Chromed Leather Dyeing Peculiarities when Deliming with Peracetic Acid

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The research was aimed to investigate the influence of deliming with peracetic acid on leather dyeing kinetics. Hydrophobic *C.I. Acid Red 213* and hydrophilic *C.I. Acid Red 423* dyes were used. Sorption of dye depends on hydrophobicity/hydrophility of dye and dyeing temperature. Equilibrium of process is reached faster using hydrophobic *C.I. Acid Red 213* at 45 ℃. However, both control and experimental leather fibres adsorb more hydrophilic dye *C.I. Acid Red 423* and this fact does not depend on temperature. The diffusion coefficient of dye *C.I. Acid Red 423* calculated according to Weisz model is higher when dyeing conventional leather. The change of deliming method has influence on chromed leather dyeing but this influence is not significant. The adsorption ability of control leather fibres at 30 ℃ and 45 ℃ is higher using both dyes as compared to the dyeing the experimental one. The increase of dyeing temperature increases the adsorption ability independently on the sort of leather fibres. Such dependence of the adsorption ability on the temperature shows that hydrophobic action and van der Waals forces prevail between dye and fibres during dyeing process. The Gibbs energy changes show that adsorption of both dyes by leather fibres independently on their sort is a spontaneous process. The affinity of both dyes to conventional leather fibres is higher comparing with experimental one. The change of enthalpy is positive in all cases, and it means that the driving force of the dyeing is the change of entropy.
Keywords: leather, peracetic acid, chroming, dyeing, adsorption, diffusion, kinetics, thermodynamics.

INTRODUCTION

New and more environmentally friendly method of deliming of limed with $Ca(OH)_2$ and Na_2S pelt was developed in [1, 2]. Peracetic acid was employed as deliming agent. The adaptation of this method in practice allows processing of qualitative chromed leather.

It is known that changes of derma structure, which go on during unhairing and opening up of derma structure, influence a run of subsequent technological processes [3, 4]. Dyeing process is not an exception. Duration of beamhouse processes and concentration of materials used have influence on adsorption of dyes and intensity of colour [5].

Investigation has proved that modification of beamhouse processes influences intensity of leather coloration and light resistance. The colour of dyed chromed leather is more intensive and adsorption of dye decreases when short liming is carried out as compared to dyed leather after long liming [6]. Kutjin et al. [7] suggested that leather capability of dye sorption decreases when interfibriliar substances, which have high sorption power, are removed.

The influence of factors such as initial amount of dye, pH of leather, and temperature on the dyeing of lime-free leather was established. The results have shown that lime-free leather absorbs lesser amount of dye during dyeing but dye penetrates more deeply compared to conventional leather [8].

The dyeing process and dyeing quality depend not only on the beamhouse processes. Knaflic [9] found that unsatisfactory removing of scud during deliming has influence on colour of leather after dyeing. The chromed leather distinguishes by surface adsorption when it is manufactured without bating [6].

Tanning process also has significant influence on dyeing quality. It was established that affinity of dyes to leather, adsorption and even coloration depend on tanning process properties [10].

Tanning materials used for production of leathers may vary, according to the properties required and the field of use. Simple acid dyes gave good consumption and fastness values for dyeing of mineral tanned leathers; however these values for vegetable tanned leathers were relatively bad. 1 : 1 metal complex dyes were tried as an alternative and the results of the trials were rather good for both the mineral and vegetable tanned leathers [11].

Overall, the inconsiderable deviation from determined parameters of leather processing can markedly deteriorate the quality of dyed leather. The main aim of this research was to investigate the dyeing of chromed leather manufactured after deliming with peracetic acid.

EXPERIMENTAL PROCEDURES

Preparation of leather samples and fibres

The soaked and washed hide was cut into pieces (5×10) cm and a series of samples was prepared from these pieces. The samples for the investigation were taken from lower part (cattle rump) of hides.

Control chromed leather was processed according to the conventional technology. Experimental leather was processed according to the same technology except deliming and bating processes, which were carried out as described in literature [2]. Both leathers were chromed in one bath. The conventional and experimental leather were chopped, mixed with water (1 : 200) and roll milled for 15 min.

The mass of fibres was filtered through a Buchner filter (moisture capacity 90 %) and then used for experiments.

