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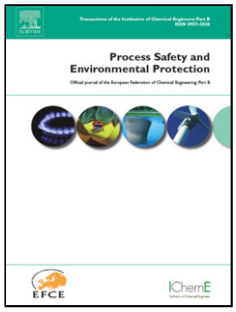


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# Technological-economic optimization of enzymatic hydrolysis used for the processing of chrome-tanned leather waste

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**Abstract**

Chrome-tanned solid waste generated in large quantities by the leather industry poses a major threat not only to the environment, but also to living organisms including humans because of its potential toxicity. The crucial issue determining viable industrial processing and valorisation of this waste is the process economy. In this work, a mathematical model that enables technological simulation of complete process for chrome shavings utilization by alkali-enzymatic hydrolysis was developed and incorporated into an economic optimization model. The model includes experimentally verified quantitative description of the dependence of reaction rate on enzyme concentration, an important factor which so far has not been addressed in this context. The simulation calculation showed that the enzyme optimal concentration usually lies in a relatively narrow area between 0.2 and 0.4 % wt. of the

feedstock dry matter. Such optimization can save considerable portion of the processing costs – as much as 43 % at given calculation parameters – and improve the plant capacity and annual profit leading to the reduction of payback period from initial 4.7 years to final 1.5 year. The results obtained through this engineering approach are valuable not only for the processing plant operation, but also for the overall process desfn including the design of process control algorithms, and therefore are applicable and adjustable for a wide range of cases, from individual waste producers to centralized leather waste processing.

**Keywords**

Chrome-tanned waste; Enzymatic hydrolysis; Enzyme kinetics; Techno-economic optimization; Process simulation;

**Nomenclature**

| Symbol | Unit | Description |
|---|---|---|
| $a$ | (1) | Constant of reaction rate expression |
| $b$ | (1) | Constant of reaction rate expression |
| $C_{CHEM}$ | (USD) | Costs of chemicals |
| $c_{DM}$ | (% wt.) | Dry matter concentration in reaction mixture |
| $c_E$ | (% wt.) | Concentration of enzyme in the reaction mixture |
| $c_H$ | (% wt.) | Concentration of protein hydrolysate in the reaction mixture |
| $c_p$ | (% wt.) | Concentration of hydrolysable protein fraction in the reaction mixture |
| $c_{PROT}$ | (% wt.) | Content of hydrolysable protein fraction in the feedstock |
| $c_{p0}$, $c_{p3}$ | ($J \cdot kg^{-1} \cdot K^{-1}$) | Specific heat capacity of the stream 0, 3 |

| | | |
|---|---|---|
| $c_{2W}$ | (% wt.) | Content of water in the filter cake |
| $DM_{SH}$ | (% wt.) | Dry matter content of the shavings |
| $F_{ME}$ | (m/m) | Multiple effect evaporator efficiency |
| $F_{MI}$ | (W/kg) | Input power per unit of reaction mixture |
| $F_{WY}$ | (m/m) | Efficiency of filter cake washing |
| $F_W$ | (m/m) | Proportional amount of washing water to the estimated weight of moist filter cake (Washing factor) |
| $\Delta H_{vap}$ | (MJ/kg) | The enthalpy of vaporization of water |
| $k$ | ($[m/m]^{1-a-b} \cdot min^{-1}$) | Reaction rate coefficient |
| $L_1$, $L_2$ | (1) | Heat losses coefficients |
| $m_i$ | (kg) | Weight of the *i*-th stream |
| $m_{SH}$ | (kg) | Input weight of the moist shavings |
| $P$ | (W) | Stirrer input power |
| $P_E$ | (USD/kWh) | Unit price of electric energy |
| $P_{ENZ}$ | (USD/kg) | Unit price of enzyme |
| $P_H$ | (USD/kg) | Unit factory selling price of final product |
| $P_{ST}$ | (USD/GJ) | Unit price of steam used for heating |
| $P_W$ | (USD/kg) | Unit price of waste streams utilization |
| $Q_{TOT}$ | (J) | Costs of thermal energy |
| $\Delta T_1$ | (°C) | Temperature difference for heating the reaction mixture to the reaction temperature |
| $\Delta T_2$ | (°C) | Temperature difference for heating the filtrate to its boiling point in the evaporator |
| $V_R$ | ($m^3$) | Volume of hydrolysis reactor |
| $\tau$ | (min) | Time |
| $\tau_{FIN}$ | (min) | Total time of hydrolysis reaction |

| | | |
|---|---|---|
| $\tau_{PREP}$ | (min) | Overall time necessary for reactor preparation for hydrolysis (charging/discharging operations, heating) |

## 1. Introduction

The leather industry has long been considered as highly polluting, generating huge amounts of liquid and solid waste in all production steps (Kanagaraj et al., 2015). The solid waste is mainly composed of fibrous structural proteins collagen and keratin. Since this protein waste also contains other chemicals, it represents significant environmental burden, especially if left unutilized. Around 35-40 % of proteinous solid wastes from tanneries are chrome shavings (Kanagaraj et al., 2006; Pati et al., 2014), which are produced when the tanned hide is shaved to a uniform thickness. They are mainly composed of collagen cross-linked with trivalent chromium (CrIII) complexes. The content of chromium in chrome shavings may vary, but according to various literature sources ranges from 2 to 4 % (related to dry matter content) (Cabeza et al., 1998; Famielec, 2020; Pati et al., 2014; Sharaf et al., 2013).

The production of chromium-containing solid wastes (including chrome shavings) in tanneries has been recognized as a problem for many years but recent pressure from environmental authorities has given the problem increasing urgency (Ozgunay et al., 2007; Parisi et al., 2021; Pati et al., 2014; Yang et al., 2019).

It is particularly the presence of chromium that makes this waste potentially hazardous for both the environment and living organisms including humans because of the possibility of oxidation to hexavalent form under various external conditions such as temperature, pH or the presence of strong oxidizing agents (Apte et al., 2005; Kolomaznik et al., 2008).

Hexavalent chromium is highly toxic and associated with many diseases from dermal irritation to carcinogenicity (Pavesi and Moreira, 2020). The precise mechanisms of its action,

as well of other heavy metal pollutants, is still a subject of extensive research, since it is suggested to be related with epigenetic factors such as DNA methylation (Sharavanan et al., 2020).

Landfilling and incineration, still the dominating methods of chrome shavings disposal (Jiang et al., 2016), both carry the risk of secondary pollution of air, soil and groundwater with hexavalent chromium. Especially landfilling, though forbidden in many countries, leaves behind huge sites of contaminated soil and consequently ground waters, which require extensive remediation (Muthusaravanan et al., 2018; Rambabu et al., 2021) that may last for generations.

As a result, sustainable and cost-effective processing of this potentially hazardous waste globally remains at the forefront of concern of major leather producers.

