Mathematical simulation for optimization of tanning processes; deliming of white hide

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Abstract: - In this paper, the authors show the usefulness of theoretical tools of chemical engineering in natural polymer processing, namely on the example of white hide deliming. White hide is a consequent product in the processes in which raw hide is transformed into leather. It is produced in the de-hairing stage which follows the soaking operation. For next operation, tanning, it is necessary to remove calcium hydroxide from white hide. Mathematical descriptions of both non-chemical and chemical deliming are presented, concentration fields of the reacting chemicals described and the importance of the acido-basic boundary inside the white hide shown. Experimental determination of the effective diffusion coefficient is also included. The presented mathematical models can serve as a very good basis for rationalization of the deliming process, save considerable amounts of energies, deliming chemicals and technological water, and make the whole process more environmentally friendly.

Key-Words: - Mathematical modeling, deliming, white hide, free boundary, diffusion

1 Introduction

White hide is a consequent product in the processes in which raw hide is transformed into leather. It is produced in the de-hairing stage which follows the soaking operation. In the de-hairing process, sodium sulphide reduces cystein – the dominant amino-acid present in keratin – to cystin, which is accompanied by the destruction of the keratin protein. The result of the operation is the so-called white hide. The de-hairing process takes place in a strongly alkali conditions of calcium hydroxide (lime). The most important process is tanning reaction in which collagen is stabilized mostly with basic chromium salts. This reaction starts in acid conditions. For this reason it is necessary to remove excess sodium sulfate and calcium hydroxide from white hide. This operation is realized in two steps – plain washing with pure technological water and the second is chemical deliming in which strongly bonded calcium hydroxide is removed by neutralization using the appropriate deliming agent. The plain water washing process can performed either by decantation or through-flow washing. Decantation is used in the beginning when surface calcium hydroxide is removed in the form of suspension. Until recently, rationalization of natural polymers processing, especially of collagen type, had been performed on the basis of direct experimental measurements and long-time practical experience. Application of theoretical tools of chemical engineering was rather an exception in description of operations in which raw material is converted into final products. Production concentration, rising prices of energies, auxiliary agents and technological water, and especially strict environment protection requirements have forced researchers to deal with mathematical-physical description of individual operations and thus to reduce demanding and often expensive experimental measurements and especially their disputable extrapolation to industrial practice. In this article, mathematical simulations of individual steps of white hide deliming process are presented.

2 Mathematical models

2.1. Non-chemical deliming

The following mathematical model of decantation washing is based on the mass balance:

$$c_i V = c_{i+1} V + c_{i+1} V_{0i} \tag{1}$$

there follows

$$c_{i+1} = \frac{c_i}{1+Na_i},\ Na_i = \frac{V_{0i}}{V} \tag{2}$$

The efficiency of decantation (y) for ith-step can be presented as follows:

$$y_i = \frac{c_i Na_i}{c_p},\ y = Na_i \sum_{i=1}^{n} \frac{c_i}{c_p} = 1 - \left(\frac{1}{1+Na_i}\right)^n \tag{3}$$

where

c_i	calcium hydroxide concentration in i[th] step of decantation	[kg m $^{-3}$]
c_{i+1}	calcium hydroxide concentration in (i + 1)[th] step of decantation	[kg m^{-3}]
Na_i	dimensionless consumption of technological water in i[th] step (soaking number)	[1]
c_p	initial concentration of calcium hydroxide in white hide	[kg m^{-3}]

After decantation, through-flow washing takes place. The following mathematical model for through-flow washing is again based on the mass balance of calcium hydroxide:

$$O = \dot{V} c + V \frac{dc}{d\tau} + V_0 \frac{dc_0}{d\tau} \qquad c > 0\ ;\ \tau > 0 \tag{4}$$

$$c(0) = \frac{c_p}{1+Na_0} \tag{5}$$

Integration of differential equation 4 using the initial condition (5) we get:

$$c(\tau) = \frac{c_p \exp\left(-\frac{\dot{V}\tau}{Vo+V}\right)}{1+Na_0} = \frac{c_p \exp}{1+Na_0}\left(\frac{Na_0 - Na}{1+Na_0}\right) \tag{6}$$

where

$$Na = Na_0 + \frac{\dot{V}\tau}{V}\ ;\ Na_0 = \frac{V_0}{V} \tag{7}$$

The efficiency (y) for through-flow washing is as follows:

$$y = \frac{\dot{V}\int_o^\tau c(\tau)d\tau}{c_p V} = 1 - \frac{1}{1+Na_0}\exp\left(\frac{\dot{V}\tau}{V_0+V}\right) =$$
$$= 1 - \frac{1}{1+Na_0}\exp\left(\frac{Na_0 - Na}{1+Na_0}\right) \tag{8}$$

Na_0 – relative hold-up of technological water

$\dot{V}$ - volume through-flow of technological water[m^3/s]

Eq. 8 is valid in the case that *(Na_0 - Na) < 0* is fulfilled.

