Mathematical model and control system for chromium recycling process

Dagmar Janáčová, Vladimír Vašek, Ondrej Líška, Karel Kolomazník, Pavel Mokrejš, Petr Doležel

Abstract— The paper deals with application of computer controlling and displaying system of the technological recycling process of both liquid and solid wastes from the tanning industry. The chrome tannery wastes are potentially dangerous to the environment. A proposal for chrome recycling technology, realization of the laboratory equipment and programming possibility are likewise presented. The idea of recycling technology lies in using reaction of non - environmentally friendly chrome liquid and solid wastes and creating new products that are not toxic and can be used in the other industrial applications.

Described mathematical model for the recycling technology is based on the chemical - physical engineering description of a heterogeneous kinetics. The method of regressive analysis was used for determining of parameters for each kinetic equation from the experimental data. The proposed model was used for a simulation test and an optimum calculation in the connection with minimum procedural costs of recycling technology.

The real process presentations are built with laboratory equipment for a closed recycling technology of real chrome liquid and solid wastes taken from the tanning company TAREX.

The computer controlling and displaying system has two levels. The technological level is composed on a PC with the technological extension card Advantech PCL-812PG ensuring the direct control over the real process. The software for this level was created in the C language with the real time library RTMON. The supervisory level creates a personal computer with professional displaying software by Wonderware InTouch. The parts of software are DDE server

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic under the Research Plan No. MSM 7088352102 and by the European Regional Development Fund under the project CEBIA-Tech No. CZ.1.05/2.1.00/03.0089.

D. Janáčová, Tomas Bata University in Zlín, Faculty of Applied Informatics, Department of Automation and Control Engineering, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic; phone: +420 576 035 274; fax: +420 576 032 716; e-mail: janacova@fai.utb.cz

V. Vašek, Tomas Bata University in Zlín, Faculty of Applied Informatics, Department of Automation and Control Engineering, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic (e-mail: vasek@fai.utb.cz)

K. Kolomazník, Tomas Bata University in Zlín, Faculty of Applied Informatics, Department of Automation and Control Engineering, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic (e-mail: kolomaznik@fai.utb.cz)

O. Líška, Technical University of Kosice Faculty of Mechanical Engineering, Department of applied mechanics and mechatronics, Letná 9,042 00 Košice, Slovakia (email: <u>ondrej.liska@tuke.sk</u>)

P. Mokrejš, Tomas Bata University in Zlín, Faculty of Technology, Department of Polymer Engineering, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic (e-mail: mokrejs@ft.utb.cz)

P. Doležel, Tomas Bata University in Zlín, Faculty of Applied Informatics, Department of Automation and Control Engineering, nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic. (e-mail: vasek@fai.utb.cz) module ensuring the communication between both levels of the control system via the serial link RS 232.

Keywords— chrome waste treatment, continual reaction model, curve determination, control system.

I. INTRODUCTION

THE leather industry belongs to significant producers of material waste. By treatment of both liquid and solid waste, the great quantity of chrome sludge is produced. The chrome can be potential highly toxic for the environment. Concerning the chrome toxicity, the trivalent chrome Cr^{3+} is natural part of environment.

On the contrary, the hexavalent chrome Cr^{6+} at concentration in air amounting to 2 $\mu g/m^3$ implicates helt troubles in humans. Some compounds of hexavalent chrome have carcinogenic effects.

In the soil, the hexavalent chrome can be fast reduced into the trivalent chrome that is subsequently aglomerated and bound [1].

II. METHODS OF THE CHROME WASTE TREATMENT

Methods of the liquid waste treatment are based on the agglomeration chrome in the form of hydroxide by the instrumentality of alkali chemicals.

One of the numerous possible solutions to the problem of chrome-tanned wastes is their enzymatic dechromation. This is the most effective method from economic point of view. In comparison with the traditional technology, the yield increase is about 30 %. The proteolytic enzymes are more active at mild temperature. They are also effective by protein dissolving. The chrome stays insoluble to the moment of reaction in alkalic pH conditions. The research deals with finding the optimal conditions that will speed up reaction and decrease amounth of enzymes which will reduce economical costs [2].