Chrome shavings can be directly utilized as absorbent materials for cleaning soils or wastewater from oils and other chemicals. They can be further processed in many ways – e.g. via thermal processes such as incineration, pyrolysis including high temperature carbonization, anaerobic digestion for the production of biogas, production of leather/polymer composites and various types of hydrolysis (Famielec, 2020; Ma et al., 2019; Parisi et al., 2021; Pati et al., 2014; Priebe et al., 2016).

The latter includes hydrolysis in either acid or alkaline medium or hydrolysis using enzymes. Especially enzymatic hydrolysis based on the action of alkaline proteases has been intensively investigated by researchers since it represents an environmentally friendly way and can be carried out at milder conditions compared to chemical hydrolysis. However, utilization of mere enzymatic hydrolysis is limited by several shortcomings, from which temperature tolerance of enzymes and enzyme selectivity are the most important, according to (Jiang et al., 2016). A two-step process was invented by (Taylor et al., 1993), which included treatment of chrome shavings with inorganic alkalis (mostly hydroxides) and removal of gelatable protein

in the first step, followed by enzymatic hydrolysis. The drawback of this procedure was relatively high content of ash in the resulting protein hydrolysate. Further progress in this field was achieved by the development of modified alkaline-enzymatic hydrolysis, where for the maintenance of alkaline conditions were used low-molecular amines in combination with reduced amount of inorganic base (magnesium oxide, hydroxides of alkali metals or alkali earth metals) (Kolomazník et al., 2000). The technology was successfully implemented on the industrial scale, with the yield of low-ash protein hydrolysate of up to 80 %, and a filter cake containing high portion of chromium. The reaction takes place at a temperature no higher than 80 °C and a pH value between 8 and 9.

Though the chemical composition of chrome shavings makes them suitable for processing to recover their constituents, it is the entire process economy that needs to be taken into account for sustainable industrial implementation (Cabeza et al., 1999). As was pointed out by (Jiang et al., 2016), even combined (multi-step) methods of chrome-tanned waste processing suffer from high cost operations.

Regarding the processing economy, there are two major aspects: first is the quality, application and commercialization of final products, which is a subject of intensive research; e.g. (Arcibar-Orozco et al., 2019; Gaidau et al., 2009; Kolomazník et al., 2000; Kumar et al., 2015; Langmaier et al., 2008). Other crucial aspects are the operating and investment costs of the technology itself. Proper assessment and optimization of parameters for automatic control of the process can substantially reduce the operating costs and make the process flexible to produce final products with specific customer-tailored parameters (e.g. the molecular weight of protein hydrolysate can be altered by the composition of the reaction mixture and the concentration of enzyme). There are several factors (variables) affecting the economy of the process, many of them antagonistic, such as price of the enzyme vs. its concentration vs. reaction rate, the overall time of the process and the resulting yield vs. the maximum

performance of the entire technological equipment. Very few publications can be found dealing with a detailed study of hydrolysis conditions and their mutual dependence and relation to the economic parameters. From most recent literature (Sasia et al., 2019), the authors studied the effect of enzyme concentration and time on the degradation of chrome shavings (expressed as Total Kjeldahl Nitrogen content). They replaced the commonly used protease Alcalase with a bating enzyme to reduce the process costs, however, the process required longer time and the yield of the protein fraction was lower than in the case of commercial proteases. Other work related to the topic provides kinetic data only for further processing of the insoluble product of chrome shavings hydrolysis, the filter cake (Hrncirik et al., 2005). Cost optimization of the hydrolysate obtained from leather waste was described in (Vaskova and Kolomaznik, 2018). Nevertheless, experimental verification of the kinetics model was not presented and pure modelling and simulation approach was employed. In addition, the authors did not include concentration of enzyme as one of the key factors affecting the reaction kinetics. Let note that the relation between enzyme price and its optimal amount is usually significant factor for the overall process economy as was recently stressed in techno-economy study of enzymatic hydrolysis of switchgrass (Larnaudie et al., 2019). Assessment of a technology from the economic point of view is mostly performed via techno-economic analysis. This well-established approach is usually aimed at examining feasibility of new processes in terms of plant size, comparison of different process designs, identification of key processes and factors affecting the overall economy and even identification of most important research areas as is illustrated by recent papers adopting this approach (Larnaudie et al., 2019; Lim and Foo, 2017; Lundberg et al., 2018; Thaore et al., 2018). In case of batch processes, the throughput analysis and bottleneck identification can substantially increase the overall plant performance (Koulouris et al., 2000). In addition, key processes can be rigorously optimized to determine technical parameters which correspond to economic

optima. For such purpose, specific mathematical optimization models are usually formulated and solved. For instance, (Jolliffe and Gerogiorgis, 2017) suggested nonlinear optimization model for minimization of total costs of liquid-liquid extraction process in ibuprofen manufacturing and employed surrogate equations describing thermodynamic equilibria in order to decrease computational load. Similar surrogate optimization approach was used in paper (Ho et al., 2019) for maximizing the reactor productivity. The authors stressed that sole determination of optimal parameters of subprocess(es) can be suboptimal from the entire technology point of view. Consequently, optimization of the entire production process shall be addressed if the overall plant economic performance is to be optimized. Genetic algorithm working with results from external simulations was employed for minimization of total annual costs in (Ge et al., 2020), whereas authors of study (Larnaudie et al., 2019) used statistical model based on experimental data and limited number of simulations to find optimal technology conditions (enzyme dosage and solids content in reaction mixture) corresponding to minimal selling price of ethanol. Discussed analyses and optimizations were aimed at economy assessment and optimization of processes, which are to be realized in industrial praxis. However, during plant lifetime (20 – 30 years) many factors like prices of chemicals and feedstock or utilities do change which affects specific values of optimal technology conditions. In other words, one can expect shift of optima during long-term operation of plant. Despite importance of this issue for maintaining maximal economic performance of the processing plant during its lifetime, it has been rarely addressed.

The objective of this study was therefore to build a mathematical model facilitating technological-economic simulation of the entire process for utilization of chrome-tanned solid waste in order to perform technology optimization. The study particularly includes experimental verification of reaction kinetics of alkali-enzymatic hydrolysis of chrome shavings and its dependence on enzyme concentration, which to the best of author's

knowledge so far has not been addressed in literature. The verified kinetic model presents a cornerstone of the overall technological-economic model used for determination of optimal values of key process parameters.

## 2. Material and Methods

### 2.1 Material

Chrome shavings for hydrolytic treatment were collected in a local tannery in Vietnam. Proteolytic enzyme Alcalase® 2.5 L was purchased from Novozymes A/S. Magnesium oxide (MgO) was of analytical grade, n-Butylamine purity was 99.5%. Demineralized water was prepared on the AQUAL 29 system, its conductivity was lower than 1 μS/cm. All other chemicals were of analytical grade.