By the above mentioned decantation and through-flow washing we completely remove the excess sodium sulphide, unbound calcium hydroxide and also partially bound calcium hydroxide. The mathematical model for partially bound $Ca(OH)_2$ (through-flow washing) is shown in the following system of equations. In this case it it necessary to include the inner diffusion of $Ca(OH)_2$ in the mathematical description.

$$\frac{\partial c(x,\tau)}{\partial \tau} = D\frac{\partial^2 c(x,\tau)}{\partial x^2} - \frac{\partial c_A(x,\tau)}{\partial \tau} \qquad 0 < x < b \quad \tau > 0 \tag{9}$$

$$c_A = \frac{Ac}{1+Bc} \tag{9a}$$

$$-S\frac{Dc(b,\tau)}{\partial x} = V_0 \frac{\partial c_o(\tau)}{\partial \tau} + \dot{V} c_0(\tau) \tag{9b}$$

$$\frac{\partial c(b,\tau)}{\partial x} = 0 \tag{9c}$$

$$c(b,\tau) = \varepsilon c_0(\tau) \tag{9d}$$

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

$$c_0(0) = \frac{c_p}{\varepsilon + Na_0} = c_{0p} \tag{9f}$$

c	volume concentration of non-bound calcium hydroxide in white hide	[kg m $^{-3}$]
c_0	volume concentration of calcium hydroxide in leaving technological water	[kg m $^{-3}$]
c_A	volume concentration of calcium hydroxide in white hide (bound calcium hydroxide – Eq. 9a)	[kg m $^{-3}$]
x	coordinate (position from the white hide center)	[m]
τ	time	[s]
D	effective diffusion coefficient of calcium hydroxide in white hide	[m ^{2} s $^{-1}$]
A	sorption parameter (bond strength of $Ca(OH)_2$ on white hide)	[1]
B	sorption parameter	[m ^{3} kg $^{-1}$]
S	total surface area of white hide	[m ^{2}]
V_0	volume of hold-on liquid in the drum	[m ^{3}]
$\dot{V}$	volume through-flow of technological water	[m ^{3} s $^{-1}$]
b	half-thickness of white hide sample	[m]
c_p	initial volume concentration of non-bound calcium hydroxide in white hide	[kg m $^{-3}$]

Eq. (9) describes a non-stationary one-dimensional concentration field of calcium hydroxide in white hide. Eq. (9a) expresses the dependence of bound equilibrium volume concentration of calcium hydroxide on its unbound equilibrium concentration (Langmuir's adsorption isotherm). Eq. (9b) is a mass balance equation describing the equality between the boundary diffusion flow and the sum of mass accumulation in washing drum and exiting mass flow. Eq. (9c) represents isotropic diffusion properties of white hide (axis symmetry). Eq. (9d) is the condition of ideal stirring of liquid phase in the washing drum and the final equations (9e,f) are boundary conditions. Partial differential equation (9) together with the boundary conditions (9a-f) represents a non-linear system and therefore it has only a numerical solution.

If it is possible in Eq. (9a) to neglect Bc against 1, it means that Eq. (9a) takes the form $c_A = Ac$, we obtain a linear model which can be solved analytically. In this case, the value of the effective diffusion coefficient (k) equals:

$$k = \frac{D}{(1+A)}$$

Thus, Eq. (9) takes the form:

$$\frac{\partial c(x,\tau)}{\partial \tau} = k\frac{\partial^2 c(x,\tau)}{\partial x^2} - \frac{\partial c_A(x,\tau)}{\partial \tau} \quad 0<x<b \quad \tau<0 \qquad (10)$$

