Application of Kinetics Models in Leather Processing

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Abstract

Kinetics are present in almost all industrial processes. Its study is the key to clarify the behavior of many chemical systems. Understanding how a reaction occurs, its elementary steps, reaction pathways and kinetic mechanisms, enables the processes improvement. In leather processing, the study of kinetics provides important information about the necessary operating time in beamhouse, tanning, dyeing and fatliquoring stages, so that energy and resources can be saved. In experimental kinetic study, a model can be fitted to the data so that it numerically reproduces the experimental measurements of the process in a satisfactory way. The model fit is important because it allows the optimization of the process without the need for more experiments to be done. In literature, (i) phenomenological kinetic models are found, obtained through the laws of physics and chemistry, as well as the laws of conservation of mass, energy and movement and (ii) empirical models, based on experimental data obtained in the process, which are generally correlated by statistical and mathematical methods, such as regressions. For leather processing, few works use kinetic models, even though a wide variety of studies performing kinetic experiments are found. The aim of this work was to evaluate which kinetic models are used in the leather process, as well as to identify whether the hypotheses made in these models correspond to what occurred experimentally. The most used models are: pseudo-first order, pseudo-second order, Weber-Morris, Cegarra-Puente and modified Cegarra-Puente. These models were applied in the stages of unhairing, tanning and dyeing.

Key words: kinetics, kinetics modeling, leather processing

1 Introduction

The effective utilization of chemical products is an important factor for a sustainable industry as it decreases the effluent volume and the environmental impact (Kanagaraj, 2016). The optimization of the process of leather manufacturing allows the use of the properly amount of chemical needed, reducing the amount of hazardous chemicals and the pollution load of wastewater (Spivak, 2019). This can be achieved using kinetic models that permit simulations and prediction of the evolution of the system under the studied working conditions. With mathematical models, it is possible to scale-up without repeating experiments (Kanagaraj, 2011).

In leather processing, kinetic studies provide important information about the necessary operating time to complete the reaction in beamhouse, tanning and wet-finishing operations so that energy and resources are saved. The nature of the reactants can influence the speed of certain chemical reactions, due to the different process inputs in leather processing, such as raw material (skin/hide - species, race), chemicals (supplier, choice, environmental problems), fashion/trends.

Over the years, a wide variety of kinetics models (Langmuir, Pseudo-first order, Pseudo-second order, Elovich, Crank, Boyd, Bangham, Weber and Morris) have been formulated (Largitte, 2016). In applying such models, it is extremely important to follow the assumptions of the models to obtain a consistent result. In literature, kinetic models are often used in the data processing of wastewater of leather process (Piccin el al., 2012), however few papers use kinetic models for leather processing. The aim of this work was to evaluate which kinetic models have been used to study the steps of unhairing, tanning, and dyeing, as well as to identify whether the hypotheses made in these models correspond to what occurred experimentally. This paper identified the main kinetic models used in leather processing, their hypotheses, conditions in which they are valid and their type (phenomenological or empirical) and verified the utilization of the kinetic models in the literature according to their hypotheses.

2 Methodology

The Scopus and ScienceDirect databases were used to survey the most used kinetic models in leather processing. For the search, the following terms were considered in the title, abstract and keywords: “kinetics” and “leather’’, “kinetics” and “tanning’’, “kinetics” and “dyeing’’, “kinetics” and “unhairing”.

Searches were made in August 2021, and only articles that made the kinetic modeling of leather processing were considered in this work, those that addressed the topic in the treatment of effluents from the tanning process were discarded. The results of the databases research were analyzed to eliminate duplicate articles and exclude inappropriate articles. After this evaluation, the articles remained categorized as to the stage of leather processing in which the kinetics was evaluated (unhairing, tanning, dyeing).

3 Kinetics of leather processing

Leather manufacturing requires several steps, with sequential additions of chemicals, intercalated by washes and mechanical processes (Aquim, 2009). The steps that involve adding chemicals and washing are usually done in wet medium performed in drums. These steps require mass transfer from the bath to the hide. For the unhairing diffusion of chemical products is involved. Tanning and dyeing steps involve the diffusion and fixation of tanning agents and dyes, respectively. It is very important to know the kinetics of the process (Gutterres and Mella, 2015).