### 2.2 Methods

Chrome shavings were subjected to hydrolytic treatment according to the following procedure. A sample of approximately 13 g of chrome shavings of known dry matter content was placed in a laboratory flask and after addition of water (approximately 165 g), the mixture was gradually heated under constant stirring and reflux up to 65 °C. The pH of the mixture chrome shavings/water (reaction mixture liquid phase, more precisely) was 3.9 in all cases. After the temperature reached 65 °C, magnesium oxide (MgO) was added in the amount of 0.4 g (in the form of a suspension in water), which increased the pH up to 8.5. To keep the pH around this value (8.2-8.5), n-butylamine was gradually added to the reaction mixture. After 30 min after the addition of MgO, a sample of approximately 5 ml was taken from the mixture using a syringe. The sample was filtered and analysed for dry matter content. Immediately after taking the first sample, proteolytic enzyme Alcalase was added in each reaction mixture in the amount of 0.056, 0.11 and 0.56% wt. (related to dry matter of the

shavings), respectively. Other samples were taken in the time of 30, 60 and 120 min after the addition of Alcalase and treated in the same way as the first sample. The reaction was stopped after 180 min, the reaction mixture was filtered through a filter paper KA-1 and the obtained filtrate and filter cake were weighted and analysed for the dry matter content.

The dry matter of the samples was determined gravimetrically, by drying the samples to constant weight at a temperature of 103 °C; the method is based on ISO 662. The ash content was determined using a method based on standard ČSN 14775. The total chromium content was determined from the overall elemental composition of the samples measured on the XRF spectrometer SPECTRO iQ II, with evaluation made by the method of fundamental parameters. The nitrogen content was determined by Dumas method by a Thermo FLASH 2000 N/Protein Analyser. Determination of hexavalent chromium ($Cr^{VI}$) content was performed according to standard ISO 17075-1. The pH of the reaction mixture was measured using a G20 automatic titrator equipped with a SC-115 electrode.

### 2.3 Mathematical Modelling

At the beginning, it is essential to summarize the basic processing scheme, process streams and compounds involved. The first process in batch utilization of chrome shavings is alkali hydrolysis followed by reaction mixture filtration. Obtained filtrate is further concentrated, usually by means of water evaporation, in order to manufacture the final product – protein hydrolysate with desired content of dry matter. The process flow diagram (PFD) including numbering of process streams is presented in Fig. 1. In order to simplify the real process for the purposes of its simulation employing mathematical modelling, it is assumed that all streams can contain only the following compounds: water (W), protein hydrolysate (H), hydrolysable protein fraction (P) and other compounds which are inert and do not interfere with the hydrolysis (R).

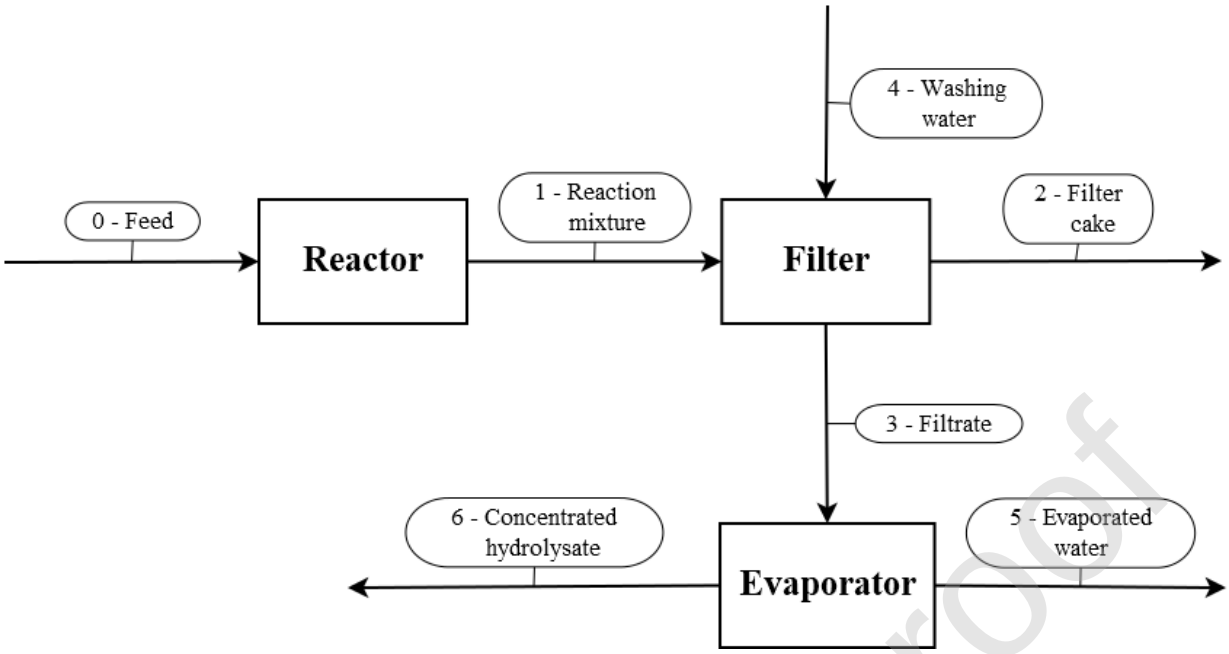


Fig. 1. Process flow diagram of chrome shavings utilization.

*2.3.1 Hydrolysis*

First process employed in chromium shavings processing is hydrolysis of the protein fraction. The reaction mixture is heterogeneous, the feedstock – chrome shavings – forms the solid phase of the reaction mixture. Hydrolysable fraction of the solid phase (especially collagen protein) is gradually disintegrated by the action of hydrolysis reaction catalysed by enzymes, the thickness of shavings particles is decreased by the course of the reaction and smaller protein macromolecules, which are soluble in the reaction mixture liquid phase, are released to the liquid phase. The hydrolysis continues even in the liquid phase and leads to a gradual decrease in average molecular weight of protein macromolecules until the limit value is reached (usually 5-10 kDa). Other reactions take place during hydrolysis (e.g. neutralization of free carboxyl groups of amino acids), the reaction rate of hydrolysis is notably sensitive to changes in pH of the reaction mixture and its temperature due to the used catalyst – enzyme.

Even the mechanism of the hydrolysis reaction catalysed by enzyme subtilisin (used in this study – commercial product Alcalase) is not completely understood yet and is a subject of studies (Valencia et al., 2014). It should also be mentioned that the reaction rate is significantly influenced by the mass transfer between the solid and liquid phase. Consequently, the exact quantitative description of the reaction is complicated and a model incorporating all mentioned factors would not be suitable for the purpose of technological-economic simulation. In addition, such model requires determination of a number of physical parameters, which are in many cases difficult to measure. For said reasons, an engineering approach was applied and several, rather empirical models, were tested. Since mass transfer can play an important role, it is necessary to point out that such models are valid for specific feedstock only and it is necessary to employ stirring at a level of intensity, which ensures that a so-called kinetic region is achieved from the viewpoint of outer mass transfer. In other words, the data can be transferred to a larger scale provided that the same mixing conditions and size distribution of the feedstock are ensured.