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Table 1. Chemical and physical indexes of leather and leather fibres

Index	Chromed leather		Fibres of chromed leather	
	control	experimental	control	experimental
Value of pH	3.24	3.31	3.26	3.22
Shrinkage temperature, oC	111.0	111.5	–	–
Moisture content, %	58.5	60.7	54.1	56.0
Cr_2O_3 content, %	4.3	4.7	3.7	4.0
Porosity, %	55.0	57.0	–	–

Dyes

In the experiments series of $1:2$ metal complex dyestuffs (Ciba-Geigy): *C.I. Acid Red 423* ($M = 960$ g/mol) and *C.I. Acid Red 213* ($M = 765$ g/mol) were used.

Determination of chemical and physical indexes of leather

Shrinkage temperature was determined using special equipment [12]. PH, moisture and Cr_2O_3 content were determined according to the standards [13 – 15]. Porosity was determined by measuring real and apparent leather volume [12]. Before porosity determination the leather samples were fixed using acetone [12].

Determination of hydrophobicity/hydrophily of dyes

Hydrophobicity/hydrophily of dyes was determined as follows: 0.02 g of dye was mixed with 25 ml of cyclohexanone and 25 ml of distilled water. The mixture was shaken for 2 hrs, transferred into a separating funnel and left to separate. The fractions were separated and their optical densities were measured. The coefficient of estimation of hidrophobicity/hydrophility was calculated according to equation:

$$H = D_{cyclohexanone} / D_{water};\qquad(1)$$

$D_{cyclohexanone}$ is the optical density of dye solution in cyclohexanone; D_{water} is the optical density of dye solution in distilled water.

Concentrations of dyes in solutions were determined by the photo colorimetric method using spectrometer "Genesys 8" (Spectronic, USA).

Determination of dyeing kinetics

Dyeing kinetics was determined as follows: 5 g of leather was dyed for 10 hrs in 500 ml of dye solution with a initial concentration 18 g/l at 30 °C or 0.1 g of leather fibres was dyed no less than 8 hrs with a starting concentration (0.9 – 9) g/l at 30 °C and 45 °C. During dyeing the optical density was measured and concentration was calculated using calibration curves. The amount (C) of dye adsorbed by leather was taken as a difference between initial and equilibrium concentration and expressed as the % of this difference. The apparent diffusion coefficient (D_1 or D_2) was calculated by two ways: D_1 – according to the equation, which describes the diffusion of dyes into pores filled by solution [16] and D_2 – according to a formula, which is mostly used in textile dyeing [17]:

$$D_1 = \alpha \cdot D_T / K, \text{ cm}^2/\text{s};\qquad(2)$$

where D_t is the diffusion coefficient, which is close to diffusion coefficient of dye in water: 10^{-6} cm^2/s; α is the coefficient of porosity; D_T is the diffusion coefficient in

solution, cm^2/s; K is the coefficient of adsorption equilibrium.

$$K = D_2 \cdot t / b^2, \text{ cm}^2/\text{s};\qquad(3)$$

where K is the coefficient, which is found from the curve $f(C_t / C_\infty) = gK$; here C_t is the amount of dye adsorbed by leather during time t, mmol/g; C_∞ is the amount of dye adsorbed by leather when equilibrium was reached, mmol/g; D_2 is the apparent diffusion coefficient, cm^2/s; t is the time, during which leather adsorbed the amount of dye C_t, s; b is the thickness of leather, cm.

Thermodynamics of dyeing

A sample equivalent to 0.1 g of absolutely dry fibres was dyed for 8 hours at 30 °C and 45 °C, at a concentration of (0.9 – 9) g/l. The isotherms of sorption were drawn according to the concentrations of dyes in fibres and solution after reaching equilibrium.

The Langmuir adsorption model [18] was used for a description of the isotherms:

$$q_e = \frac{K_L Q_L C_e}{1 + K_L C_e};\qquad(4)$$

where q_e is the equilibrium concentration of dye in fibres, mmol/g; C_e is the equilibrium concentration of dye in solution, mmol/l; Q_L is the ultimate amount of dye, which taken for a unit of fibres adsorbent mass, when surface of fibres is completely covered by monolayer of dye (Langmuir adsorption capacity), mmol/g; K_L is the equilibrium constant of Langmuir, l/mmol.

