The Journal of Supercritical Fluids 181 (2022) 105492

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Subcritical water hydrolysis of poultry feathers for amino acids production

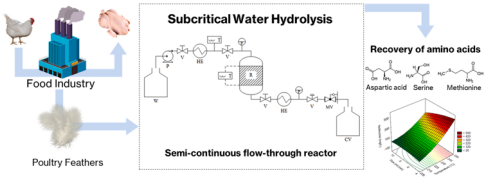
Henrique Di Domenico Ziero [a], Larissa Castro Ampese [a], William G. Sganzerla [a], Paulo C. Torres-Mayanga [b], Michael T. Timko [c], Solange I. Mussatto [d], T. Forster-Carneiro [a,*]

[a] School of Food Engineering (FEA), University of Campinas (UNICAMP), Monteiro Lobato St., n.80, 13083-862 Campinas, SP, Brazil
[b] Professional School of Engineering in Food Industries, Department of Engineering, National University of Barranca, Barranca, Lima, Peru
[c] Department of Chemical Engineering, Worcester Polytechnic Institute (WPI), Institute Road, Goddard Hall, 123, Worcester, MA, USA
[d] Department of Biotechnology and Biomedicine, Technical University of Denmark, Søltofts Plads, Building 223, 2800 Kongens Lyngby, Denmark

HIGHLIGHTS

- Subcritical water hydrolysis (SWH) was used to obtain amino acids from poultry feathers.
- Hydrolysis temperature and water flow rate were investigated.
- The highest amino acid yield was 2.7 ± 0.2 g L^{-1} at 250 °C and 5 mL min^{-1}.
- Alanine, proline, and tryptophan were the main amino acids recovered.
- SWH is a chemical-free alternative to produce amino acids from poultry feathers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Hydrothermal technology
Pressurized fluid
Animal waste
Protein residue

ABSTRACT

This study assessed the subcritical water hydrolysis (SWH) of poultry feathers to recover amino acids. Experiments were conducted in a semi-continuous flow-through subcritical reactor (110 mL), which was operated over a range of temperatures (210–250 °C) and water flow rates (5–15 mL min^{-1}), combined through a 2^2 central composite design, at constant feed (10 g) and pressure (15 MPa). The results demonstrated that non-essential and essential amino acids were obtained from SWH of poultry feathers. The highest hydrolysis temperature resulted in the highest concentrations of valine, methionine, tryptophan, phenylalanine, isoleucine, leucine, and lysine. Otherwise, threonine, histidine, and arginine were obtained more effectively at lower temperatures. The response surface methodology was adopted to identify the best conditions for amino acid production, and it was possible to identify the ranges of temperatures and water flow rates to be used to recover specific amino acids. This study allowed concluding that SWH is a promising eco-friendly technology to recover amino acids from protein-rich wastes.

1. Introduction

Responsible disposal and re-use of agro-industrial residues are critical for the economy and the environment [1]. The circular economy attempts to place an added value on wastes to divert them from environmental disposal, incineration, or landfills, representing a new concept for the re-use and valorization of agro-industrial residues [2,3]. Successful implementation of the circular economy will require judicious use of existing technologies and the development of new ones, especially for the valorization of wastes with unusual properties [4].

* Corresponding author.
E-mail address: taniafc@unicamp.br (T. Forster-Carneiro).

https://doi.org/10.1016/j.supflu.2021.105492
Received 18 June 2021; Received in revised form 19 November 2021; Accepted 21 November 2021
Available online 25 November 2021

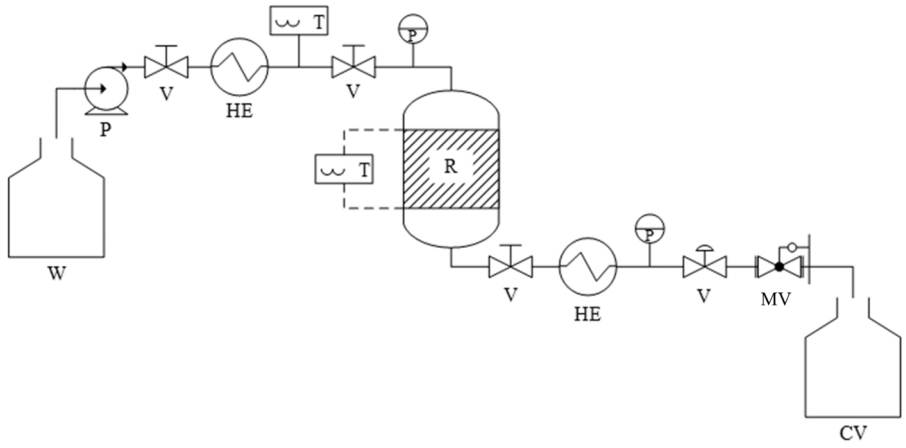


Fig. 1. Schematic diagram of experimental apparatus for SWH of poultry feathers: (W) water tank; (P) High-pressure pump; (V) block valves; (P) manometer; (T) thermocouples; (R) subcritical reactor; (HE) heat exchanger; (MV) micrometric valve; (CV) collecting vessel.

Table 1
Experimental conditions used for SWH of poultry feathers.

Sample	Codified variables		Non-codified variables	
	X_1	X_2	Temperature (°C)	Flow (mL min^{-1})
SWH 1	−1	−1	210 (−1)	5 (−1)
SWH 2	−1	0	210 (−1)	7.5 (0)
SWH 3	−1	+1	210 (−1)	10 (+1)
SWH 4	0	−1	230 (0)	5 (−1)
SWH 5	0	0	230 (0)	7.5 (0)
SWH 6	0	+1	230 (0)	10 (+1)
SWH 7	+1	−1	250 (+1)	5 (−1)
SWH 8	+1	0	250 (+1)	7.5 (0)
SWH 9	+1	+1	250 (+1)	10 (+1)

Table 2
Characterization of poultry feathers.

