTC Official Methods of Analysis, **1996**.
25. American Society for Testing and Materials (ASTM), **2005**.
26. SAKA E.E., GULER C. The effects of electrolyte concentration, ion species and pH on the zeta potential and electrokinetic charge density of montmorillonite, Clay Miner., **41**, (4), 853, **2006**.
27. WANG Y.L., LIAO X.P., GU Y.C., ZHAO S.L., SHI B. Alternative utilization of skin wastes: preparation of a Fe(III)-loaded adsorbent for anionic dyes in aqueous solution, J. Soc. Leath. Tech. Ch., **90**, (5), 205, **2006**.
28. OLIVEIRA L.C.A., GONCALVES M., OLIVEIRA D.Q.L., GUERREIRO M.C., GUILHERME L.R.G., DALLAGO R.M. Solid waste from leather industry as adsorbent of organic dyes in aqueous-medium, J. Hazard. Mater., **141**, 344, **2007**.
29. ARAVINDHAN R., FATHIMA N.N., RAO R., NAIR U. Utilization of calcium alginate beads as adsorbent for removal of dyes from tannery wastewaters, Journal of the American Chemists Association, **101**, 223, **2006**.
30. COT J., ARAMON C. Waste processing in the tannery: production of gelatin, reconstituted collagen and glue from chrome-tanned leather splits and trimmings subjected to a modified detanning process, J. Soc. Leath. Tech. Ch., **70**, (3), 69, **1986**.
31. HEIDEMANN E. The principle of binding mechanism, binding forces of chemical compounds on collagen, Fundamentals of Leather Manufacture, Printed by Roetherdruck, Darmstadt, ISBN 3-7929-0206-0, pp. 259-261, **1993**.
32. KANAGARAJ J., VELAPPAN K. C., CHANDRA BABU N. K., SADULLA S. Solid wastes generation in the leather industry and its utilization for cleaner environment - A review, Journal of Scientific and Industrial Research (JSIR), **65**, (07), 541, **2006**.
33. BITLISLI B. O., KARACAKI E. Utilisation of leather industry solid wastes in the production of porous clay brick, J. Soc. Leath. Tech. Ch., **90**, (1), 19, **2006**.