The very basic idea of the hydrolysis reaction employed in this study is depicted in the following equation:

$$P \xrightarrow{enzyme} H \qquad (1)$$

In other words, hydrolysable protein fraction (P) of the feedstock is turned into soluble protein hydrolysate (H) by the action of the hydrolysis reaction. The content of hydrolysable protein fraction (P) in the feedstock is determined analytically and incorporated in the model as input value $c_{PROT}$.

As was mentioned, several empirical and semi-empirical models (like Michaelis–Menten kinetics) were tested to fit the data; however, the best results were achieved with the following expression:

$$r = k \cdot c_E^a \cdot c_P^b \quad (2)$$

The influence of pH and temperature on the reaction rate was not incorporated in the model because in practice the reaction is led at stable conditions, which correspond to the optimal values of these parameters for applied enzyme.

The parameters of the rate equation were found with the help of the simplex method incorporated in Matlab software "fminsearch" function. Similar procedure with more details on the kinetic model data fitting and model parameters optimization procedure can be found in (Pecha et al., 2016). The sum of the squares of relative errors was used as an objective function.

Mass balance of the batch reactor leads to the following differential equations (Eqs. (3-4)), with the solution of which a reaction mixture composition can be calculated.

$$\frac{dc_P}{d\tau} = -k \cdot c_E^a \cdot c_P^b \quad (3)$$

$$\frac{dc_H}{d\tau} = k \cdot c_E^a \cdot c_P^b \quad (4)$$

*2.3.2 Filtration*

In the next step, a suspension forming the reaction mixture is filtered. Let assume for the purposes of the mathematical model that the solid phase is completely separated from the liquid phase and that the filtrate therefore contains only hydrolysed protein (H) and water

(W). This is justified by the fact that the ash content of the hydrolysate is usually low by the employed procedure and protein content in final hydrolysate is about 90 % of its mass.

As is obvious from the PFD (Fig. 1), filter cake washing is employed in order to increase the yield of the filtrate. The moisture content of filter cake is usually known from the experiments and is dependent on the type of filter used and filtration conditions employed. Therefore, the consumption of washing water will be estimated from the presented mass balance, where numbers stand for process streams and capital letters for compounds present in the modelled system:

$$m_4 = \frac{m_1(c_{1P}+c_{1R})}{1-c_{2W}} F_W \quad (5)$$

The estimation of washing water consumption ($m_4$) is based on the assumption that the filter cake contains no hydrolysate; $F_W$ stands for washing factor governing the proportional amount of washing water to the estimated weight of moist filter cake. Said assumption (zero hydrolysate content in the filter cake) is used just for the $m_4$ calculation.

Since it is reasonable to use relatively limited amount of washing water in order to prevent notable dilution of the filtrate, some hydrolysate will remain in the filter cake. The liquid phase is composed solely of the hydrolysate and water. Consequently, the relation between the hydrolysate composition in liquid phase in stream no. 1 (Reaction mixture) and stream no. 2 (Filter cake) can be expressed by the following equation:

$$\frac{c_{1H}}{c_{1H}+c_{1W}} F_{WY} = \frac{c_{2H}}{c_{2H}+c_{2W}} \quad (6)$$

Factor $F_{WY}$ stands for the efficiency of filter cake washing. Without washing, it is equal to 1 because of aforementioned composition of liquid phase. Its precise value and its dependency on the amount of washing water can be determined experimentally for used filter system. Equations (5-6) then enable easy completion of the mass balance of filtration and calculation of a detailed composition of all process streams involved.

### *2.3.3 Filtrate evaporation*

In the last step, the filtrate is concentrated by means of water evaporation. Let assume that stream no. 5 (Evaporated water) contains only water, which is reasonable due to the fact that protein hydrolysate is non-volatile. Volatile compounds, which can be present or formed during evaporation, are negligible in amount and not significant for the technological-economic study. As a result, the mass balance of the evaporator leads to the following expressions quantifying the amount of evaporated water (Eq. (7)) and concentrated protein hydrolysate (Eq. (8)), *i.e.* the final product of the processing technology.

$$m_5 = m_3 \left(1 - \frac{c_{3H}}{c_{6H}}\right) \tag{7}$$

$$m_6 = m_3 - m_5 \tag{8}$$

With the help of introduced equations, it is possible to complete the mass balance of the whole process, which presents the technology core of the model.

### *2.3.4 Process economy*

In the next step, it is necessary to address the economic side of the modelling of leather waste processing technology. The main focus is on the unit operating costs because for example the

labour costs related to the unit mass of product are heavily dependent on the location of the processing plant, its size and level of applied automation.

There are four basic components of the unit operating costs in the processing of leather waste – costs of chemicals, costs of electrical energy, costs of thermal energy and costs of waste stream processing, as is summarized in the following expression Eq. (9).

$$C = C_{CHEM} + P \cdot P_E \cdot \tau_{FIN} + Q_{TOT} \cdot P_{ST} + m_2 \cdot P_W \quad (9)$$

In the presented study, the costs of chemicals include only the cost of the enzyme because it presents the major component of chemical costs in the applied technology, thus the costs of chemicals are dependent on enzyme price $P_{ENZ}$ and its overall amount in the reaction mixture, as is captured in the following equation:

$$C_{CHEM} = m_0 \cdot c_E \cdot P_{ENZ} \quad (10)$$

Regarding the electrical energy, the costs are given in Eq. (9) and represent consumption of electrical energy by the reactor stirrer because these costs are directly influenced by the reaction time and size of the reactor. The costs are calculated for prescribed amount of input feedstock – chromium shavings. As a result, if the shavings dry matter concentration in the reaction mixture is decreased, the overall reaction mixture weight necessary for the processing of the shavings prescribed amount is increased. Consequently, a stirrer with higher input power should be used. This proportional relation is governed by the constant value of input power per unit of reaction mixture – $F_{MI}$, and the final stirrer input power $P$ is calculated simply as:

$$P = m_0 \cdot F_{MI} \quad (11)$$

The thermal energy is used in several steps, specifically to heat up the reaction mixture to the reaction temperature ($Q_1$), to heat the filtrate to its boiling point in the evaporator ($Q_2$) and to evaporate the water ($Q_3$) in order to concentrate (thicken) the final product, protein hydrolysate aqueous solution. Although $Q_2$ and $Q_3$ are transferred in one equipment (evaporator), they are calculated separately:

$$Q_1 = m_0 \cdot c_{p0} \cdot \Delta T_1 \cdot L_1 \quad (12)$$

$$Q_2 = m_3 \cdot c_{p3} \cdot \Delta T_2 \cdot L_2 \quad (13)$$

$$Q_3 = \frac{m_5 \cdot \Delta H_{vap}}{F_{ME}} \quad (14)$$

$$Q_{TOT} = Q_1 + Q_2 + Q_3 \quad (15)$$

Factor $L$ was incorporated in order to include thermal losses in the economic calculations, factor $F_{ME}$ stands for multiple effect evaporator efficiency. Multiple effect evaporators are able to evaporate more kilograms of water per one kilogram of steam used as a source of thermal energy; for more detailed discussion see e.g. (Hackett, 2018).