Parameters	Content (%, dry basis)
Moisture	7 ± 2
Ash	2.1 ± 0.2
COD	1.9 ± 0.1
Total Nitrogen	14 ± 1
Protein	87.4 ± 0.6

Results expressed as mean ± standard deviation. Analysis conducted in triplicate.

Protein-rich residues, including poultry feathers, have potential as a feed for the production of amino acids [5,6]. Poultry feathers are generated in large quantities during chicken and turkey production [7]. Worldwide, approximately 8.5×10^7 tons of chicken are annually produced in the poultry industry, and roughly 10% of the chicken mass are feathers, resulting in approximately 8.5×10^6 tons of chicken feathers [8]. Unfortunately, poultry feathers are treated as wastes without commercial value. Innovative technologies to waste management must be studied to decrease the environmental impact caused by the generation and disposal of poultry feathers.

Valorizing poultry feathers requires some understanding of their composition [9]. Feathers are a keratin-based material composed of α-keratin and β-keratin [10]. The crude protein content ranges from 85% to 90% [8,10]. The substantial protein content of feathers suggests valorization avenues in feed and nutrition applications [11,12].

Commercial practices handle poultry feathers in several different ways [13]. Most feathers have been landfilled or incinerated, and in some cases, part of the feathers is processed into meals for use in the poultry industry and fertilizers [14]. Unfortunately, this meal contains low-quality proteins resulting from the hydrolytic and thermal processes that the feed undergoes. Accordingly, converting feathers into meals results in the degradation of amino acids while consuming large amounts of energy [12]. More energy-efficient methods are required for poultry feather valorization to yield valuable products than low-quality meals.

Converting the protein in chicken feathers directly into amino acids can solve the problems associated with meal production. Amino acids present several applications for medical, food, pharmaceutical, animal, and cosmetic purposes [15]. Regarding food applications, amino acids can be used as flavor enhancers and specialty nutrients. Amino acids can also be used as animal feed additives [16]. In addition, in the pharmaceutical and cosmetic industries, the main use of amino acids is as an ingredient for various products, such food supplements, infant formula, masks, and skin moisturizers [16].

Several technological routes can be used to obtain amino acids from chicken feathers, and the most common methods are chemical and enzymatic hydrolysis, followed by extraction [17,18]. Unfortunately, both methods have substantial disadvantages, including the high cost of enzymes and the generation of toxic wastes from chemical hydrolysis. Therefore, a new environmentally friendly approach for amino acid conversion with high efficiency is urgently required. In this context, green techniques using environmentally benign solvents have been studied as an efficient recovery method that eliminates waste generation, inspiring amino acid recovery from poultry feathers [19].

Among several plausible solvent options like alkalis and acids, subcritical water is attractive for transforming protein residues into amino acids. Water at subcritical conditions (typically defined as temperature ranging from 100° to 374°C and pressures higher than the corresponding saturation point) has received particular attention as an environmentally benign reaction and extraction solvent [20]. Subcritical water behaves as a non-polar solvent that hydrolyzes and extracts organic molecules from complex matrices, including bio-based compounds [21–23]. Simultaneously, the ionic product of subcritical water is much greater than in water at ambient temperature and pressure, resulting in the promotion of both acid and base-catalyzed reactions [24,25]. The result is rapid hydrolysis of the peptide bonds responsible for linking amino acids into proteins without adding acid or base catalysts that would otherwise contribute to waste production [26].

Several studies evaluated the use of subcritical water hydrolysis (SWH) to convert biomass residues into amino acids. For instance, Park et al. [27] treated *Pyropia yezoensis* (a type of edible seaweed) with hot water, ethanol, and SWH, finding that SWH treatment resulted in the most significant number of bioactive compounds, such as amino acids with antioxidant activity. Similarly, Ahmed and Chun [28] reported SWH treatment of tuna skin and collagen to decompose proteins to release peptides and amino acids. Lee et al. [29] recovered amino acids