3.1 Unhairing

In the unhairing step the hair can be destroyed (hair-burning) or saved (hair saving). In order to preserve the hair, enzymes are used and attack the hair roots and the epidermis (Dettmer et al., 2013). Firstly, to get into the hair roots, the enzymes must diffuse into the hide. The diffusion through the hide matrix takes 70% of the total enzymatic time (Yates, 1969).

3.2 Tanning

The tanning process takes place in two sequential steps: first, the diffusion of the tanning molecules into the hide and the subsequent fixation, in which the tanning agent reacts with the collagen (Fuck, 2008). The reaction mechanism of collagen with tanning agents varies with their chemical characteristics. Carboxylic groups, for example, normally react with mineral tanning agents (chromium). On the other hand, the peptide groups include the carbonyl in which there is interaction by strong hydrogen bonding

with vegetable tannins (Gutterres and Silva, 2010). Factors influencing diffusion are the size of the molecule responsible for tanning, solution viscosity, temperature, pH, tanning concentration, mechanical actions, etc. (Faber, 1990). The pH, for example, causes changes in the collagen stereostructure that influence the binding of certain tanning agents (Schroepfer and Meyer, 2015).

The hide is pickled with acidic pH so that the carboxylic groups that make up the collagen structure are protonated taking low affinity with chromium. This low affinity allows a better diffusion of chromium throughout the hide preventing superficial fixation. For diffusion to occur, the hide remains in the drums with chromium salt for about 5 hours, during which time the chromium molecules penetrate the hide matrix due to the difference in chromium concentration (concentration gradient) between the hide's internal matrix and the external matrix of the hide affected in turn by the movement of the drum (Gutterres and Mella, 2014; Sathish, 2016). After the chromium has penetrated the hide, the fixation step can be started. To fix the chromium, it is necessary the carboxylic groups of the collagen structure to be ionized and the chromium salt changes the charge of its complex, going from anionic to cationic. Basifying agents are added to the bath to gradually raise the for pH 2,5 – 3,0 to pH 3.8 - 4.2 with increase of temperature to about 50°C, during the movement of the drum for 1-2 h when the chromium fixes (Gutterres and Mella, 2014).

Tanning with vegetable tannins also takes place in two stages, diffusion and fixation. The conditions for the process to take place are, however, different from those for chrome tanning. Vegetable tannin tanning requires a pre-tanning to open the collagen fibers. Bonding with collagen occurs through the hydrogen bonds of phenolic groups in tanning substances with certain basic groups attached to the polypeptide chain. Fixation occurs at a temperature ranging from 30 to 40°C after the tannin has passed through and at a pH in the range of 3 to 6, to avoid tearing and oxidation of the leather (Auad, 2018, 2020).

3.3 Dyeing

The dyeing process occurs with the distribution of a dye in the solution and its adsorption on the collagen matrix (Püntener, 2000; Kanagaraj et al., 2016). The kinetic behavior of a dye during its transfer from the bath to the leather occurs in at least five steps. They are: 1. Diffusion of dye from the bath to the leather surface; 2. Diffusion through the boundary layer between water / leather; 3. Surface adsorption; 4. Diffusion in the leather matrix (Püntener, 2000) and 5. Fixation (Fuck, 2008).

Diffusion is one of the most important phenomena (Püntener, 2000). Different types of dyes have different rates of adsorption, due the difference in their chemical structure, and this can lead to problems in achieving levelness and shade consistency (Kanth et al., 2009; Kanagaraj et al., 2016). Dye fixation happens due to the chemical reactions between the amine molecule of collagen and the dye molecule (Fuck, 2008). It is not always necessary for the dye to be crossed in all leather cross-section/thickness. Depending on the purpose of the leather article, only superficial dyeing can be done.

Thus, the two steps may or may not occur in sequence. Nonetheless, the high-grade leathers are throughout dyed so that they have the same shade on the cut edge and on the back (flesh side) as on the more compact grain side (Püntener, 2000). Efforts have been made to understand the phenomena involved in the dyeing process, however the physico-chemical mechanisms in leather dyeing are not yet clearly understood. Even if the same procedure and the same chemicals are used, differences in depth and shade level can occur from batch to batch (Muralidharan and Rao 1990; Püntener, 2000).