The technology produces only one by product (stream no. 2, Filter cake) whose utilization is still subject of research. As a result, the filter cake usually presents waste which is in many countries considered as hazardous due to its high chromium content and its processing brings additional costs to the process as is included in Eq. (9). Note that the purpose of hydrolysis is

to utilize valuable protein fraction of the chrome shavings on one hand and to concentrate the chromium for further potential utilization on the other hand.

Presented equations form the main economic part of the leather waste processing mathematical model. Finally, key economic indicators can be calculated and further evaluated – unit operating costs, unit gross profit, annual profit and production. Note that annual operating time of 6 240 hours was used for calculation of annual number of batches and related annual production.

Both parts, i.e. technological and economic, were incorporated into an in-house software written in Matlab environment for the purposes of process simulation. The model contains a set of nonlinear ordinary differential equations (Eqs. (3-4)), which were solved by numerical methods. Specifically, function "odes15s" of Matlab environment was used for said purpose. Calculation of processing plant economic parameters (e.g. total capital investment or total manufacturing costs) was done separately with Microsoft Excel according to key input data obtained from the technological-economic model – unit operating costs and annual production. This calculation reflects location of processing plant in the Czech Republic. Detailed description of these calculations is given in Supplementary Material.

## 3. Results and discussion

An integral part of the model is simulation of chromium shavings hydrolysis reaction kinetics. Especially this part needs to be based on experimental data in order to produce reliable results in simulations. As was described in the section of mathematical modelling, the influence of temperature and pH was not studied because these variables are given by their optimal values for used enzyme, and the purpose of the process control is to ensure that the optimal values of reaction temperature and pH are kept constant without notable fluctuations throughout the reaction. The reaction rate is, however, substantially influenced by the concentration of

enzyme and consequently this factor was experimentally investigated. The course of the reaction was studied by determining the dry mass of the product – protein hydrolysate – in the reaction mixture liquid phase. The experimental data and their comparison with kinetics model prediction are summarized in Fig. 2. The error bars in Fig. 2 mark a 10% deviation from measured value. This deviation is typical with the used feedstock – partially because of experimental error arising from the work with heterogeneous reaction mixture and mainly because of the fact that the properties of the waste feedstock are heterogeneous in their nature as well (variable thickness/grain size and especially fluctuations in feedstock composition). The agreement between measured data and the model is satisfactory and reasonable for the purposes of further process modelling. In fact, the data set description by the model can be considered very good, taking into account all simplifications made and the complexity of the real system as described in the modelling section.

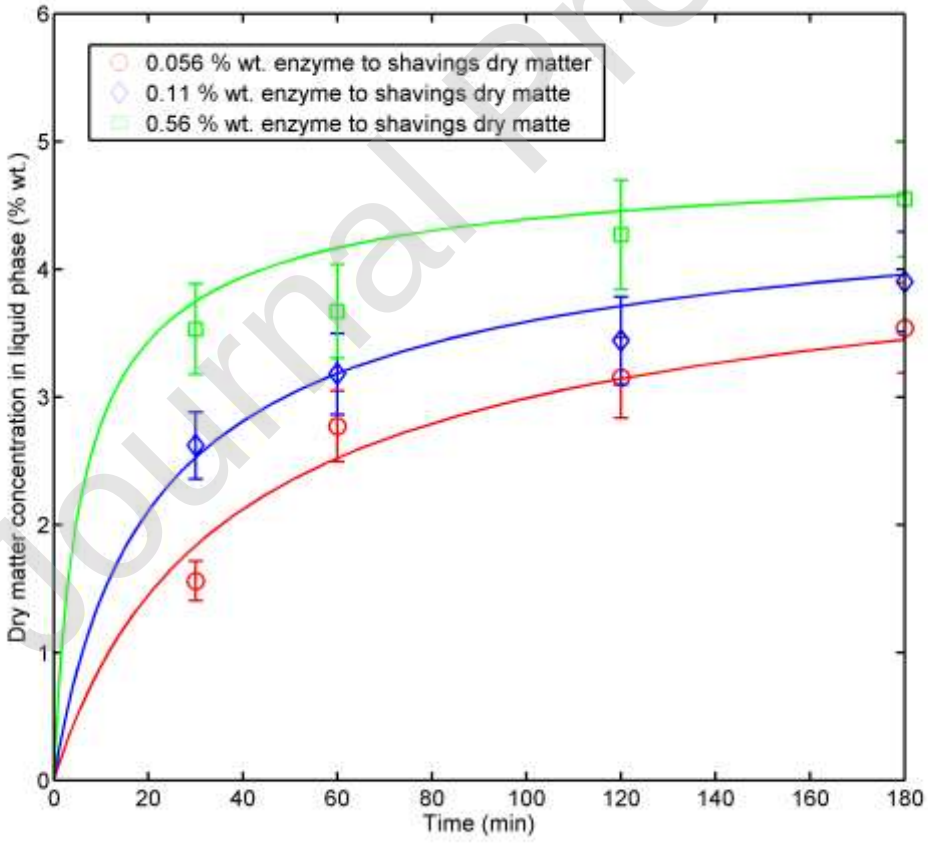

Fig. 2. Dependency of the hydrolysis course on the enzyme concentration and comparison of experimental data (points with 10% error bars) and model prediction (lines); 65 °C, pH 8.2-8.5.

For the sake of completeness, basic properties of the used feedstock – chrome shavings – are summarized in Table 1. Chrome shavings composition reported by other authors are in similar range; see e.g. (Arcibar-Orozco et al., 2019; Cabeza et al., 1998; Sharaf et al., 2013).

Table 1

Chrome shavings composition.

| **Parameter** | **Unit*** | **Value** |
|---|---|---|
| Dry matter | % wt. | 68.1 |
| Ash content | % wt. in DM | 8.8 |
| Nitrogen | % wt. in DM | 15.7 |
| Total chromium | % wt. in DM | 2.0 |
| $Cr^{VI}$ | mg/kg of DM | <3 |

*DM stands for Dry Matter

Table 2

Values of general input model parameters.

| **Parameter** | **Unit** | **Value** |
|---|---|---|
| *a* | 1 | 0.756 |
| *b* | 1 | 2.60 |
| $c_{PROT}$ | % wt. | 87 |

| | | |
|---|---|---|
| $c_{p0}$, $c_{p3}$ | $J \cdot kg^{-1} \cdot K^{-1}$ | 4180 |
| $c_{2W}$ | % wt. | 80 |
| $c_{6H}$ | % wt. | 30 |
| $DM_{SH}$ | % wt. | 50 |
| $F_{ME}$ | m/m | 2.5 |
| $F_{MI}$ | W/kg | 1.5 |
| $F_{WY}$ | m/m | 0.2 |
| $F_{W}$ | m/m | 0.75 |
| $\Delta H_{vap}$ | MJ/kg | 2.3 |
| $k$ | $[m/m]^{1-a-b} \cdot min^{-1}$ | 9402.2 |
| $L_1$, $L_2$ | 1 | 1.1 |
| $m_{SH}$ | kg | 1000 |
| $P_E$ | USD/kWh | 0.2 |
| $P_H$ | USD/kg | 0.75 |
| $P_{ST}$ | USD/GJ | 20 |
| $\Delta T_1$ | °C | 50 |
| $\Delta T_2$ | °C | 40 |
| $V_R$ | $m^3$ | 5 |
| $\tau_{PREP}$ | min | 90 |