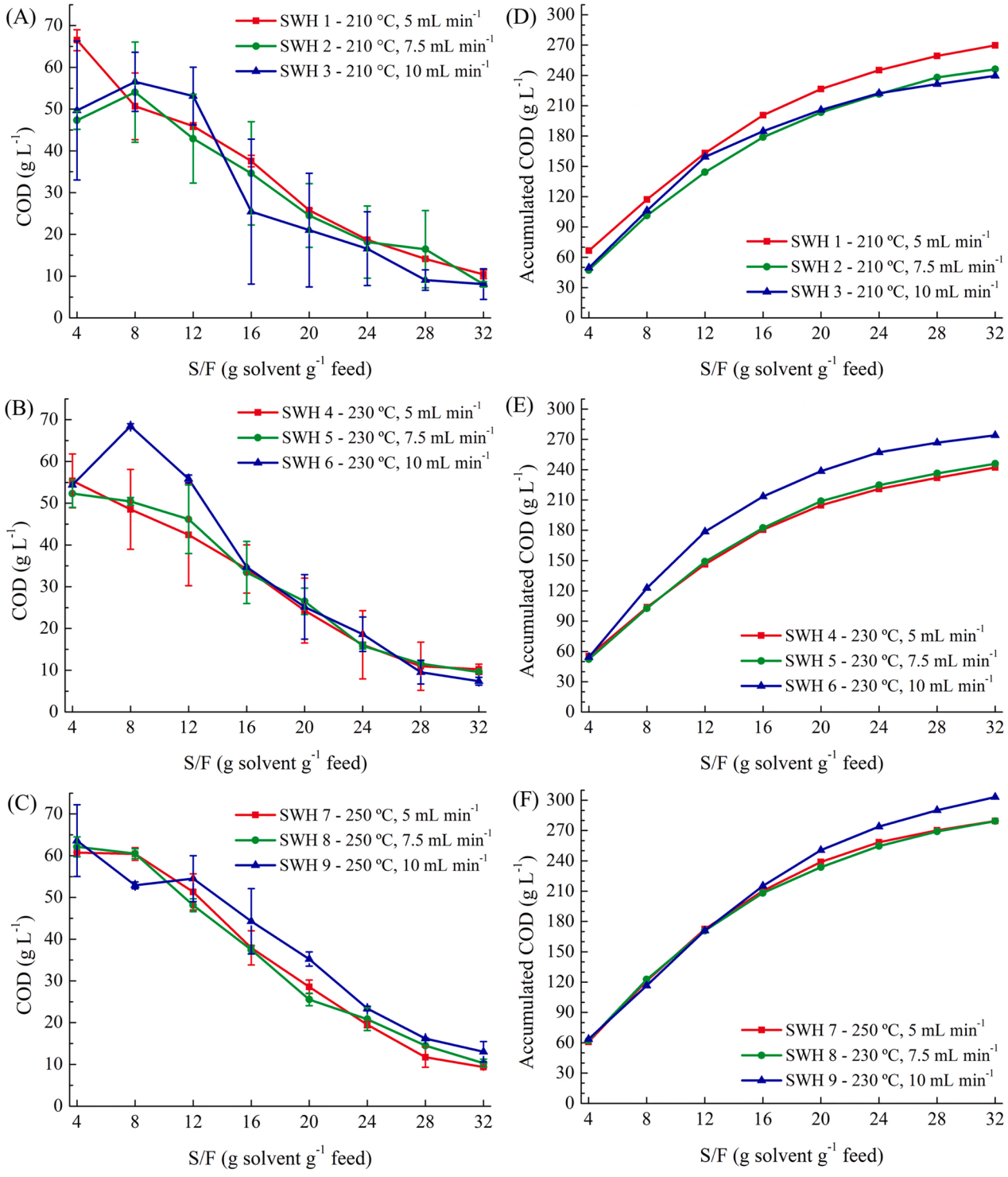


Fig. 2. Kinetics of chemical oxygen demand (COD) for the hydrolysates collected at different temperatures and flow rates.

from comb pen shell (*Atrina pectinata*) by SWH. The highest amount of crude protein was obtained at 200 °C (36.14 mg g^{-1}). In comparison, the highest amino acid yield was observed at 230 °C, (74.80 mg g^{-1}), which indicated that temperature in the range of 170–230 °C is suitable for obtaining protein-rich compounds using SHW [29]. Therefore, SWH has been considered a promising technology to recover amino acids for application in the food and pharmaceutical industries [30].

The poultry feathers composition indicates its feasibility for amino acid recovery [8,15]. Still, studies considering the use of SWH are insufficient. Fortunately, abundant literature describes the use of subcritical water to hydrolyze vegetable wastes containing lignocellulosic biopolymers [31]. Previous studies of SWH of lignocellulosic materials demonstrate that temperature and water flow rates are critical variables defining performance that must be balanced for optimal performance [32–35]. Biopolymer hydrolysis rates increase with increasing reaction temperature, thereby releasing soluble monomers for extraction [36]. Unfortunately, monomer degradation rates also increase with increasing temperature, meaning a balance between hydrolysis and

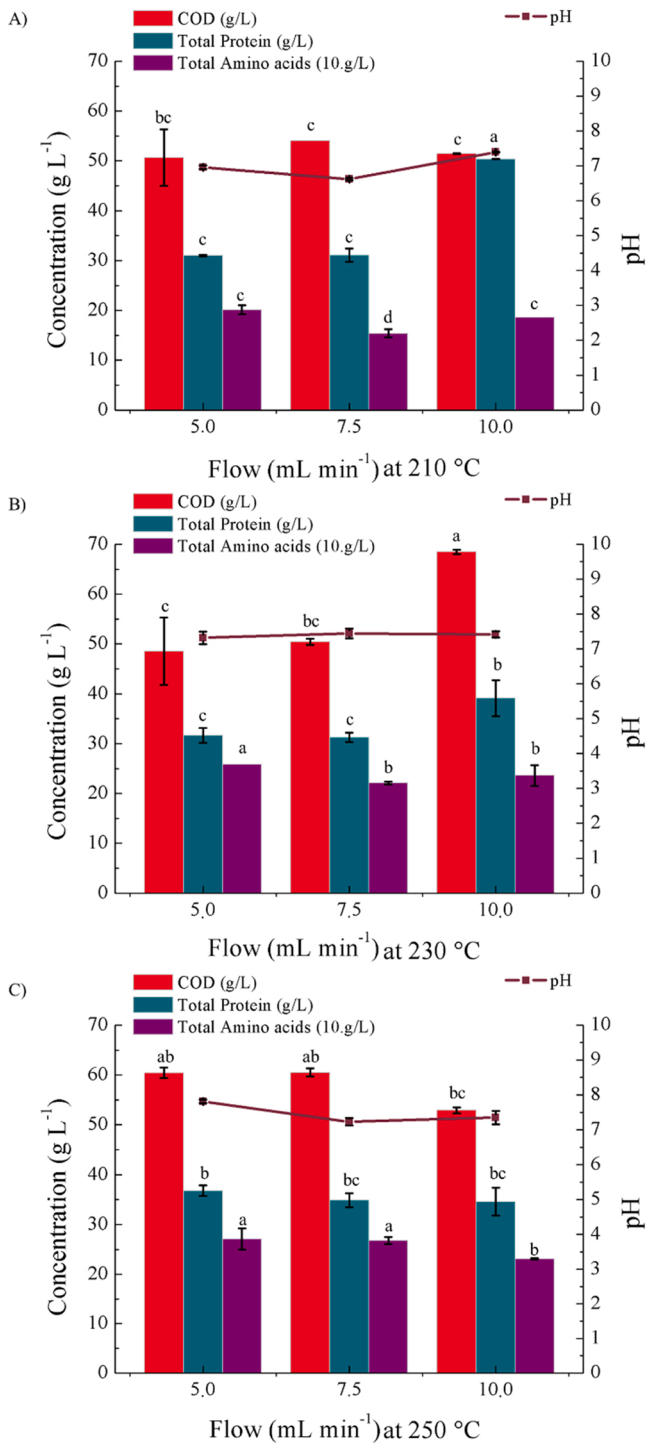


Fig. 3. Average value plots of Chemical Oxygen Demand (COD, g L^{-1}), total protein (g L^{-1}), total amino acids (×10 g L^{-1}) and pH values at the S/F of 8 g solvent g^{-1} feed: A) 210 °C and 5.0, 7.5, 10.0 mL min^{-1}; B) 230 °C and 5.0, 7.5, 10.0 mL min^{-1}; and C) 250 °C and 5.0, 7.5, 10.0 mL min^{-1}. Different letters in each graph represent significant difference by Tukey's test ($p < 0.05$).