4 Kinetics models applied to leather processing

The kinetic models applied to leather processing are models usually considered in the kinetic modelling of solid-liquid adsorption. This may happen because the steps in which they are used in leather processing resemble diffusion/adsorption process inside porous adsorbent solids. In unhairing, the chemicals need to diffuse until they reach the hair. In tanning, in a bath containing chromium or vegetable tannin, the tanning agent diffuses into the hide fiber due to concentration gradient, and fixation occurs very similarly to a chemisorption. Similarly, in cross-dyeing, dye molecules in a bath diffuses to the interior of the leather fibers, and the driving force is again a concentration gradient. In literature about leather, most used kinetic models are empirical, based on experimental data obtained in the process, which are generally correlated by statistical and mathematical methods, such as regressions. On the other hand, phenomenological kinetic models are obtained through the laws of physics and chemistry, and the laws of conservation of mass, energy and movement, are rarely used in this application.

The adsorption kinetic models that have been also used in leather processing, are commonly classified as based on reaction control, as the pseudo-first order and pseudo-second order models (Qiu, 2009; Souza, 2017) and based on diffusional control, as the Weber-Morris model (Qiu, 2009). In the

reaction control models the adsorption is considered to be the most time-consuming process, so the intraparticle diffusion and external mass transfer can be neglected. Otherwise in models with diffusion control, the diffusion is the rate limiting step. There are still other models used in the leather processing, such as the Cegarra-Puente, modified Cegarra-Puente and Vickerstaff. Some of the most commonly used models in the lather process are presented in the sequence.

4.1 Weber and Morris model

Weber and Morris (1963) have studied the batch adsorption of alkyl benzene sulfonates by activated carbon. The mass transfer into the interior of the particle, characterized by an intraparticle diffusion coefficient, can be the slowest step (Largitte, 2016), as seen in the Equation 1:

$$q_t = k_i \sqrt{t} + C \tag{1}$$

Where q_t is the amount of adsorbent in the adsorbent (mg/g) at time t, that varies linearly as a function of the square root of time t; k_i is constant of the intraparticle diffusion rate and C is a constant that normally is associated to the degree of the boundary effect.

In the work of Schwaab (2017), it was observed that this relationship between the adsorbed concentration versus the square root of time is obtained when a semi-infinite solid is considered, a linear adsorption isotherm and with constant liquid phase concentration. With similar assumptions, it also can be obtained for finite solid, but in this case this relationship in only valid at the beginning of the process, that is, very low time values. For this reason, Weber-Moris model must be used carefully, particularly if the validity of the assumptions cannot be assured.

4.2 Cegarra-Puente

Cegarra and Puente (1967) did the dyeing tests in a bath with a constant capacity. In order to keep the bath concentration constant in the dye bath, an amount greater than that needed to saturate the polyester fiber was used. The process of dyeing polyester fibers with dispersed dyes has the diffusion as the slowest reaction, consequently, is the one which sets the rate of the process.

The Cegarra-Puente equation is based on heterogeneous reactions delayed by the reaction chemicals where a desorption rate appears. This empirical equation relates the rate of dye absorption to the

amount of dye absorbed by the substrate at any time during the dyeing process (Cegarra and Puente, 1967; Kanth et al., 2009). Equation 3 was proposed by Cegarra and Puente.

$$\ln\left[1-\frac{C_t^2}{C_\infty^2}\right]=-Kt \tag{2}$$

Where $C\infty$ is the concentration in the adsorbate at the equilibrium, C_t is the concentration of adsorbate in solution at time t and K is the constant proposed by Cegarra and Puente.