In this case it is useful to set up the following dimensionless variables:

$$C = \frac{c_p - c(x,\tau)}{c_p} \; ; \quad C_0 = \frac{\left[c_{0p} - c_0(\tau)\right]\varepsilon}{c_p} \; ;$$

$$X = \frac{x}{b} \; ; \quad Fo = k\frac{\tau}{b^2}$$

(11a,b,c,d)

which gives us the dimensionless model of through-flow washing:

$$\frac{\partial C(X,Fo)}{\partial Fo} = \frac{\partial^2 C(X,Fo)}{\partial X^2} \quad 0<X<1 \quad Fo>0 \qquad (12)$$

$$\frac{\partial C(0,Fo)}{\partial Fo} = 0 \qquad (12a)$$

$$C(X,0) = 0 \qquad (12b)$$

$$C_0(0) = 0 \qquad (12c)$$

$$C(1,Fo) = C_0(Fo) \qquad (12d)$$

$$\frac{\partial C(1,Fo)}{\partial X} = \frac{Na_0}{\varepsilon}\;\frac{\partial C_0(Fo)}{\partial Fo} + L\left[1 - C_0(Fo)\right] \qquad (12)$$

$$L = \frac{b^2\dot{V}}{DV_0\varepsilon} \; ; \quad Na_0 = \frac{V_0}{V} \qquad (13a,b)$$

Where D is the diffusion coefficient of calcium hydroxide.

Solving of the above stated model gives:

$$C = 1 - 2L\sum_{n=1}^{\infty} \frac{\cos(Xq_n)e^{-Fo\,q_n^2}}{q_n \sin(q_n)\left(1 + L - q_n \frac{Na_0}{\varepsilon}\right) + q_n^2 \cos(q_n)\left(1 + \frac{Na_0}{\varepsilon}\right)} \quad (14)$$

$$C_0 = 1 - 2L\sum_{n=1}^{\infty} \frac{e^{-Fo\,q_n^2}}{q_n\, tg(q_n)\left(1 + L - q_n \frac{Na_0}{\varepsilon}\right) + q_n^2 \left(1 + \frac{Na_0}{\varepsilon}\right)} \quad (15)$$

Where q_n are the roots of Eq. (16):

$$\left(L - q_n^2 \frac{Na_0}{\varepsilon}\right)\cos(q_n) - q_n \sin(q_n) = 0 \quad (16)$$

2.2. Chemical deliming

For the tanning operation, however, it is necessary to remove calcium hydroxide completely. If we continue with plain water washing, the operation costs increase rapidly (while the efficiency remains practically constant). For this reason, plain water washing has to be replaced with a deliming agent solution (chemical deliming) which, as already said in the introduction, breaks the bond between calcium hydroxide and the collagen matrix by neutralization reaction, which results in creation of unbound neutral calcium salt. For example, using lactic acid as deliming agent gives unbound calcium lactate. Mathematical description of chemical deliming of white hide is based on the non-reacted nucleus model:

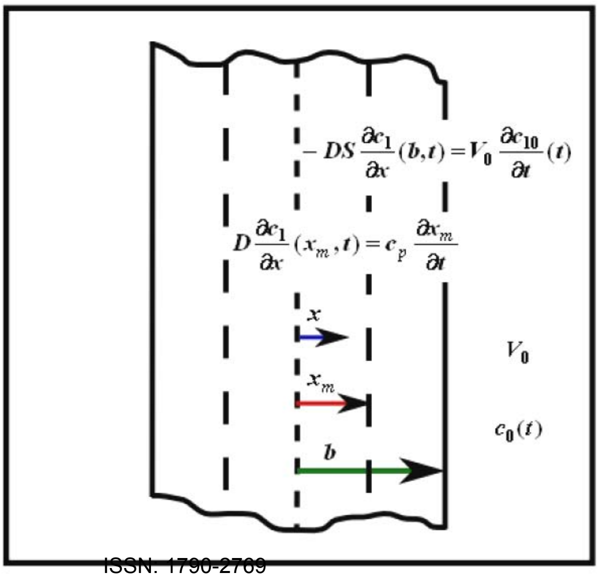


Fig. 1 Model of chemical deliming.