degradation must exist. Minimizing monomer retention in the heated zone – for example, by continuous removal in an extraction flow – can reduce degradation and maximize monomer yields [37]. Otherwise, operating SWH at high flow rates has the disadvantage of product dilution, complicating the recovery and purification processes [36]. No theory can predict the tradeoffs between these factors, meaning that the response of each feedstock must be evaluated on its own.

Based on the above, this study evaluated the use of SWH of poultry feathers to recover amino acids. The objective was to determine the best operational parameters of the semi-continuous hydrolysis process and the amino acid composition of the hydrolysates obtained. A complete factorial experimental design and the Response Surface Methodology (RSM) were used to examine the effects of temperature and flow rate on amino acid content. The values of temperature and flow rate selected for this analysis were based on previous studies on SWH of protein-rich wastes [29,38,39]. The results presented here can guide future efforts to use SWH for chemical-free poultry feather valorization as amino acids without waste generation, acting as a strategic and sustainable mechanism for the circular economy approach in the poultry industry.

2. Material and methods

2.1. Raw material

Poultry feathers were supplied by the Oriente Company (Videira City, São Paulo, Brazil). Before use, the poultry feathers were shredded in a knife mill (Marconi Equipment, model MA 340, Piracicaba, SP, Brazil). The resulting particles were sifted by a Tyler magnetic vibratory stirrer (Bertel, model N1868, Caieiras, SP, Brazil). Due to the high surface area to volume ratio, dried particles between 297 and 710 μm in diameter were selected as the feed to SWH experiments. The milled material was stored at 25 °C until use.

2.2. Characterization of poultry feathers

The poultry feathers were analyzed for their content of moisture, ash, nitrogen, protein, and chemical oxygen demand (COD), using methods recommended by the Association of Official Analytical Chemists (AOAC) and Standard Methods for the Examination of Water and Wastewater [40,41]. The moisture (105 °C for 24 h) and ash (550 °C for 12 h) contents were determined by the gravimetric method [40]. The nitrogen quantification was determined according to the methodology of Micro Kjeldahl [40]. Protein content was quantified based on the nitrogen content, using a conversion factor of 6.25 [40]. The soluble COD was performed according to the method 4520 D of APHA [42].

2.3. Experimental design for SWH of poultry feathers

SWH of poultry feathers was performed in a semi-continuous flow-through subcritical reactor (Fig. 1). The system is equipped with a high-pressure liquid pump (double piston pump, Model 36 preparation pump, LabAlliance, Apple Valley, MN, USA) to pressurize and feed water to the reaction vessel. The reaction vessel is a 316-stainless steel tube with an internal volume of 110 mL (Autic Industrial Instrumentation, Campinas, SP, Brazil). A thermal jacket rated to deliver 1500 W heats the reactor insulated by ceramic fiber (RSA Equipment and Instrumentation, Campinas, SP, Brazil). The temperature was controlled using two thermocouples (type K) located in the entrance and outlet of the reactor (RSA Equipment and Instrumentation, Campinas, SP, Brazil). The product exiting the reaction vessel is cooled in a shell-and-tube heat exchanger coupled to a thermostatic bath (Marconi Equipment, model MA184, Piracicaba, SP, Brazil). The system's pressure is controlled by a micrometering valve (Parker Autoclave Engineers, model 10VRMM2812, Erie, PA, USA) located after the heat exchanger. The pressure in the system is measured by pressure gauges (0–51 MPa) from WIKA company (Klingenberg am Main, Bavaria, Germany), with an accuracy of up to 0.1%.

In each experiment, 10 g of milled poultry feathers were loaded into the reactor. The reactor was filled with water from the pump to reach the final pressure, held constant at 15 MPa for all experiments. The flow was maintained constant at the desired rate, and samples were collected at solvent/feed (S/F) ratios ranging from 4 to 32 g solvent g^{-1} feed, which resulted in eight samples. These samples were stored at −18 °C for

Table 3
Characterization of amino acids obtained from subcritical water hydrolysis of poultry feathers at S/F of 8 g g^{-1}.