4.3 Modified Cegarra-Puente / Cegarra-Puente-Valdeperas

Some modifications were proposed to the Cegarra-Puente model, one of them was carried out in the doctoral thesis of J. Valdeperas, in which it was assumed that the direct velocity, in relation to what it would have in a bath of constant concentration, would decrease over time. Valldeperas suggested that the forward speed be proportional to a power of time, which would also affect the speed of the inverse reaction. The equation is adapted to tannin baths with varying exhaustion, introducing the appropriate modification, where 'a' is the coefficient depending on exhaustion (Sánchez, 1981). The modified equation is presented in Equation 3:

$$\ln\left[-\ln\left[1-\frac{C_t^2}{C_\infty^2}\right]\right]=a\ln t+a\ln K \tag{3}$$

Another way to write Equation 3 is as shown below in Equation 4:

$$\frac{C_t}{C_\infty}=\left[1-e^{-(kt)^a}\right]^{1/2} \tag{4}$$

This equation allows the calculation of Ct for different times, knowing the velocity constant and the exponent. Where $C\infty$ is the concentration in the adsorbate at the equilibrium, C is the concentration of adsorbate in solution at the moment t, K is the constant proposed by Cegarra and Puente, t is the time, and a is the coefficient depending on exhaustion.

4.4 Vickerstaff

Using a diffusion model, Vickerstaff developed an approximation to Crank's equation to describe dyeing (Jian et al., 2011), as shown in Equation (5).

$$C_t = 2C_\infty \sqrt{\frac{Dt}{\pi}} \tag{5}$$

Where *Ct* was the concentration of released total protein, *C*∞ is the concentration at the equilibrium, *D* was the diffusion coefficient and *t* was the time.

4.5 Pseudo-first-order

The pseudo-first-order is an empirical model proposed by Lagergren (1898) to describe the kinetic process of adsorption in the liquid-solid phase of oxalic acid and malonic acid on charcoal. It is commonly used for liquid-solid adsorption systems. The pseudo-first-order model describes the adsorption kinetics of a species on an adsorbent particle by the first order differential equation (6).

$$\frac{dq_t}{dt} = k_1 \left(q_e - q_t \right) \tag{6}$$

According to this model, the adsorption capacity is proportional to the "distance to equilibrium" which is expressed by the difference between the equilibrium concentration and the amount adsorbed at time *t* (Rodrigues and Silva, 2016). Its integrated form is commonly used, by integrating this differential equation Eq. (7) for the boundary conditions: qt = 0 at = 0 and qt = qt at = t, the following equation can be obtained (Benjelloun, et al. 2021):

$$q_t = q_e \left(1 - k_1 e^{-k_1 t} \right) \tag{7}$$

Where *qe* is the amount of adsorbate in the equilibrium adsorbent (mg/g); *qt* is the amount of adsorbent in the adsorbent at time *t* (mg/g); *k1* is Lagergren's first order constant rate; and *t* is the contact time (min).

4.6 Pseudo-second-order

The pseudo-second-order model was proposed by Ho (1998) to describe a kinetic process of adsorption of divalent metal ions onto peat. The model's assumptions were that the adsorption can be of

second order and the rate limiting step can be chemical adsorption involving valence forces through the sharing or exchange of electrons between the peat and the divalent metal ions. Furthermore, the adsorption follows the Langmuir equation. Kinetics can be expressed by the following second order differential equation Eq. (8)

$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t \right)^2 \tag{8}$$

Its integrated form is commonly used, by integrating this differential equation Eq. (8) for the boundary conditions: qt = 0 at = 0 and qt = qt at = t, the mathematical equation of the following pseudo-second order kinetic model Eq. (9) was obtained:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{9}$$

Where *qe* is the amount of adsorbate in the equilibrium adsorbent (mg/g); *qt* is the amount of adsorbent in the adsorbent at time *t* (mg/g); K_2 is the pseudo-second-order constant rate; and *t* is the contact time (min).

Table 1 presents the main hypotheses made in the deduction of the models and which step is the limiting of the considered model are presented. In this compilation of the kinetic models is indicated its use in different steps of leather processing as found in the literature.

Table 1: Kinetic models applied in leather processing referenced in the literature.