The verified model describing the reaction system kinetics including its dependence on the concentration of catalyst – proteolytic enzyme – was further incorporated into the model of the overall process for chrome shavings utilization. As can be assumed, the concentration of enzyme is an important factor influencing the hydrolysate yield at a given reaction time and having significant impact on the processing costs because the price of this agent presents

notable fraction of the operating costs (see Table 3S in Supplementary Material). Results of simulation calculations aimed at capturing the dependence of the unit operating costs on applied enzyme dose and its current price are presented in a 3D graph (Fig. 3). As evidenced by the Figure, there is a relatively narrow area of minimal unit operating costs and its precise location is dependent on current price of the enzyme; the range of enzyme optimal concentration at given model parameters lies in the range between 0.2 and 0.4 % wt. of the feedstock dry matter for most enzyme prices. Similar dependency is obtained also for annual gross operating profit (see Fig. 1S in Supplementary Material).

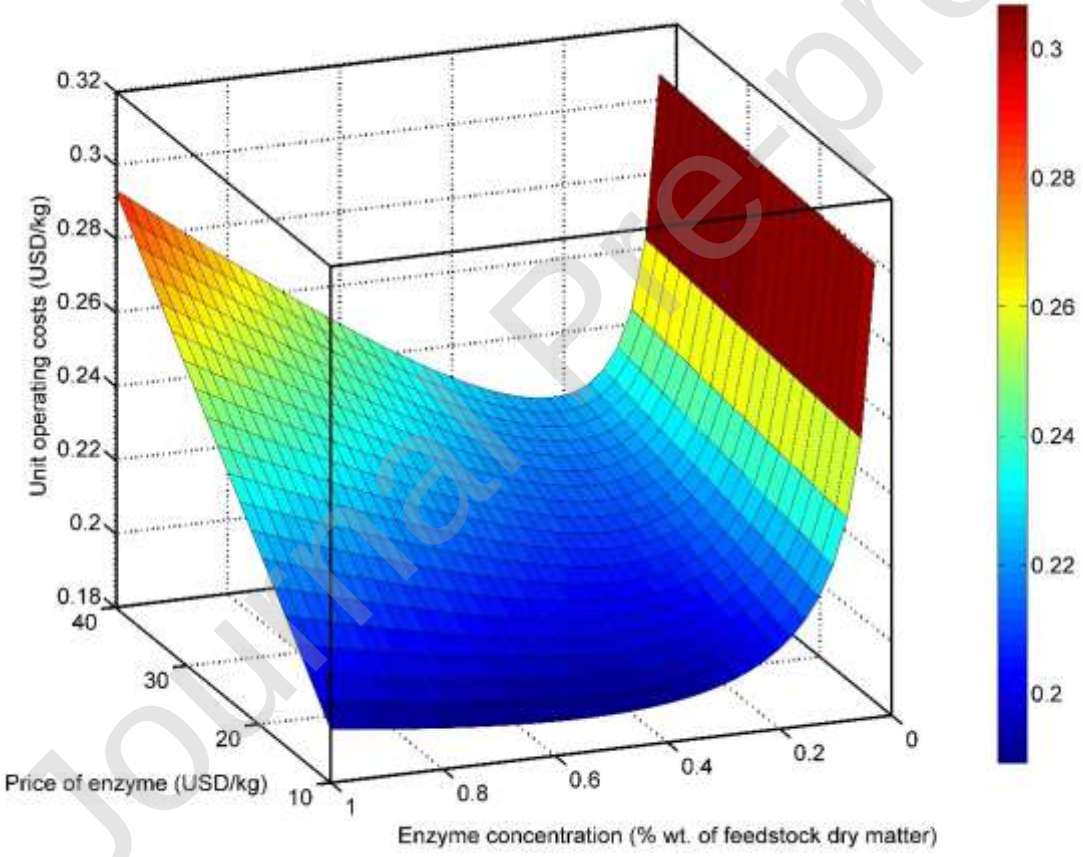


Fig. 3. Dependency of unit operating costs on price of enzyme and its concentration; Simulation parameters were: $c_{DM}$ = 6 % wt., $\tau_{FIN}$ = 180 min, $P_W$ = 0.2 USD/kg, other general input parameters are given in Table 2.

Another important factor is the concentration of dry matter of the feedstock in the reaction mixture. It is apparent from the mass balance that adding more feedstock into the reactor results in higher concentration of hydrolysate in the reaction mixture and consequently the amount of evaporated water during the phase of hydrolysate concentration is lower. Reading this, one can easily come to a conclusion that an increase in feedstock concentration should lead to reduction of the processing costs as well as to improvement of plant performance. Although the mathematical model allows to calculate results for any concentration of the feedstock, the reality is not so smooth. In fact, (as revealed by many experiments), each feedstock is slightly different, with different content of dry matter, and a certain amount of water is necessary in order to ensure that the reaction mixture can be stirred satisfactorily in the laboratory and especially in industrial conditions. In addition, also the reaction proceeds differently at different ratios of feedstock and water. Consequently, relatively limited range of feasible feedstock concentrations is achievable in practice, which is often difficult to predict without proper experimental measurement with the specific feedstock to be processed. It is therefore of value to calculate optimal enzyme concentration, which corresponds to the minimal unit operating costs, and its dependence on feedstock dry matter concentration in the reaction mixture. Summary of said calculations is depicted in Fig. 4. As can be seen, an area of minimal operating costs exists at each level of feedstock concentration in the reaction mixture and its location is a function of enzyme concentration. As was stated above, increasing the feedstock concentration in the reaction mixture leads to the decrease of unit operating costs. Nevertheless, even at the level of the highest feedstock concentration in the reaction mixture (10 % wt. of dry matter), the optimal enzyme load can save considerable portion of the processing costs – as much as 43 % as documented by Fig. 4.

The model therefore enables to dynamically determine the technological conditions (like enzyme loading) corresponding to economic optimum (minimal costs or maximal profit) according to current economy inputs – prices of energies, product or waste treatment – which usually do fluctuate in time during long-term operation of a processing plant. Such optimization can be valuable even as a part of reaction control algorithm – which will dose the enzyme according to the real dry matter concentration in the reaction mixture and its current price besides other important parameters. The form of the model, i.e. set of mathematical expressions, supports its discussed utilization for standard operation of the processing plant, allows straightforward application of optimization algorithms facilitating numerical determination of optima location and the model can be relatively simply implemented in many custom made software including mentioned control algorithm. Let note that utilization of common simulation approach and software, e.g. (Koulouris et al., 2000) or (Lundberg et al., 2018) for the described purpose of process optimization could be cumbersome especially due to large number of simulation calculation required (e.g. Fig. 3. is based on 800 unique simulations) and more complicated implementation of such simulation software into optimization/control algorithms. On the other hand, standard simulation software shall provide more detailed data during the phase of designing a processing unit. However, presented relatively simple model of chrome shavings utilization can also bring important insight into decision about the size of the equipment in view of investment costs and the processing unit production performance, as is discussed below.