The value of Q_L was determined from a plot C_e / q_e versus C_e figure of one dividing by interception of straight line. The values of K_L were calculated as proportion between the interception and slope of straight line. Value of index R_L, which shows how conditions are opportune to adsorption, was calculated according to equation [19]:

$$R_L = \frac{1}{1 + K_L C_0};\qquad(5)$$

where C_0 is the initial concentration of dye in solution, mmol/l.

Conditions are favourable for sorption when value of R_L is between 0 and 1; when $R_L > 1$ conditions are not favourable for adsorption; when $R_L = 1$ adsorption is linear and when $R_L = 0$ adsorption is irreversible.

Thermodynamic parameters of adsorption: change of Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated according to equations [20]:

$$\Delta G = -RT \ln K_C;\qquad(6)$$

$$\ln K_C = \Delta S/R - \Delta H/RT;\qquad(7)$$

where K_C is the thermodynamic distribution constant; T is the temperature of dyeing solution, K; R is the universal

gas constant, J/mol·K; ΔH is the heat of dyeing, J/mol; ΔS is the entropy change, J/mol·K.

The value of thermodynamic distribution constant was obtained experimentally from the slope and intercept of plot $\ln(q_e/C_e)$ versus q_e. The slope of the obtained straight line is equal of $\ln K_C$. The values of, ΔH and ΔS were determined from the slope and intercept of $\ln K_C$ versus $1/T$.

RESULTS AND DISCUSSION

Dyeing kinetics

During dyeing dyes interact with free groups of collagen or collagen and tanning material or with both groups at the same time. Covalent, ionic, hydrogen bonds, and van der Waals forces form in such case [21].

In textile dyeing, the diffusion coefficient changes from 10^{-12} cm^2/s up to 10^{-7} cm^2/s. When dyeing a fibre the diffusion coefficient varies from 10^{-12} cm^2/s to 10^{-7} cm^2/s as well. Such wide interval of values depends on dye affinity to textile and structure of fibres [6, 16].

The dyeing of chromed leather, which was manufactured using different technologies, was investigated by evaluating dyeing parameters, which show a rate of dye sorption and diffusion into substrate.

Firstly, coefficients of hidrophobicity/hydrophility for dyes used in work were determined. The values of coefficients were 27.3 for *C.I. Acid Red 213* (hydrophobic) and 0.71 for *C.I. Acid Red 423* (hydrophilic), respectively.

The structure of leather is very complicated and for this reason it is difficult to describe mathematically the diffusion coefficient. In the literature there are only several methods meant for calculation of diffusion coefficient, in which the diffusion is linked to an investigation of leather structure and to equations describing this diffusion.

In order to evaluate apparent diffusion coefficient for dye *C.I. Acid Red* 423, the leather dyeing kinetics was determined and curves obtained (Fig. 1) were used for the calculation of diffusion coefficients (presented in Table 2).

Table 2. Apparent diffusion coefficients of dye *C.I. Acid Red 423*

Diffusion coefficient, cm^2/s	Chromed leather	
	control	experimental
$D_1 \cdot 10^{-7}$	2.39	2.25
$D_2 \cdot 10^{-6}$	2.42	2.61

The diffusion coefficient (D_2) calculated according to Krenk model [16] had higher value when the experimental leather was dyed. Supposedly, a thickness of leather influenced the values of calculated diffusion coefficients: thickness of sample was 0.17 cm for the control leather and 0.18 cm for the experimental one.

Calculation of diffusion coefficient (D_1) according to Weisz model [15] provided the value of diffusion coefficient, which was higher when the control leather was dyed. This correlates with the results presented in Fig. 1. The equilibrium was reached faster when dyeing the control sample: 8 hrs for the sample and 9 hrs for the experimental one. Since the porosity of leather influences the values of diffusion coefficients calculated according to Weisz model it can be supposed that exactly the porosity of leather determines the sorption process.
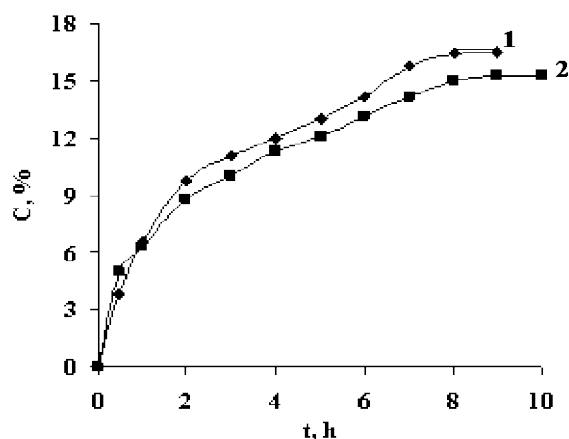