Kinetic Model	Equation	Hypothesis	Reference
Cegarra and Puente	$\ln\left[1-\frac{C_t^2}{C_\infty^2}\right]=-Kt\,*$	Bulk phase concentration remains constant Process reversibility	Kanth 2009 Kanth 2010
Modified Cegarra and Puente	$\ln\left[-\ln\left[1-\frac{C_t^2}{C_\infty^2}\right]\right]=a\ln t+a\ln K\,*$	Varying exhaustion	Kanth 2009 Kanth 2010
Weber-Morris	$q_t=k_i\sqrt{t}+C$	Bath concentration is constant The adsorption kinetics is instantaneous The equilibrium isotherm is linear	Kanth 2009 Sathish 2019
Pseudo-first order	$\frac{dq_t}{dt}=k_1\left(q_e-q_t\right)$ $\ln\left(q_e-q_t\right)=\ln q_e-k_1t\,*$	The adsorption driving force is the difference between the solid phase concentration at any time and at equilibrium	Sathish 2019
Pseudo-second order	$\frac{dq_t}{dt}=k_2\left(q_e-q_t\right)^2$ $q_t=\frac{q_e^2k_2t}{1+q_ek_2t}$	The adsorption driving force is the square of the difference between the solid phase concentration at any time and at equilibrium	Sathish 2019 Kanagaraj 2011 Kanagaraj 2016
Vickerstaff	$Ct\ =\ 2C\sqrt{\frac{Dt}{\pi}}$	Infinite bath	Jian 2011

*linearized equation

5 Results and discussions

Table 2 presents the application of the kinetic models to each leather processing step. In the literature, the models used are mostly empirical (Cegarra-Puente, modified Cegarra-Puente, Pseudo-first order and Pseudo-second order). They are easy to use, but are subjected to operational and process conditions in which they were deduced and, therefore, cannot be used to describe the system with conditions different from those determined for its adjustment, which limits its application for prevision.

It can be seen that kinetics is studied mainly in the tanning and dyeing steps, steps that involve the incorporation of materials into the hide. These two steps of processing lead to pollution of effluent. In the tanning step, not all chromium salt is fixed in the leather, and the remaining chromium go to the effluent (Kopp 2021). At dyeing, 1 to 5% of the dye applied in the leather dyeing remains in the effluent (Fuck et al. 2018) and the effluents from dyeing are difficult to treat by conventional methods (Ortiz-Monsalve et al. 2019).

The influence of pseudo-first and pseudo-second order and Weber-Morris models when it comes to kinetics is notorious, being present in most works, even though these models are very restricted and depend on specific conditions for their application.

The pseudo-first order, pseudo-second order, Cegarra-Puente and Cegarra-Puente modified models used in the analyzed articles were used in their linearized form. The correlation coefficient or sum of squares was used as an index of quality in fitting the data to the model. Transforming the nonlinear equation into a linear form involves assumptions, and the obtained results can be very undermined. This leads to data distortion and, consequently, results that violate the standard least squares assumption of variance and normality. The linearization of the pseudo-second model results in more than five different linear equations as a result one can get different parameters when using different forms of the same model for a given process. Using the non-linear form of the function results in the error being distributed along the curve (Chowdhury and Saha, 2011; Kajjumba, et al 2018).

Unhairing

Jian (2011) used enzymes in the unhairing step. The enzyme protease did little harm on skin at the first 3 h, and after this time it degraded collagen and resulted in serious injury to skin. Using a different enzyme

extract of *Bacillus subtilis* BLBc, samples started to show some damages to the hide grains above 6 h of reaction (Dettmer et al., 2013). The kinetics of released collagen protein indicates that the injury to skin took place in 3-6 h. Therefore, it's necessary to control the time of protease unhairing within an appropriate limit. The good fit of Vickerstaff model suggests that enzymatic unhairing by protease is a diffusion-controlled process at the initial stage. Where Vickerstaff can be used only in a short time. An alternative was studied by Andreoli et. al. (2015) in which enzymatic-oxidative hair removal with enzyme extracted from two strains of Bacillus subtilis (BLBc 11 and BLBc 17) and hydrogen peroxide was used, obtained as a result a hair removal that does not promote degradation for hair removal.