When seeking ways of processing chrome-tanned wastes in the Czech Republic we decided to employ the enzymatic dechromation technology worked out at the USDA in Philadelphia [3]. To fit conditions in the factory manufacturing auxiliary tanning agents where the technology was applied, we modified the American process by using organic volatile bases such as isopropylamine, diisopropylamine, cyclohexylamine, ammonia and others [4]. Usage of the mentioned volatile amines has the following advantages:

- a) Ash content in hydrolysis products is considerably reduced. (From an initial 25% to a maximum 7% in the first stage of hydrolysis and from 15% to a maximum 3% in the second stage). A reduced ash content gives a higher quality product and in case desalting by ion exchangers13 or membrane filtration14 is employed, the working cycle of ion exchanger columns or filtration plants is prolonged.
- b) It increases the content of chromic oxide in filter cake, thus facilitating its processing into regenerated tanning salt.
- c) When concentrating diluted solutions of protein hydrolysates, a certain regeneration of organic base takes place. In laboratory and pilot-plant conditions we achieved 60% regeneration, on an industrial scale the

regeneration of organic base varied within the range of 20 - 40%.

 d) The efficiency of protein yield increases from 60% to 80% and more. Table I presents results we obtained in USDA laboratory conditions.

From this point of view we worked up method of two stage process (Fig. 1). In the first one happened downtrend of the chromite capacity in the ground down leather swill by the help of the magnesium operation which is contained in the filtrate cake. Total chromium ion removing we can obtain by the using caustic soda or carbonate aqueous.



FIRST STAGE

Fig. 1 Scheme of two stage of enzymatic hydrolysis [2]

The modified technology of enzymatic hydrolysis was then employed in a plant of the TANEX Company, now KORT fastes. AN, in Hrádek nad Nisou in north part of Czech Republic, with a daily capacity of 3 metric tons for processing chrome shavings. The most important operation in the whole process of leather manufacturing from pelt is tanning when basic complexes chrome salts form strong coordinating bonds between carboxyl groups of the collagen protein. However, this reaction goes to equilibrium, i.e. some of the available of chrome does not link to the collagen protein by tanning reaction and thus, according to the specific technological procedure, outgoing liquid contains 0.2 - 0.4 % of chrome ions. Prudent practice is to use alkaline precipitation to remove chrome from this "spent" liquor. In our process a chrome sludge was isolated after enzymatic dechromation of tanned solid scraps. It contained 10-15 % of magnesium oxide (on the free moisture base) and also a small amount of organic base. This fact led us to explore the possible utilisation of chrome sludge to remove and recover chrome ions in spent tanning liquors.

III. MATHEMATICAL MODEL OF CHROMIC WASTE ENZYMATIC DECHROMATION

Enzymatic hydrolysis of shavings is heterogeneous protheolytic enzymes katalytic chemical reaction, by which the solid phase reacts with liquid. This products or reaction are other solid and liquid phases. For quantitative description of the enzyme hydrolysis, we used model of the bound component washing.

The chemical reactor capacity depends on the enzyme hydrolysis kinematics. Under the mentioned conditions, the process can be described by following equations [1], [9]:

$$D_{ij}\nabla^2 c_i = \frac{Dc_i}{D\tau} + r \tag{1}$$

where

$$\frac{Dc_i}{D\tau} = \frac{\partial c_i}{\partial \tau} + \frac{c_i}{\partial x} v_x + \frac{\partial c_i}{\partial y} v_z + \frac{\partial c_i}{\partial z} v_z$$
(2)

The reaction rate is function of the reactive components concentration:

$$r_i = f(c_i c_j \dots) \tag{3}$$

Concrete form of function (3) depends on the chemical reaction mechanism. If the concentration gradients are inconsiderable (i.e. chemical reaction is slow, or the solid phase elements are very small), the equation (3) can be simplified into the form:

$$r_i = \frac{\partial c_i}{\partial \tau} \tag{4}$$

The process rate depends on the enzyme hydrolysis kinetics. The second limit case occurs if the chemical (enzyme) reaction is very rapid or the solid phase elements are very large. Then the chemical reaction can be neglected and the reaction rate depends on diffusion of reactive substance into the inner volume of solid phase.