Fig. 1. Kinetics curves of dye *C.I. Acid Red 423* adsorption at 45 °C by chromed leathers: 1 – control; 2 – experimental

In order to eliminate the influence of porosity on the dyeing process, leather fibres were dyed. The obtained kinetics curves are presented in Figs. 2 and 3.

The results presented in Fig. 1 show that sorption of dyes into conventional leather is greater than that into produced after deliming with peracetic acid leather: the control sample absorbs approx. 6 % higher amount of *C.I. Acid Red 423* as compared to the experimental one. The same trend remains during dyeing of leather fibres (Fig. 2 and Fig. 3) and it does not depend on the sort of dye and temperature. This let us to suppose that other factors than porosity of leather or diameter of pores play leading role in leather dyeing process. On the other hand, type of dye has influence on the amount of dye in leather fibres when equilibrium is reached: the adsorption of hydrophilic dye *C.I. Acid Red 423* by both samples was higher in comparison with adsorption of hydrophobic *C.I. Acid Red 213* at the same temperature.

Dye sorption thermodynamics

The second step of the investigation was to establish the thermodynamic parameters, which characterize a distribution of dye between solution and substrate when equilibrium is reached, show an adsorption ability of substrate and allow estimation of dyeing process driving forces.

In order to estimate the driving forces of dyeing, the experiments of leather fibres dyeing by hydrophobic *C.I. Acid Red 213* and more hydrophilic *C.I. Acid Red 423* were carried out at 30 °C and 45 °C. The fibres were used to avoid the influence of leather topography and to reach more rapidly the process equilibrium. The adsorption isotherms are presented in Fig. 4. The equilibrium isotherms of dyeing adsorption were described according to the Langmuir sorption model [17] presented in Fig. 5.

After calculation of the saturation concentration using curves in Fig. 5, it was found that the concentrations for *C.I. Acid Red 213* practically did not depend on the temperature of dyeing and type of leather and were equal to $(0.32-0.43)$ mmol/g. The saturation concentration of *C.I. Acid Red 213* at 30 °C and 45 °C was 0.46 mmol/g and 0.68 mmol/g for the experimental leather and $(0.37-0.54)$ mmol/g for the conventional one.

Linear relationship obtained according to Langmuir equation (Fig. 5) was used to calculate sorption ability Q_L and equilibrium constant K_L, which estimates a ratio of sorption and desorption velocities. Index R_L, which shows how favourable conditions are to sorption process, was calculated as well. The results are presented in Table 3.

The data in Table 3 show that sorption ability (Q_L) is higher when dyeing with hydrophobic *C.I. Acid Red 213* and does not depend on temperature and sort of leather fibres as compared to dyeing by hydrophilic *C.I. Acid Red 423*. On the other hand, the adsorption ability of control sample is higher in all cases of dyeing when compared with the experimental one.