2.2.1. Diffusion of the deliming agent (index *i*)

$$D_i \frac{\partial^2 ci}{\partial x^2}(x,\tau) = \frac{\partial c_i}{\partial \tau}(x,\tau) \quad x_m < x < b \quad \tau > 0 \quad (17)$$

$$c_{pi}\frac{\partial x_m}{\partial \tau}(\tau) = \frac{1}{2} D_i \frac{\partial c_i}{\partial x}(x_m,\tau) \quad (17a)$$

$$V_0 \frac{\partial c_{i0}}{\partial \tau}(\tau) = -D_i S \frac{\partial c_i}{\partial x}(b,\tau) \quad (17b)$$

$$c_i(x_m,\tau) = 0 \quad (17c)$$

$$c_i(b,\tau) = \varepsilon c_{i0}(\tau) \quad (17d)$$

$$c_i(x,0) = 0 \quad 0 < x < b \quad (17e)$$

$$c_{i0}(0) = c_{i0p} \quad (17f)$$

The following Figure 2 shows the concentration field of the deliming agent in solid phase:

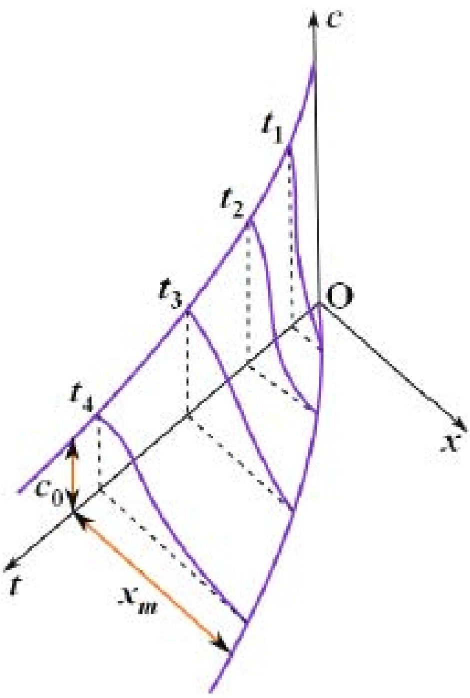


Fig. 2 Concentration field of the deliming agent in solid phase.

2.2.2. Diffusion of the neutral calcium salt (index *j*)

$$D_j \frac{\partial^2 c_j}{\partial x^2}(x,\tau) = \frac{\partial c_j}{\partial \tau}(x,\tau) \quad x_m < x < b \quad \tau > 0 \tag{18}$$

$$c_{pj} \frac{\partial x_m}{\partial \tau}(\tau) = \frac{1}{2} D_j \frac{\partial c_j}{\partial x}(x_m,\tau) \tag{18a}$$

$$V_0 \frac{\partial c_{j0}}{\partial \tau}(\tau) = -D_j S \frac{\partial c_j}{\partial x}(b,\tau) \tag{18b}$$

$$c_j(x_m,\tau) = c_{jp} \tag{18c}$$

$$c_j(b,\tau) = \varepsilon\, c_{j0}(\tau) \tag{18d}$$

$$c_j(x,0) = 0 \tag{18e}$$

$$c_{j0}(0) = 0 \tag{18f}$$

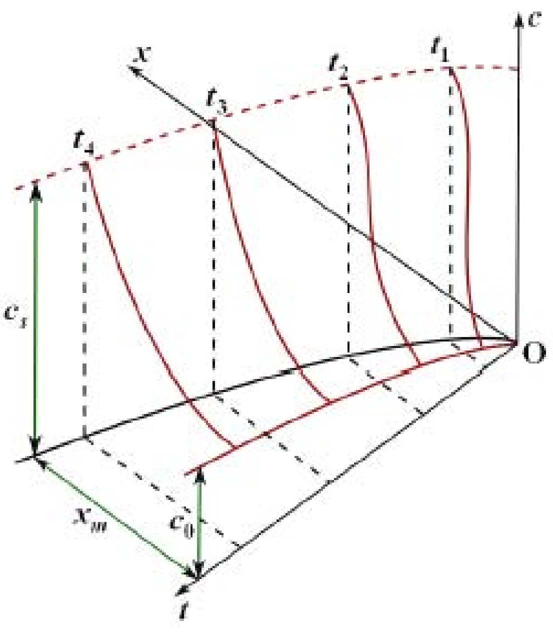


Fig. 3 Concentration field of calcium salt extraction from solid phase (white hide).

Only two transport parameters, effective diffusion coefficients of deliming agent and neutral calcium salts, are necessary to be determined experimentally. In this case, it is possible to use quasistationary model of chemical deliming. It is valid in the case of small concentrations both of both components (deliming agent and salt) and small values of diffusion coefficient.