The research proved, that diffusion mechanism occurs more often than kinetic mechanism.

For following quantification we will suppose onedimensional system. The reaction will proceed in the immobile solid material and concentrations the reactive substances will be very low.

The chrome shavings denaturation proceeds on the first stage of hydrolysis. By this process, the uniform distribution of pH in the cross profile of shavings have to be achieved. The pH value has to by such that the enzyme reaction will be fastest.

Denaturation can be described by the continual reaction model [5], [9]:

$$D\frac{\partial^2 c(x,\tau)}{\partial x^2} - r(x,\tau,c) = \frac{\partial c(x,\tau)}{\partial \tau}, \ 0 \le x \le b$$
(5)

$$c(b,\tau) = \varepsilon \ c_0(\tau) \tag{6}$$

$$\frac{\partial c}{\partial x}(0,\tau) = 0 \tag{7}$$

$$-DS\frac{\partial c}{\partial x}(b,\tau) = V_0 \frac{\partial c_0(\tau)}{\partial \tau}$$
(8)

$$c(x,0) = 0 \tag{9}$$

$$c_0(0) = c_{0p} \tag{10}$$

Equation (5) represents washed component diffusion from material in the direction of washing liquid. Equation (6) holds under condition of a perfectly mixed liquid phase. Boundary condition (7) denotes that field of concentration in solid material is symmetric. Boundary balance condition (8) denotes the equality of the diffusion flux at the boundary between the solid and the liquid phases with the speed of accumulation of the diffusing element in the surrounding. Equation (9) describes initial concentration of reactive component in liquid phase. Condition (10) shows the initial distribution of washed component concentration in solid material.

If transporting alkali is sorbited by the solid phase, the reactive rate can be described by equation (11):

$$r = \frac{\partial c_A}{\partial \tau} \tag{11}$$

The sorbited alkali concentration (c_A) is function of the unbound alkali concentration (c). It can be determined by use of Langmuir sorption isotherm (13) [12] (Case of very rapid hydrolysis)

$$c_A = \frac{Ac}{1+Bc} \tag{12}$$

If the unbound alkali concentration is very slow than the equation (12) can be simplified into the form:

$$c_A = A.c \tag{13}$$

By substitution of equations (11) and (13) into equation (5) we obtained:

$$k\frac{\partial^2 c}{\partial x^2}(x,\tau) = \frac{\partial c}{\partial \tau}(x,\tau), \ 0 \le x \le b, \quad \tau > 0$$
(14)

where

$$k = \frac{D}{1+A} \tag{15}$$

By substitution of dimensionless variables

$$C = \frac{c - c_{0p}}{c_p - c_{0p}}, X = \frac{x}{b}, \ F_0 = \frac{k\tau}{b^2}, Na = \frac{V_0}{V}$$
(16)

we obtained by Laplace transformation method analytical solution describing dimensionless concentration field in the solid phase (17):

$$C(X, F_{\circ}) = \frac{\varepsilon(1+A)}{\varepsilon(1+A) + Na}$$

-2Na $\cdot \sum_{n=1}^{\infty} \frac{\cos(q_n X) \exp(-q_n^2 F_{\circ})}{\varepsilon(1+A)\cos(q_n) - \frac{\varepsilon(1+A)}{q_n}\sin(q_n) - Na \cdot q_n \sin(q_n)}$

and real concentration field in solid phase (18):

$$c(x,\tau) = c_{0p} + (c_p - c_{0p}) \left(\frac{\varepsilon(1+A)}{\varepsilon(1+A) + Na} - 2Na \cdot \sum_{n=1}^{\infty} \frac{\cos(q_n X) \exp(-q_n^2 F_o)}{\varepsilon(1+A) \cos(q_n) - \frac{\varepsilon(1+A)}{q_n} \sin(q_n) - Na \cdot q_n \sin(q_n)} \right)$$
(18)

where q_n are roots of equation (19):

$$\tan(q) = -\frac{Na \cdot q}{\varepsilon (1+A)} \tag{19}$$

Practically, the stable state will come, if value of dimensionless time $F_0 = 1$. Then time necessary to optimal pH profile setting can be estimated from equation (20):

$$\tau_d = \frac{b^2}{k} \tag{20}$$

In the Fig. 2 and Fig.3 are described real concentration fields for sorption coefficients values A = 5, A = 50. The other parameters are:

soaking number Na = 5,

initial alkali concentration in liquid phase $c_{0p} = 5 \text{ kg/m}^3$, half thickness of solid phase b = 1 mm, diffusion coefficient $D = 3.10^{-9} \text{ m}^2/\text{s}$.