Sample	Experimental conditions of SWH								
	SWH 1 (210 °C, 5 mL min^{-1})	SWH 2 (210 °C, 7.5 mL min^{-1})	SWH 3 (210 °C, 10 mL min^{-1})	SWH 4 (230 °C, 5 mL min^{-1})	SWH 5 (230 °C, 7.5 mL min^{-1})	SWH 6 (230 °C, 10 mL min^{-1})	SWH 7 (250 °C, 5 mL min^{-1})	SWH 8 (250 °C, 7.5 mL min^{-1})	SWH 9 (210 °C, 10 mL min^{-1})
Essential amino acids (mg L^{-1})									
Histidine	6.9 ± 0.4^{d}	7.6 ± 0.5^{cd}	7.73 ± 0.01^{cd}	9.1 ± 0.4^{ab}	8.4 ± 0.4^{bc}	7.7 ± 0.1^{cd}	6.7 ± 0.1^{d}	9.8 ± 0.3^{a}	7.3 ± 0.4^{cd}
Threonine	6.8 ± 0.3^{b}	6 ± 5^{b}	12.74 ± 0.01^{a}	2.8 ± 0.2^{d}	3.5 ± 0.2^{d}	4.9 ± 0.7^{c}	0.7 ± 0.6^{e}	2.02 ± 0.06^{d}	1.5 ± 0.9^{e}
Arginine	57 ± 3^{a}	51 ± 1^{b}	40.06 ± 0.01^{c}	45.25 ± 0.03^{c}	52.1 ± 0.2^{ab}	43 ± 7^{c}	7.9 ± 0.2^{f}	18 ± 4^{e}	30 ± 4^{d}
Valine	64 ± 4^{de}	56 ± 2^{e}	60.38 ± 0.01^{de}	79 ± 3^{cd}	72 ± 3^{cde}	82 ± 15^{cd}	135 ± 1^{a}	113 ± 8^{b}	85 ± 3^{c}
Methionine	148 ± 9^{b}	138 ± 1^{b}	145.08 ± 0.01^{b}	151.74 ± 0.04^{b}	151 ± 2^{b}	154 ± 3^{b}	198 ± 30^{a}	166 ± 6^{ab}	159 ± 11^{b}
Tryptophan	172 ± 3^{e}	165 ± 1^{d}	186.14 ± 0.01^{c}	196.59 ± 0.02^{bc}	193 ± 2^{bc}	199 ± 7^{bc}	230 ± 7^{a}	231 ± 13^{a}	209 ± 1^{b}
Phenylalanine	47 ± 3^{cd}	42.3 ± 0.3^{e}	49.13 ± 0.01^{bcd}	52.2 ± 0.5^{bc}	45 ± 1^{e}	52 ± 8^{bc}	58 ± 2^{a}	54 ± 2^{ab}	47.5 ± 0.7^{cd}
Isoleucine	68 ± 12^{c}	29.1 ± 0.1^{d}	29.76 ± 0.01^{d}	189 ± 2^{bc}	149 ± 7^{bc}	143 ± 32^{bc}	423 ± 166^{a}	418 ± 44^{a}	263 ± 59^{ab}
Leucine	68 ± 5^{cd}	60 ± 3^{d}	68.46 ± 0.01^{cd}	85 ± 3^{b}	69 ± 2^{cd}	78 ± 19^{bc}	115.12 ± 0.06^{a}	105 ± 5^{a}	84 ± 3^{b}
Lysine	6.8 ± 0.5^{bc}	5.5 ± 0.5^{c}	8.65 ± 0.01^{bc}	8.8 ± 0.6^{bc}	7.6 ± 0.5^{bc}	9 ± 3^{b}	13 ± 1^{a}	12.9 ± 0.7^{a}	9.0 ± 0.9^{b}
Non-essential amino acids (mg L^{-1})									
Aspartic acid	50.8 ± 0.3^{c}	86 ± 11^{b}	121.43 ± 0.01^{a}	23 ± 2^{def}	34 ± 2^{cde}	41 ± 20^{cd}	10.7 ± 0.4^{f}	15 ± 2^{ef}	20 ± 4^{def}
Glutamic acid	10.1 ± 0.6^{bc}	12 ± 2^{b}	14.50 ± 0.01^{a}	7.6 ± 0.1^{de}	9.0 ± 0.5^{cd}	10.2 ± 0.5^{bc}	6.1 ± 0.1^{e}	7.1 ± 0.8^{de}	8 ± 1^{cd}
Cysteine	3.10 ± 0.01	–	–	–	–	–	–	–	–
Asparagine	4.03 ± 0.05^{b}	8.5 ± 0.5^{a}	8.40 ± 0.01^{a}	2.02 ± 0.02^{cde}	2.5 ± 0.2^{bcd}	3 ± 1^{bc}	$0.6 \pm 0.5^{2\,f}$	1.24 ± 0.08^{ef}	0.9 ± 0.6^{ef}
Serine	121 ± 5^{ab}	111 ± 38^{bc}	159.97 ± 0.01^{a}	72 ± 4^{cde}	84 ± 3^{bcd}	74 ± 30^{cde}	10.8 ± 0.3^{g}	30 ± 6^{fg}	43 ± 10^{def}
Glutamine	0.23 ± 0.03^{d}	–	–	–	–	0.34 ± 0.04^{c}	–	0.76 ± 0.04^{a}	0.64 ± 0.01^{b}
Glycine	238 ± 39^{cd}	155 ± 6^{d}	168.42 ± 0.01^{d}	392 ± 15^{b}	237 ± 2^{cd}	314 ± 69^{bc}	547 ± 3^{a}	482 ± 33^{a}	366 ± 13^{b}
Alanine	628 ± 38^{c}	402 ± 1^{d}	481.50 ± 0.01^{d}	868 ± 15^{a}	744 ± 9^{b}	772 ± 90^{ab}	680 ± 3^{bc}	736 ± 17^{bc}	694 ± 52^{bc}
Tyrosine	38 ± 3^{b}	40 ± 2^{b}	47.13 ± 0.01^{a}	40.7 ± 0.7^{b}	41.2 ± 0.7^{b}	47 ± 3^{a}	41 ± 1^{b}	40.7 ± 0.9^{b}	36 ± 1^{b}
Proline	275 ± 13^{c}	205 ± 2^{f}	254.70 ± 0.01^{cd}	359 ± 7^{a}	303 ± 1^{b}	321 ± 17^{b}	221 ± 10^{ef}	236 ± 14^{de}	243 ± 24^{de}

Results expressed as mean ± standard deviation. Analysis conducted in triplicate. Different letters in each line represent significant differences by Tukey's test ($p < 0.05$).

further analysis.