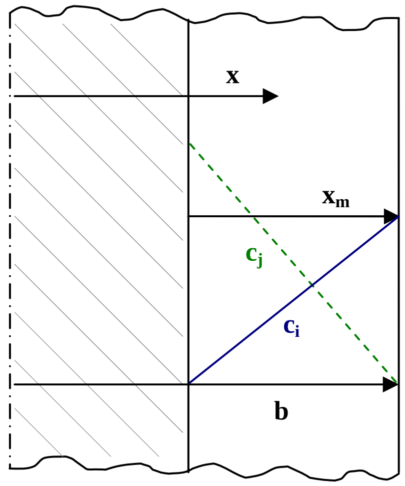


Fig. 4 Quasistationary model of diffusion of the deliming agent. The term x denotes the position of the free acid-hydroxide boundary, and b denotes half of the sample cross-section.

Mass balance for the moving of acido-basic boundary:

$$+S\ c_{pj} \frac{dx_m}{d\tau} = \frac{S\ D\ c_{p0i}}{2x_m} \tag{19}$$

Integration of the previous equation gives:

$$x_m = \sqrt{\frac{D\ c_{p0i}\tau}{c_{pj}}} \tag{20}$$

3 Experimental part

3.1. Determination of the effective diffusion coefficient of HCl

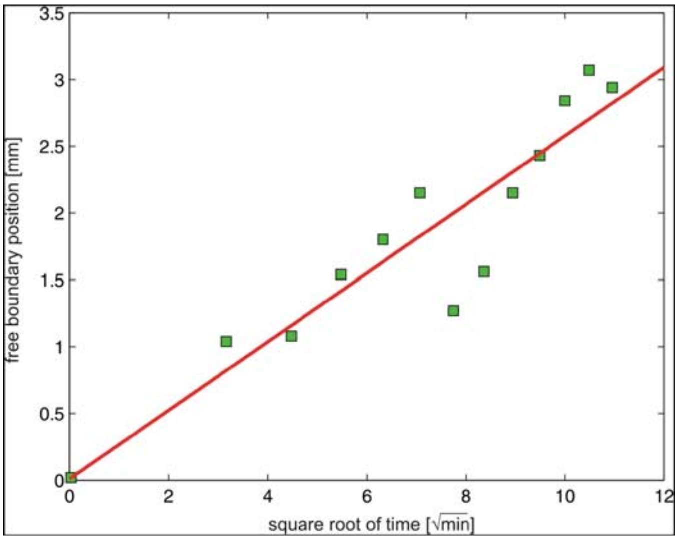
Let us assume again that the diffusion coefficient is small enough. Then we can assume that the concentration field of the acid inside a calcimine sample (between the acid-hydroxide boundary and the surface of the sample) is linear (see Figure 4 above).

The results of our experimental measurements are shown in Table 1:

time (hour:min)	free boundary position $x_m(\tau)$ (mm)
00:00	0.00
00:10	1.04

00:20	1.08
00:30	1.54
00:40	1.80
00:50	2.15
01:00	1.27
01:10	1.56
01:20	2.15
01:30	2.43
01:40	2.84
01:50	3.07
02:00	2.94

By plotting $x_m(\tau)$ against the square root of time with the use of linear regression we received the following graph:



It enables us to estimate the slope of the straight line:

$$k = 0.2566 \frac{mm}{\sqrt{\min}}$$

With the use of the slope of the straight line, we can determine the effective diffusion coefficient of HCl:

$$D = 4.64 \times 10^{-9} m^2 s^{-1}$$

4 Conclusions

As already stated in the introduction, description of white deliming can be based either on experimental practice or on the usage of theoretical tools of chemical engineering. Our contribution deals with the second option. It was shown that even this very complicated process – transport of chemicals in a natural polymer accompanied by a chemical reaction – allows a mathematical description and, moreover, the description reflect reality well (within given precision). In our contribution we present mathematical models of both non-chemical and chemical white hide deliming. In the case of chemical deliming, our approach includes the use of non-reacted nucleus model and the free acido-basic boundary position. Our work is supported by experimental determination of the effective diffusion coefficient of the deliming agent, in our case hydrochloric acid. The presented mathematical models can serve as a very good basis for rationalization of the deliming process, save considerable amounts of energies, deliming chemicals and technological water, and make the whole process more environmentally friendly.