Fig. 2 Concentration field in the solid phase for sorption coefficient A = 5



Fig. 3 Concentration field in the solid phase for sorption coefficient A = 50

IV. OPTIMAL PROCESSING COSTS DETERMINATION

Main aim to the enzyme hydrolysis optimization consists in minimization of the total operating costs which can be determined from computed costs curve under the given conditions. For this purpose we assumed that total processing costs N_T include costs of hydrolysis N_R , costs of the protein solution concentrate N_{EV} and other costs N_0 [8]:

$$N_T = N_R + N_{EV} + N_0 (21)$$

By substitution

$$N_R = \frac{P.K_E.\tau}{m_p} \tag{22}$$

and

$$N_{EV} = \frac{V.r.K_s}{m_p}$$
(23)

we obtained

$$N_{T} = \frac{P.K_{E}.\tau + V.r.K_{S}}{m_{p}} + N_{0}$$
(24)

Weight of evaporated water we computed from balance equation (25):

$$V = m_p \left(\frac{a_{s,P}}{a_{s,D}} - 1\right) \tag{25}$$

By using balance equation of hydrolytic reactor, filtration and evaporation, we computed weight of product by equation (26):

$$m_{p} = \frac{\left(C\left(a_{s,C} - a_{s,FK}\right) - \left(AB + V1\right).a_{s,FK} + M\right).a_{s,D}}{a_{s,P}\left(a_{s,D} - a_{s,FK}\right)}$$
(26)

By substitution of equations (25) and (26) into equation (24), we obtained

$$N_{T} = \frac{P.K_{E}.\tau(a_{s,D} - a_{s,FK})a_{s,P}}{\left(C(a_{s,C} - a_{s,FK}) - (AB + V1)a_{s,FK} + M\right).a_{s,D}} + \left(\frac{a_{s,P}}{a_{s,D}} - 1\right).r.K_{s} + N_{0}$$
(27)

The total operating costs depend also on alkali cost and on other costs that can be computed as

$$N_{0} = a_{s,P} \frac{\left(C\left(a_{C}.K_{Mgo} + a_{s,B}.K_{SB} + a_{v}.K_{v}\right) + \alpha.\Delta t.S\tau.K_{s} + n.K_{L}.\tau\right)\left(a_{s,D} - a_{s,FK}\right)}{\left(C\left(a_{s,C} - a_{s,FK}\right) - (AB + V1)a_{s,FK} + M\right).a_{s,D}}$$
(28)

Concentration of dry residue $(a_{s,p})$ in the reactive mixture and in the filtrate depends on time. This function depends hydrolytic reaction mechanism.

A. Kinetic mechanism

By kinetic mechanism we suppose that chromic waste is in form of dust elements.

The reaction can be described by equation (29)

λī

$$\frac{dx}{d\tau} = k_1 \left(1 - x \right), \quad x = \frac{a_{s,D}}{a_{s,Q}} \tag{29}$$

After integration, we obtained

$$a_{s,D} = a_{s,O} \left(1 - e^{-k_{1}\tau} \right)$$
(30)

The equilibrium concentration $a_{s,0}$ can be computed by equation (31)

$$a_{s,0} = \frac{a_{s,C}.C}{V1 + SAB + C}$$
(31)

B. Diffusion mechanism

In this case we suppose that chromic waste is larger. Mathematic model of this process is more complicated

$$\frac{\partial x}{\partial \tau}(x,\tau) = k \cdot \frac{\partial^2 a}{\partial x^2}(x,\tau), \quad 0 \le x \le b, \quad \tau > 0$$
(32)

$$\frac{\partial a}{\partial x}(0,\tau) = 0 \tag{33}$$

 $a(x,0) = a_{s,C} \tag{34}$

$$a(b,0) = \varepsilon.a_{s,D} \tag{35}$$

$$-DS\frac{\partial a}{\partial x}(b,\tau) = V_0 \frac{\partial a_0}{\partial \tau}$$
(36)