The influence of the operating conditions (hydrolysis temperature and flow rate) was studied using a 2^2 central composite design containing three levels: low (−1), medium (0), high (+1), over a range of temperatures (210–250 °C) and water flow rates (5–10 mL min^{-1}) (Table 1). These experimental conditions were selected based on previous studies conducted in the laboratory [36,43,44]. Nine (9) experiments were randomly performed in triplicate to estimate experimental uncertainty and establish reproducibility. Table 1 presents all the experimental conditions used for SWH of poultry feathers.

2.4. Hydrolysate characterization

The samples were analyzed for pH, COD, total nitrogen content, and crude protein content. The pH (4500-H+ B) was measured at room temperature of approximately 27 °C (Digimed, model DM-22, São Paulo, SP, Brazil). The COD, total nitrogen, and protein content were performed according to the methods described in Section 2.2.

2.4.1. Quantification of amino acids

The amino acid composition in the hydrolysates was determined by a Dionex UltiMate 3000 HPLC (temperature: 37 °C, mobile phase: (A) 40 mM Na_2HPO_4 with 0.02% NaN_3; and (B) 45% AcN, 45% MeOH and 10% H_2O, flow rate: 1 mL min^{-1}, injection volume: 56.5 µL) equipped with a Gemini C18 column (3 µm particle size, 4.6 × 150 mm) from Phenomenex (PN 00F-4439-E0) (Torrance, CA, USA), Guard column (SecurityGuard Gemini C18, Phenomenex PN, AJO-7597, Torrance, CA, USA), and UV+fluorescence detector (Thermo Scientific, Waltham, MA, USA). A calibration curve was prepared for each individual amino acid.

2.5. Statistical analysis

Analysis of variance (ANOVA) was employed to assess statistically significant factors and interactions between the variables (temperature and water flow rate). Significant differences between the samples were evaluated by Tukey's test ($p < 0.05$). The second order mathematical model was used to determine statistical significance; ANOVA (F-values) was applied to evaluate significance at a probability of 5%. The coefficient of determination (R^2) and the adjusted coefficient of determination (R^2_{adj}) was determined. The selected experimental design is used to evaluate the curvature in the response function. Experimental results were analyzed by response surface methodology (RSM) described by the second order function (Eq. 1).

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i \quad X_i + \sum_{i=1}^{3} \beta_{ii} \quad X_i^2 + \sum_{i=1}^{3} \sum_{j>i}^{3} \beta_{ij} \quad X_i X_j \tag{1}$$

Where, Y is the studied response for amino acids, β_0 is a constant, β_i are coefficients associated with linear effects, β_{ii} are coefficients linked to quadratic effects, and β_{ij} are coefficients for second-order cross terms.

Finally, the regression coefficients were determined to the variables analyzed by RSM. The significance of the regression coefficients was also confirmed by F-test at $p < 0.05$. The statistical analysis was conducted using the Statistica® software (version 10.0, StatSoft Inc., Tulsa, OK, USA).

3. Results and discussion

3.1. Poultry feathers characterization

Table 2 presents the characterization of poultry feathers used for SWH experiments. After drying the poultry feathers, the sample presented 7% of moisture. The feather showed high protein content (87.4% ± 0.6) and low ash content, demonstrating that this feedstock can be used as a feedstock for amino acid recovery. Other studies showed that feathers generated mainly from poultry slaughterhouses are composed of more than 90% of proteins (keratin) [45].

Some proteinaceous vegetable wastes, such as defatted rice bran, beans dregs, and even microalgae, can also be used to source amino acids due to their high protein content [46,47]. Despite this, animal by-products present a greater amount of protein in their composition; for example, fish gelatin [48], squid muscle (*Todarodes pacificus*) [28], hog hair, and tuna's collagen [49], have already been studied to extract amino acids. Beyond, the use of SWH to recover amino acids can be an environmentally friendly method for the efficient valorization of animal wastes [29].