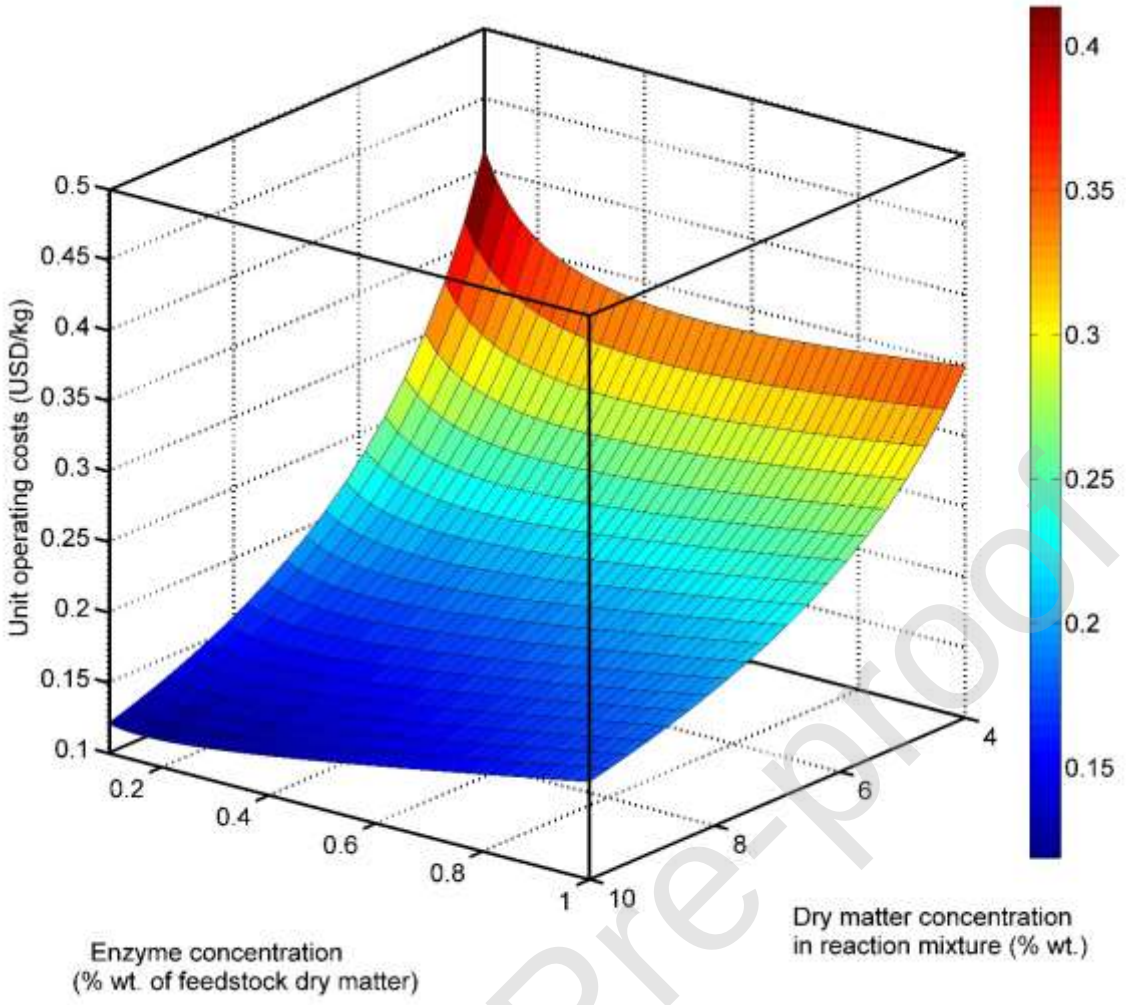


Fig. 4. Dependency of unit operating costs on concentrations of enzyme and feedstock; Simulation parameters were: $P_{ENZ}$ = 25 USD/kg, $\tau_{FIN}$ = 180 min, $P_W$ = 0.2 USD/kg, other general input parameters are given in Table 2.

As is obvious from the theory and also experimental measurements depicted in Fig. 2, there is a close relationship between enzyme concentration and reaction kinetics – reaction time necessary to achieve considerable hydrolysate concentration in reaction mixture and simultaneously considerable yield of the hydrolysate which is the main product of waste processing. In other words, the hydrolysis reaction can be accelerated by increasing enzyme concentration and consequently the reaction time can be reduced while keeping the same

yield. The costs of the production will be higher at increased enzyme loading, but shortening of the reaction time leads to increased number of batches, i.e. the overall plant processing capacity – its annual production. As a result, there is a trade-off between the reaction time (enzyme costs) and annual profit. The maximal annual profit can be determined with the help of the model, as is illustrated in Fig. 5. The simulation calculations suggest that it is worth reducing the reaction time at the cost of higher enzyme loading and even higher waste processing costs (see Table 3S in Supplementary Material) in order to maximize the plant annual profit. Note that in some cases longer reaction time can be dictated by the requirement of achieving lower molecular weight of the product. Nevertheless, even in the case of longer reaction time it is possible to determine the economically optimal reaction parameters as is shown in Fig. 5. As was stated above, discussed optimization shall be beneficial during standard operation of a processing plant for the assessment of plant optimal economic performance whenever the inputs are changed.

On the other hand, reaction time optimization is important also in the phase of processing plant designing as it affects sizing of the equipment. Impact of different reaction time on the overall plant economic performance including estimation of investment costs and related payback period is illustrated on two cases summarized in Table 3 assuming plant location in the Czech Republic. The initial case is based on usual hydrolysis time applied at industrial level (see e.g. (Kolomazník et al., 2000)), 180 min, the applied enzyme concentration is optimal from the gross annual profit point of view (0.63 % wt., see Fig. 5). The simulation is based on constant size of the reactor used for all the previous calculations (5 $m^3$ of the reaction mixture). Other equipment (especially filter and triple effect evaporator) is sized to match the reactor performance, the evaporator is designed to operate in continuous manner. In order to improve the accuracy of the presented estimates, total manufacturing costs in Table 3 include labour and other fixed costs. Detailed calculation of discussed processing plant

economic parameters is summarized in Supplementary Material. As can be seen, unit operating costs present 0.272 USD/kg, annual production is 1 244 tonnes of final hydrolysate resulting from 1 386 batches and estimated payback period reaches 4.7 years for the initial case. This presents acceptable result especially in the view of plant size. Let note that the sizing of such plant is heavily influenced by the amount of available feedstock – chrome shavings – and thus the economic viability of smaller plants is plausible for implementation of the technology in praxis.