After computing of the model described by equations (32) - (31) we obtained

$$a_{s,D} = \frac{\varepsilon a_{s,C}}{\varepsilon + Na} - 2\frac{Na.a_{s,OP}}{\varepsilon} \sum_{n=1}^{\infty} \frac{e^{-F_0 q_n^2}}{\varepsilon + Na + \frac{q_n^2 Na^2}{\varepsilon}}$$
(37)

In the Fig. 4 are shown cost curves for the hydrolyzed waste quantities 100 kg, 200 kg and 300 kg computed for diffusion mechanism. The other used parameters are shown in Table 1.



Fig. 4 Computed costs curves for various the hydrolyzed waste quantity

asFK (1):	Dk (m2/h):	aC (1):	asP (1):	delta_t (K):	asB (1):	asC (1):	aV (1):	asOP (1):	r (J/kg):
.15	.1640e-8	.2e-1	.3	50	.3e-1	.5	5	.5e-1	2260000.00
.15	.1640e-8	.2e-1	.3	50	.3e-1	.5	5	.5e-1	2260000.00
.15	.1640e-8	.2e-1	.3	50	.3e-1	.5	5	.5e-1	2260000.00
epsilon (1):	S (m2):	C (kg):	AB (kg):	KE (Euro/kWh):	KS (Euro/J):	kp (W/(m2.K)):	V0 (m3):	V (m3):	M (kg):
.5	15	100	5.00	.600000000e-2	.610000000e-9	60	5	1	2.00
.5	15	200	200*0.05	.600000000e-2	.610000000e-9	60	5	1	0.02*200
.5	15	300	300*0.05	.600000000e-2	.610000000e-9	60	5	1	0.02*300
KL (Euro/h):	KMgO (Euro/kg):	n (1):	b (m):	P (kW):	V1 (kg):	KsB (Euro/kg):	KV (Euro/k	g):	
.1510000000	.76	2	.2e-2	10	500	.910000000e-1	.130000000)e-3	
.151000000	.76	2	.2e-2	10	200*5	.910000000e-1	.130000000)e-3	
.151000000	.76	2	.2e-2	10	300*5	.910000000e-1	.130000000)e-3	

Table 1 Parameters used for costs curves determination

V. SIMULATION OF ENZYMATIC DECHROMATION

A laboratory model of the recycling process technological scheme is shown in Fig.5. As a main part, there are vessels and measuring storage tank with mixer and sensors, which are situated. The processed wastes are put into it. This equipment is fitted out with necessary sensors and valves for reading physical quantity and control of action elements.

It is necessary to control and display in recycling process:

- Filling process liquid and solid wastes with defined amount.
- Scanning discreet signals defining the position or state individual procedure parts of technological system and taking analogy values prom the process (temperature, pressure, value of concentration etc.)

- Control of the time sequence of individual operation according to technological procedure with controlling of all parameters. Regulation temperature and activity of the valves and pump in technological process.
- Communication of the control system and server via the serial link RS 232.

Control consists of the commanding of equipment and measuring out of chemicals according planed program.

Quantitatively higher-level automatic control is the using of backward connection, when action interference is made on the basis of real parameters of the process, which are just going.



Fig. 5 The simplified scheme of technological equipment

VI. PROGRAMMING METHODS IN AUTOMATION APPLICATION

Described technology is now implemented in laboratory conditions in our department by computer control system with a programmable industrial card Advantech PCL – 812/812PG, which has own A/D and D/A converters. Each part of the technology process has its own control subsystem for the direct digital control of the physical values as a temperature, water level in vessel, concentration etc. The software system is built in the C language. For the real time running of the program system there is used special pre-emptive real time operating system RTMON 4, which was built for the using of monitoring and control system for technological processes. It allows multitasking of defined number of processes. User's programs are structured on the basis of the priority hierarchically. The choosing of the program, which will be running on the processor, is carried out on the basis of its priority level. The structure of an application programs is shown in Fig. 6.