A dye can interact with free group of collagen or complex of tanning material and collagen, or with both groups at same time [22]. It was determined that chromium oxide content is higher in control sample (Table 1), and this can be the reason of higher adsorption ability of the control sample. The fact that adsorption ability increases with the increasing temperature, when dyeing with both dyes, allows the assumption that dyes and fibres interact through prevailing hydrophobic action and van der Waals forces.
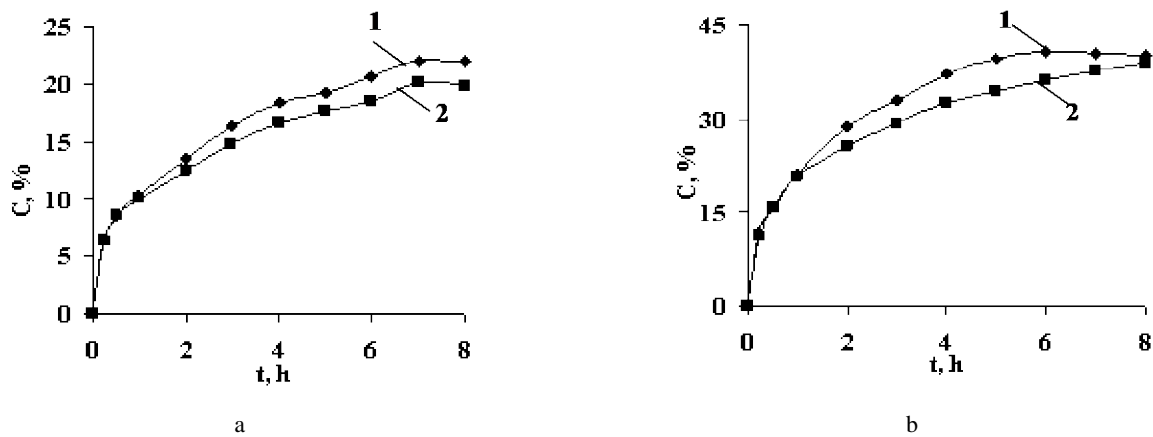

a

b

Fig. 2. Kinetics curves of dyes *C.I. Acid Red 213* (a) and *C.I. Acid Red 423* (b) sorption at 30 °C by fibres of chromed leathers: 1 – control; 2 – experimental
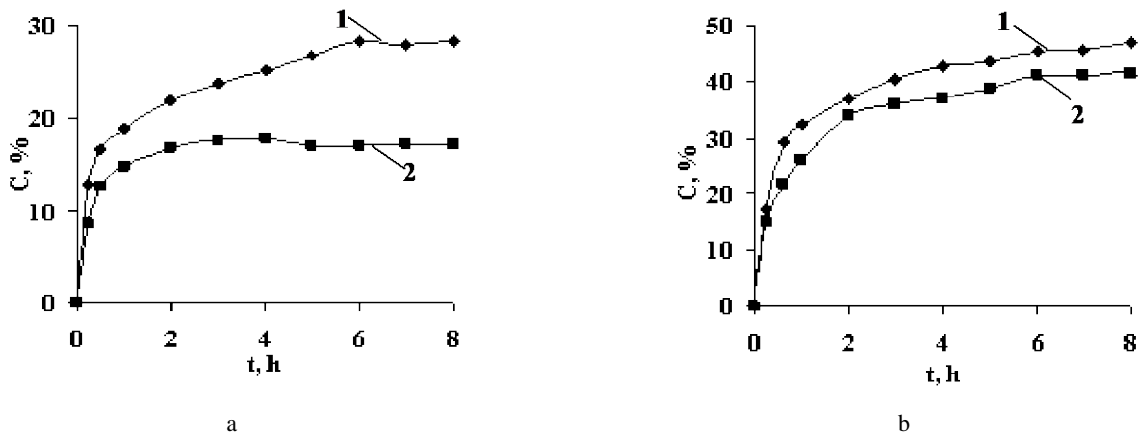

a

b

Fig. 3. Kinetics curves of dyes *C.I. Acid Red 213* (a) and *C.I. Acid Red 423* (b) adsorption at 45 °C by fibres of chromed leathers: 1 – control; 2 – experimental
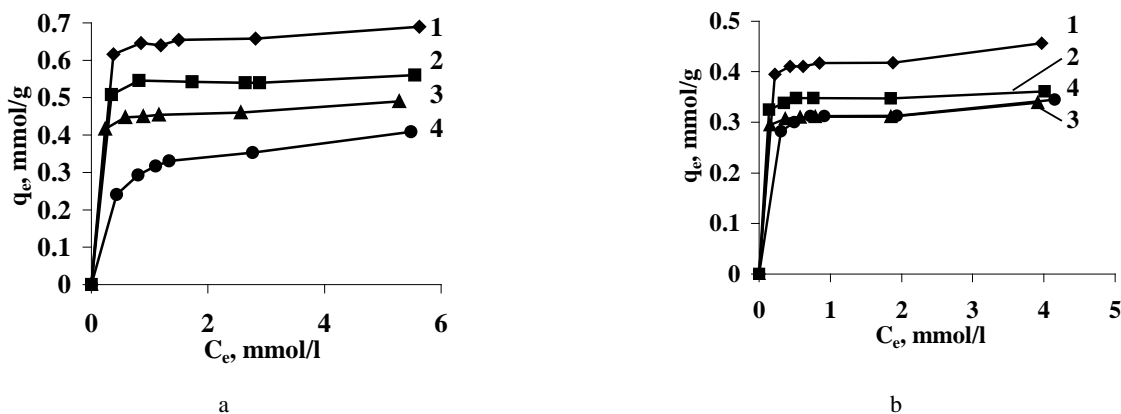