Tanning

As seen before, the tanning step, with vegetable tannins or chromium, takes place in two well-defined steps of diffusion and fixation. So, the kinetic study must be carried out taking into account these separate steps that do not occur simultaneously. The papers studied the diffusion stage, which is very important due to the crossing of the chemical to guarantee the stabilization of the hide, in the case of tanning. So, only kinetic models that are based on diffusion should be used. However, pseudo-first-order and pseudo-second-order are based on reaction (Wang 2020) and were used.

Sathish (2019) studied chrome tanning using Weber-Morris, pseudo-first-order and pseudo-second-order. The best fit model has been chosen based on a linear regression coefficient (R^2) and squared sum of errors (SSE) values and also by comparing the experimentally measured *qe* with best fitted theoretically calculated *qe*. The results indicate that the Weber-Morris was the best kinetic model. Thus, the intraparticle diffusion is controlling the sorption of Cr (III) from bulk solution. However, the process is "complex" with more than one mechanism limiting the rate of sorption. Kanth (2010) based the result on the shape of the isotherm and the R^2 values to support the modified Cegarra-Puente model for absorption of tannins.

Dyeing

Kanth (2009) reported the application of enzyme acid protease for the improvement of the exhaustion of dyes. The shape of the isotherm and the R values support the modified Cegarra-Puente model

for adsorption of both the dyes. Kanagaraj (2016) used a copolymer from trimming waste hydrolysate that has been developed using starch and poly vinyl alcohol as high performance auxiliary in dyeing. The carboxylic acid groups present in the copolymer are responsible for enhancing the adsorption of dye. Studies on kinetics of dye-uptake suggest that the dye molecules approach the collagen fiber, get adsorbed, slowly diffuse through pores and get fixed with the functional groups of collagen by electrostatic forces. The rate of absorption of dye inside the porous leather was represented by pseudo-second-order kinetics. Kanagaraj (2011) used a nanoparticle polymer to enhance the dye uptake. The reason for the improved uptake of dye may be due to the presence of carboxyl groups that play as the main functional group of interaction with dye compounds. The rate of mass absorption inside the porous leather was represented by pseudo-second-order kinetics.

Table 2: Application of kinetic models in leather processing report in the literature.

Chemical product	Process conditions	Kinetic model	According to the kinetic model?*	References
		Unhairing		
Enzymes	Enzyme: 150% (w/w) Temperature: 35°C Rotation: 8 rpm	Vickerstaff	Yes	Jian 2011
		Tanning		
Chrome	Basic chromium sulfate: 5% w/w Time: 15 to 400 min Temperature: 37°C	Weber Morris* Pseudo-first-order Pseudo-second-order	Yes	Sathish 2019
Vegetable tannin	Wattle (tannin): 20% Time: 5 to 120 min Temperature: 25, 30, 35 and 40°C	Weber Morris (Parabolic) Cegarra- Puente Modified Cegarra-Puente*	Yes	Kanth 2010
		Dyeing		
Acid Black 194 and Acid Black 210	pH: 4.5 50°C	Weber-Morris Cegarra- Puente Modified Cegarra-Puente*	Yes	Kanth 2009
Acid brown MFR	different temperature, pH, duration and concentration of dye	Pseudo-second-order	No	Kanagaraj 2016
Acid Black 20470	Dye: 1% or 2% (based on leather weight) Time: 1 h, 50, 60, 70, and 80h pH: 5.6	Pseudo-second-order	No	Kanagaraj 2011

6 Conclusions

This study identified few works focused on the study of leather processing kinetics, in contrast to the large amount that is found for the kinetics of treatment of wastewater from the leather industry. The few works found in the literature used empirical models or simplification of phenomenological models. These models have as main limitation the fact that they are only valid under specific conditions in which they were deduced, or in the case of simplified models under the conditions considered for simplification. The most used models (pseudo-first order, pseudo-second order, Cegarra-Puente and modified Cegarra-Puente) are usually used in their linearized forms. However, it is not very appropriate to use the linear method to determine kinetic parameters, because transforming a non-linear kinetic model into a linearized form tends to change the error distribution and therefore distort the parameters. Thus, it is advised that more research in this regard should be carried out, in order to better understand the kinetics of the unhairing, tanning and dyeing steps. Furthermore, the use of phenomenological models should be encouraged.

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