Program system includes the basic part of the real time operating system is created by process modules. Initialization process INIC defines data structure of the real time operating system and fills the program variables by the initial values; another process SNI reads periodically the binary and analogue input values. The control algorithms processes REG calculate optimal time to filling it into the bath from the measured values of temperatures, value of turbidity. The process COM ensures the communication between both levels of the control system via the serial link RS 232. The visualization process ZOB allows to send and to get back the information and important parameters with DDE server and software Wonderware InTouch.



Fig. 6 Real time control system

VII. TEMPERATURE CONTROL

For the identification of the controlled system we have generated inputted unit signal. Reaction of this signal is the step response. The identification was created by means of personal computer. The program was written in C language. This program archived the measured values, which can follows mass processing by means of another program. For this function was used program Excel, the part of the Microsoft Office. The thermal system has the following transfer function

$$G(s) = \frac{1,12}{(4610,1s+1)(375,2s+1)}$$
(29)

We designed different controllers for the control. The good results give the controllers with dynamic inversion. For the time period T=700s we have transfer function of discrete PID controller in the form

$$G_{R}(z^{-1}) = \frac{2,9505z^{-1} - 2,9916z^{-1} + 0,3924z^{-2}}{1 - z^{-1}}$$
(30)

The temperature control is shown in Fig. 7. We can see that time period to stabilization on the reference value is somewhere 5000s with no overshooting. This shots are necessary to system parameters determination.



Fig. 7 Real temperature control by the help controller combination

VIII. CONCLUSION

Described mathematical model for the recycling technology is based on the chemical - physical engineering description of a heterogeneous kinetics. Described method of the computer automatic control in the leather industry realizing by laboratory apparatus is workable and allows on the one hand testing new technological techniques and approach for transform of the natural hide, on the other hand testing control discreet algorithms for controlling analogue quantities. By the present experiences it can be told that the important factor affecting a lot of working results is right choice of a value of temperature to ensuring optimal reaction speed constant.

IX. LIST OF SYMBOLS

- a_{sp} weight ratio of dry matter in product, [1]
- s_{ad} weight ratio of dry matter in diluted filtrate, [1]
- $a_{s,0}$ equilibrium concentration, [1]
- a_{sk} weight ratio of dry matter in filter cake, [1]
- s_{ac} weight ratio of dry matter in hydr. chromic waste, [1]
- a_{ct} weight ratio of Mg to C, [1]
- a_{sB} weight ratio of alkali to C, [1]
- a_V weight ratio of water to C, [1]
- *A* sorption coefficient, [1]
- *AB* weight of alkaline mixture, [kg]
- *b* half thickness of shavings, [m]
- c_{op} initial chromium ions concentration in the liquid reactive mixture, [kg/m³]
- c_o chromium ions concentration in the liquid reactive mixture, [kg/m³]
- c chromium ions concentration in the swill, $[kg m^{-3}]$
- c_p initial chromium ions concentration in the swill, [kg m⁻³]
- \dot{C}_0 dimensionless concentration of chromium ions in the "liquid reactive mixture, [1]
- *C* dimensionless chromium ions concentration in the solid phase, [1]
- C weight of hydrolysed chromic waste, [kg]
- *D* effective diffusion coefficient , $[m^2/s]$
- F_0 dimensionless time, [1]
- g stoichiometric coefficient, [1]
- k velocity coefficient, $[h^{-1}]$
- K_A alkali price, [Euro. kg⁻¹]
- K_E unit price of the absorbed electrical power, [Euro. kg⁻¹]
- K_{MgO} price of Mg, [Euro /kg]
- k_p heat passage coefficient, [W.m⁻².K⁻¹]
- K_V price of water, [Euro /kg]
- K_L time rate, [Euro /kg]
- K_S heat energy price, [Euro /J]
- *m* chromium trivalent ions solidity in solution, [kg]
- m_p weight of product, [kg]
- M weight of Mg, [kg]
- N_T total processing costs, [Euro /kg]
- N_R costs of hydrolysis, [Euro /kg]
- N_{EV} costs of the protein solution concentrate, [Euro /kg]
- N_0 other costs, [Euro /kg]