a

b

Fig. 4. Sorption isotherms when dyeing with *C.I. Acid Red 213* (a) and *C.I. Acid Red 423* (b) at 45 °C (1, 2) and 30 °C (3, 4). Leather fibres 1, 3 – control, 2, 4 – experimental.
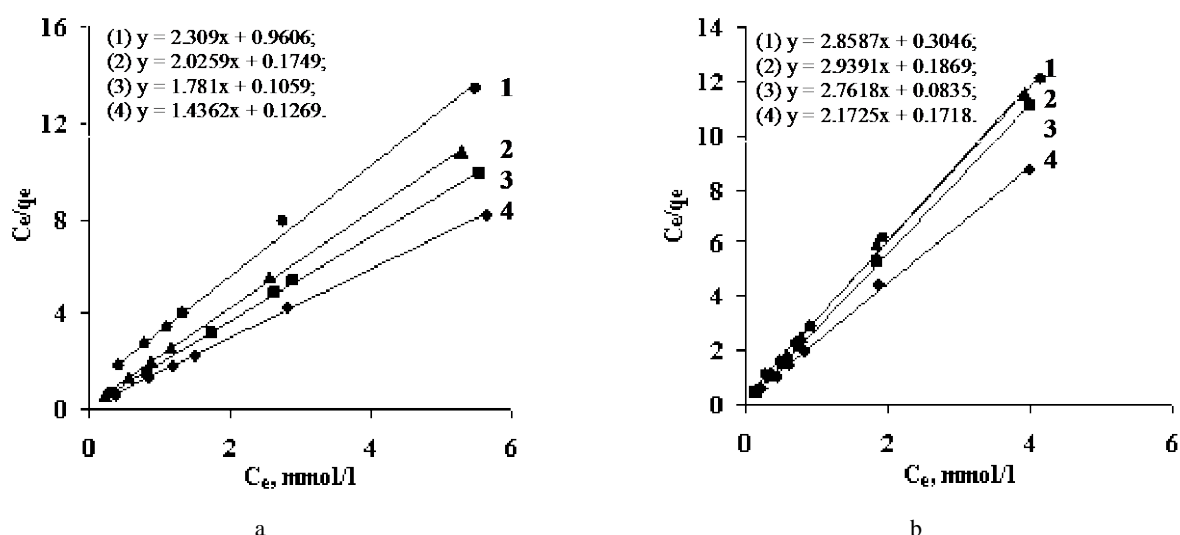
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Fig. 5. Adsorption isotherms drawn according to Langmuir equation when dyeing with *C.I. Acid Red 213* (a) and *C.I. Acid Red 423* (b) at 30 °C (1, 2) and 45 °C (3, 4). Leather fibres 1, 3 – experimental, 2, 4 – control

Table 3. Indexes of Langmuir adsorption model when dyeing at 30° and 45°C with *C.I. Acid Red 213* and *C.I. Acid Red 423* dyes

Indexes	Dye, sort of leather fibres and temperature (°C)							
	C.I. Acid Red 213				*C.I. Acid Red 423*			
	experimental		control		experimental		control	
	30	45	30	45	30	45	30	45
Q_L, mmol/g	0.433	0.561	0.494	0.696	0.350	0.362	0.340	0.460
K_L, l/mmol	2.404	16.818	11.583	11.318	9.385	33.075	15.726	12.646
R_L	0.035	0.005	0.007	0.007	0.012	0.003	0.007	0.009

Table 4. Thermodynamic indexes of dyes *C.I. Acid Red 213* and *C.I. Acid red 423* adsorption by leather fibres