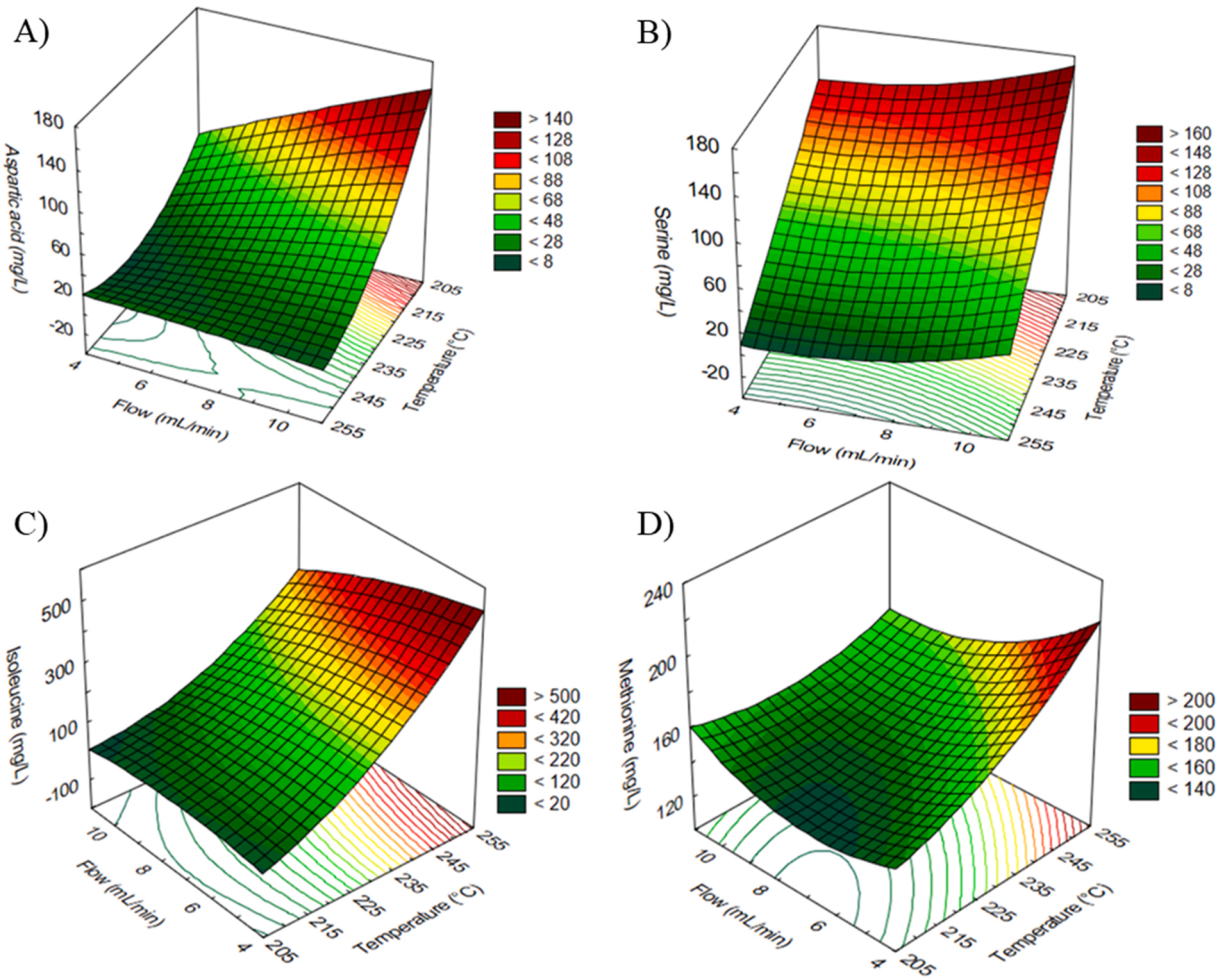


Fig. 4. Response surface plots showing the effect of temperature and flow on the concentration of aspartic acid (A), serine (B), isoleucine (C), and methionine (D) in the hydrolysates.

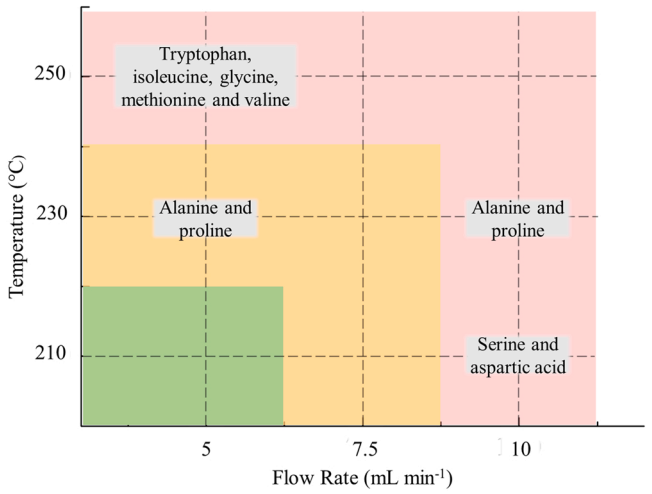


Fig. 5. The schematic diagram for amino acids production.

3.2. SWH of poultry feathers

SWH experiments were performed to evaluate the effectiveness of water flow and hydrolysis temperature on amino acid content from poultry feathers. Three levels were evaluated for both independent variables, resulting in 9 experiments. These are labeled SWH 1 through 9, as shown in Table 1. Eight samples were collected during each SWH experiment, and Fig. 2 provides plots of COD measured in the different S/F under all tested conditions. In the kinetic analysis, measurements of COD were used as an indication of organic content in the hydrolysate [50].

Fig. 2 shows that COD typically increased in the first sampling and then decreased according to the increase of reaction time. The sample collected at S/F of 8 g solvent g^{-1} feed usually exhibited an increased COD value, and after this point, COD monotonically decreased. Consequently, the S/F of 8 g solvent g^{-1} feed was chosen to evaluate total protein and amino acid content. COD indirectly measures the reducing equivalents (elements with a low oxidation number, reduced) present in the sample in question. The COD makes it possible to assess the amount of organic matter in liquid and solid waste regarding the amount of oxygen needed for its total oxidation. In this work, the hydrolysis showed a trend that indicates the importance of balancing protein hydrolysis rates with mass transfer rates to extract the amino acids and other soluble products.

Fig. 2 also includes plots of accumulated COD during the hydrolysis of poultry feathers. The final values obtained are in the range of 210–290 g L^{-1}. Interestingly, at the higher temperatures (230 and 250 °C), the greatest accumulated COD is observed at the highest flow rate (10 mL min^{-1}). In contrast, the opposite is observed at the lowest temperature (210 °C), corroborating the literature [29]. Effects of temperature and flow rate indicate a transition from reaction limited to mass transfer limited extraction at a temperature intermediate to 210 and 230 °C, as protein hydrolysis rates are fast enough at 230 and 250 °C

that recovery instead becomes mass transport limited.

3.3. Hydrolysate characterization

3.3.1. pH, COD, crude protein, and total amino acids

Fig. 3 provides COD results, total protein, total amino acids, and pH values for all flows and temperatures tested. Samples analyzed correspond to the S/F of 8 g solvent g^{-1} feed of each treatment. Overall, the pH values ranged from 6.62 (SWH 2) to 7.81 (SWH 7). Total protein content was similar for all samples and ranged from 30 to 35 g L^{-1}. The only notable outlier in this respect was SWH 3, performed at 210 °C and 10 mL min^{-1}, which contained 50.37 ± 0.03 g L^{-1} of protein. The combination of low temperature and high flow rate may have maximized partial protein hydrolysis and minimized subsequent degradation, resulting in more effective protein recovery than the other conditions tested here.

COD was measured as a complement to protein analysis. The treatments that resulted in higher COD values should coincide with higher protein and amino acid concentrations. This appears to only hold in a very rough sense. For instance, COD increased with increasing flow rate at 230 °C, however, at 210 and 250 °C the water flow rate did not affect the COD of the hydrolysate.