- *P* power requirement of the pump electrical engine, [kW]
- r vaporization heat of water, [Jkg⁻¹]
- S area of shavings, $[m^2]$
- SAB weight of the specific alkali, [kg]
- T temperature , [⁰C]
- *V* volume of evaporated water, [kg]
- V1 weight of water dosed into reactor, [kg]
- V_0 volume of liquid reactive mixture, [m³]
- *X* dimensionless space coordinate, [1]
- ε porosity of shavings, [1]
- η pump overall efficiency, [1]
- τ time, [s]
- *u* actuating signal
- *z* complex variable Z-transformation
- $G_{S}(s)$ transfer function of continuous system
- $G_R(s)$ transfer function of continuous action controller

REFERENCES

- Kolomazník, Mládek M, Langmaier F, Janáčová, D. et al. Experience in Industrial Practice of Enzymatic Dechromation of Chrome Shavings J. Am. Leather Chem. Assoc., 95 (2), pp. 55-63,2000,
- [2] P. M. Thang, "Modeling of the recycling processes in the tanning technology with the purpose of solving their automatic control", Dissertation thesis, Tomas Bata university in Zlín Zlín, 2003. (in Czech)
- [3] K. Suseela, M.S. Parvathi, , S. C. Nandy, Leder, 37, 45, 1986.
- [4] M. M. Taylor, E.J. Diefendorf. et al, J. Am. Leather Chem. Assoc., 85, 264, 1990.
- [5] H. Charvátová, *"Modeling of pelt chemical deliming"*, Dissertation thessis. Tomas Bata University in Zlin, Zlin, 2007. (in Czech)
- [6] D. Janáčová, "Modeling of Extraction Processes", Habilitation thesis, Tomas Bata university in Zlín, Zlín, 2003. (in Czech)
- [7] H. Charvátová, "Modeling of grinding process by printed circuit boards recycling", in *The 21st International DAAAM Symposium "Intelligent Manufacturing & Automation: Focus on Interdisciplinary Solutions"*. Vienna, 2010, p. 475-476.
- [8] D. Janáčová, "Enzyme hydrolysis control", *Habilitation lecture*, Ostrava, 2002.
- [9] J. Crank, *The Mathematics of Diffusion*, 2nd Ed. Clarendon Press, Oxford 1977.
- [10] M. Staněk, D. Maňas, M. Maňas, J. Javořík, "Simulation of injection molding process by cadmould rubber", *International Journal of Mathematics and Computers in Simulations*, 5, 2011, p. 422-429.
- [11] K. Kolomazník, D. Janáčová, Z. Prokopová, "Modeling of Raw Hide Soaking", in WSEAS Transactions on Information Science and Applications, Hellenic Naval Academy, Ostrava Poruba, 2005.
- [12] D. Janáčová, et al., "Washing Processes Optimization", in International Union of Leather Technologists and Chemists Societies, London, 1997.
- [13] K. Kolomazník, T. Fürst, D. Janáčová, M. Uhlířová, V. Vašek, "Three Dimensional Transport Model Using in Soaking Process", in WSEAS Transactions on Computer Research, WSEAS World Science and Engineering Academy and Science, Queensland, 2007.
- [14] J. Dolinay, et al., "New Embedded Control System for Enzymatic Hydrolysis", in *Proceedings of the 8th WSEAS International Conference* on Applied Informatics and Communications, Rhodes, Greece, 2008, p. 174.
- [15] V. Vašek, "HC11 Control Unit Applications", IFAC WORKSHOP on Programmable Devices and Systems PDS 2001, Gliwice, Poland, 2001.
- [16] T. P. Manh, V. Vašek, K. Kolomazník, Best practices scrap leather recycling, *II. workshop US Asia Environmental Partnership - Ho Chi Minh university - Nike - UTB*, Ho Chi Minh City, Vietnam, January 2003.
- [17] M. Vítečková, A. Víteček, A., M. Babiuch, "Unified Approach to Analog and Digital Two-Degree-of-Freedom PI Controller Tuning for Integrating Plants with Time Delay", *Acta Montanistica Slovaca*, 1, 2011, p. 89-94.