Indexes	Dye and sort of leather fibres			
	C.I. Acid Red 213		*C.I. Acid Red 423*	
	experimental	control	experimental	control
ΔG (30 °C), kJ/mol	−27	−44	−28	−44
ΔG (45 °C), kJ/mol	−57	−72	−48	−79
ΔH, kJ/mol	1315	217	1012	30
ΔS, kJ/mol·K	4.36	0.86	3.43	0.25

The values of equilibrium constants (K_L) show that when dyeing with both dyes the prevailing process is adsorption. The increase of K_L values shows that velocity of adsorption increases when temperature increases. Values of index R_L (Table 3) are between 0 and 1, and this means that conditions for adsorption are favourable in all cases.

The thermodynamic indexes of dyes adsorption by leather fibres were calculated according to formulas described in the chapter "Experimental procedures" and are presented in Table 4. Negative values of Gibbs energy change show that adsorption of both dyes by leather fibres is spontaneous. The higher value of Gibbs change energy indicates the higher affinity of dye to chromed leather fibres. The data in Table 4 show that affinity of both dyes to control chromed leather fibres is higher as compared to the experimental one.

It is known [23] that adsorption ability is greater when affinity of sorbent to sorbate is higher. The data in Table 3 show that the adsorption ability of control sample fibres is higher, and increases with the increasing temperature.

Since the change of dyeing heat of differently processed leather using both dyes *C.I. Acid Red 213* and *C.I. Acid Red 423* is positive, the driving force of the process is the change of entropy, which is high and positive in the case of experimental leather dyeing (4.36 kJ/mol·K and 3.43 kJ/mol·K, respectively). Klotz and Urquhart have found [24] that heat of reaction is low and the change of entropy is high and positive when complexes between nitro dyes and ox serum albumin are formed. These results have been explained by the hydrophobic interaction theory. According to this theory, molecules of dyes and chains of protein are surrounded by "icebergs" of water. During the interaction among these "icebergs" the water works free and causes a positive change of entropy. This change is the thermodynamic reason of hydrophobic interaction. Therefore, the high positive change of entropy obtained during dyeing with *C.I. Acid Red 213* might be explained by the strong hydrophobic interaction between leather and dye. This interaction is stronger in the case of experimental leather dyeing. The values of entropy change are significantly lower when dyeing with hydrophilic

C.I. Acid Red 423, and this shows that hydrophobic action is weaker in such case independently on leather processing method.

CONCLUSIONS

It was determined that dye *C.I. Acid Red 213* is hydrophobic, while dye *C.I. Acid Red 423* is hydrophilic. Adsorption of dye by leather/leather fibres depends on hydrophobicity/hydrophility of dye and temperature. Equilibrium of process was reached faster using hydrophobic dye *C.I. Acid Red 213* at 45 ℃. However, both control and experimental leather fibres absorb about 2 times more of hydrophilic dye *C.I. Acid Red 423* independently on temperature.

The diffusion coefficient of dye *C.I. Acid Red 423* calculated according to Weisz model is higher when dyeing the conventional leather. This correlates with kinetics results: the equilibrium is reached faster when dyeing the control sample.

The adsorption ability (Q_L) of control leather fibres at 30 ℃ and 45 ℃ is higher using both dyes as compared to dyeing of the experimental one. The increase of dyeing temperature increases the adsorption ability (Q_L) independently on the sort of leather fibres. Such dependence of the adsorption ability on the temperature shows that hydrophobic action and Van der Waals forces prevail between dye and fibres during dyeing process.

The values of equilibrium constants (K_L) show that when dyeing with both dyes the prevailing process is adsorption. The increase of the equilibrium constant shows that velocity of the adsorption increases when temperature increases. Conditions for adsorption process are favourable because the values of index R_L are between 0 and 1.

Negative values of Gibbs energy change prove that adsorption of both dyes by leather fibres independently on their sort is a spontaneous process. The affinity of both dyes to control leather fibres is higher in comparison with the one obtained after deliming with peracetic acid. The change of enthalpy in all cases of dyeing is positive independently on leather fibres sort, and it means that the driving force of the process is the change of entropy, which is high and positive when the experimental leather is dyed.

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