The second case is based on utilization of optimal reaction time and catalyst loading (50 min and 1 % wt., respectively, see Fig. 5). Reduction in reaction time leads to higher performance of the reactor – the annual production is nearly doubled (2 263 tonnes from 2 674 batches), investment costs are higher as larger filter and especially evaporator are necessary. Even unit operating costs are considerably increased to 0.364 USD/kg. Despite higher operating and investment costs, this option has significantly better payback period of 3.1 years, which can be expected at increased plant capacity. Furthermore, in case it would be technically viable to increase dry matter content to 8 % wt., the payback period would be 1.5 year provided that all other inputs remain the same as in the second case. Consequently, the overall plant economic performance in both design and production phase can be notably increased with the help of the developed model and presented optimization approach.

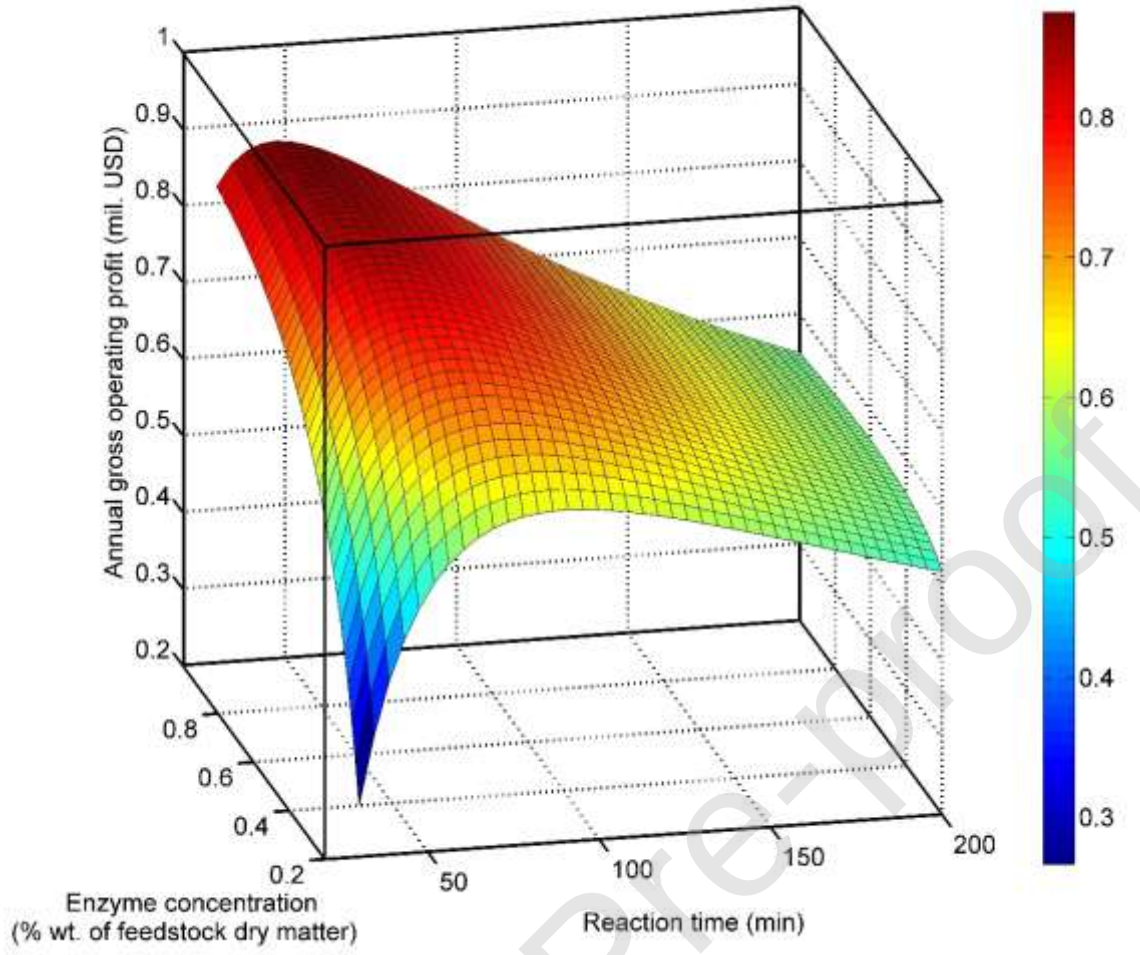


Fig. 5. Dependency of annual gross operating profit on concentrations of enzyme and reaction time; Simulation parameters were: $P_{ENZ}$ = 25 USD/kg, $c_{DM}$ = 6 % wt., $P_W$ = 0.5 USD/kg, other general input parameters are given in Table 2.

Table 3

Economic evaluation of processing plant design alternatives. Detailed calculation is given in Supplementary Material.

| **Parameter** | **Unit** | **1st (initial) case** | **2nd case** |
|---|---|---|---|
| Cycle time | (min) | 270 | 140 |
| Annual number of batches | (batch/y) | 1 386 | 2 674 |

| | | | |
|---|---|---|---|
| Annual production | kg/y | 1 244 000 | 2 263 000 |
| Unit operating costs | USD/kg | 0.272 | 0.364 |
| Unit price of product | USD/kg | 0.75 | 0.75 |
| Total capital investment | USD | 1 547 471 | 1 885 422 |
| Total manufacturing costs | USD/y | 603 249 | 1 087 663 |
| Annual revenue | USD/y | 933 000 | 1 697 250 |
| Return on investment | % | 21.3 | 32.3 |
| Payback period | y | 4.7 | 3.1 |

## 4. Conclusions

A mathematical model enabling technological simulation of leather waste processing – chrome shavings enzymatic hydrolysis – was developed and incorporated into economic model calculating the unit operating costs, annual profit and other important economy parameters. The model includes quantitative description of the dependence of reaction rate on enzyme concentration, which is based on experimental data. Despite using a simplified pseudo-homogeneous kinetic model, it was shown that the model is able to satisfactorily describe a complex real reaction system of heterogeneous nature.

The simulation calculation revealed the existence of usually relatively narrow area of optimal reaction conditions, which corresponds to the minima of unit operating costs. Presented approach to process optimization is valuable also for the design of process control algorithms facilitating adjustment of reaction conditions (e.g. enzyme concentration, time of reaction) according to current price of enzyme or feedstock concentration in the reaction mixture in order to keep the operating costs minima or maximal annual profit.

In addition, presented simulation enabled to assess parameters important for the process design – annual plant processing capacity, investment costs or payback period. Subsequent

optimization of reaction time led to notable increase in plant processing capacity (almost double) and reduction of payback period from initial 4.7 years to final 1.5 year.

In conclusion, the obtained results and presented optimization approach are valuable not only during standard operation of a processing plant, but also in the phase of process design including the design of process control algorithms. The model is therefore applicable and adjustable for a wide range of cases, from individual tanneries to centralized leather waste processing.

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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