The apparent disconnect between COD and protein measurements may be explained by several considerations. First, total protein values include protein and non-protein nitrogen [12]. Another possible reason for the incompatibility of COD and total protein comparison may reside in other molecules that affect the COD and distinctly affect the protein content. For example, considering the degradation of proteins into amino acids and then into carbonic acids and amines [51], these latter molecules are associated with COD and also with total protein values, still small molecules (compared to proteins) not necessarily affect the COD and the total protein content in the same intensity. Finally, three different treatments presented a statistically higher value for total amino acid content: SWH 4, SWH 7, and SWH 8. Moderate and higher temperatures may boost amino acid yield, and the lower and medium flow rate may provide sufficient retention time for converting protein to amino acids. Consistent with this explanation, the amino acid content of SWH 7 was nearly twice that obtained in SWH 2.

3.3.2. Amino acids composition of the hydrolysate

Table 3 summarizes amino acid composition results obtained at different experimental conditions at the S/F of 8 g solvent g^{-1} feed. It is important to highlight that the proteins presented in the feedstock are hydrolyzed during SWH, releasing the amino acids that were quantified by HPLC in the hydrolysate. Accordingly, the results demonstrate that different amino acids can be recovered at specific conditions of SWH reaction.

The reaction at the highest temperature (250 °C) resulted in the highest concentrations of many different amino acids, such as valine, methionine, tryptophan, phenylalanine, isoleucine, leucine, and lysine. Notwithstanding, some essential amino acids, like threonine (210 °C), histidine, and arginine (230 °C), were extracted more effectively at lower temperatures. This clearly shows that reaction temperature can be tuned for recovery of different amino acids, with the differences attributable either to the thermal stability of the monomer, amino acid solubility, the accessibility of the monomer in the protein itself, or the thermal stability of the peptide bonds associated with a given amino acid.

The concentration of a given amino acid in the hydrolysate is determined by several factors, including abundance in the feathers, reactivity, the water solubility of the amino acid, and stability of the amino acid. Isoleucine was the most abundant essential amino acid in these samples, and its concentration was maximized at 250 °C. Isoleucine is a moderately soluble amino acid that is highly abundant in poultry feathers [52]. The abundance of isoleucine in poultry feathers is consistent with its recovery; its moderate water solubility may explain why its concentration increased with increasing SWH temperature [52]. SWH becomes more capable of dissolving many sparingly soluble molecules with increasing temperature due to the temperature dependence of its dielectric constant. Isoleucine has a non-polar side chain, which should become increasingly water soluble with increasing temperature in the range considered here [20].

In general, the amino acids that are more hydrophobic than isoleucine – such as phenylalanine and tryptophan, both of which possess aromatic side chains – require high temperatures for obtaining better concentrations. Again, this observation is consistent with the effects of temperature on the solubility properties of water. The amino acids that are most easily recovered at 210 °C, especially arginine and threonine, possess small, polar side chains. Histidine maintains an ionizable imidazole side chain, which may explain its behavior. Observing the effects of side chains further establishes the importance of thermodynamic driving force on extraction and recovery.

For non-essential amino acids, lower and moderate temperatures were the most effective. SWH 3 contained high concentrations of aspartic acid, glutamic acid, asparagine, serine, alanine, and proline. Similarly, the amino acid concentrations in SWH 4 are much greater than the more aggressive conditions used for SWH 7 and SWH 8. Total protein concentrations (Fig. 3) corroborated with the quantification of individual amino acids, providing a degree of confidence in the two analytical techniques used, one for total amino acid content by HPLC and the other for protein quantified by the Nitrogen Kjeldahl method.

Ueno et al. [48] studied fish gelatin to produce serine, glycine, alanine, arginine, and valine in SWH at higher temperatures (240 °C). The results showed a lower concentration of amino acids when compared to the literature [48,49]. Furthermore, this study also presented different amino acids concentration when the SWH parameters were changed, and amino acids that were recovered in some temperatures were no more present in other conditions. Asaduzzaman and Chun [53] report the use of SWH in squid muscles, and the results obtained demonstrated the production of an average higher concentration of free amino acids at 250 °C. In comparison, the highest concentration of essential amino acids was obtained at 220 °C. Besides, the thermally dried squid muscles present approximately 73.26% protein content, contrasting to chicken feathers crude protein content, that is about 90%, and composed of mainly keratin, an insoluble protein [12]. Ahmed and Chun [28] evaluated the hydrolysis of tuna and collagen skin with SWH. The study reported that the collagen hydrolysate presented a high concentration of glycine, proline, alanine, and glutamic acid as the most abundant structural amino acids for all tested conditions. In addition, the authors reported a higher degradation rate of protein to peptides and peptides to free amino acids when the temperature was increased. However, after a certain point, high temperature caused decomposition of amino acid into organic acids or other products, such as carbonic acids and amines [28,51].

In addition, the yields obtained using water hydrolysis in the present study are higher than conventional methods reported in the literature (alkaline hydrolysis or enzymatic method). Stiborova et al. [54] studied digestion using semi-purified keratinase from *Pseudomonas* sp. P5 and obtained hydrolysates richer in amino acids (1191 mg L^{-1}, 56% essential ones), but peptides were present in lower amounts (up to 3.3 g L^{-1}). A reminder that the most common chemical and enzymatic extraction methods have substantial disadvantages, including the high cost of enzymes and the generation of toxic wastes from chemical hydrolysis [17–19]. A study with chicken feathers and cow hair was conducted by Coward-Kelly [55]. Firstly, the feathers were washed several times, dried, ground, and sieved, and, to characterize this initial material, the amino acid content was determined by HPLC. The results indicated that the most abundant amino acids found were glutamine (8.2 mg 100 g^{-1}), serine (8.1 mg 100 g^{-1}), proline (7.4 mg 100 g^{-1}), arginine (6.8 mg 100 g^{-1}), and cysteine (6.1 mg 100 g^{-1}) [55].

Regarding the economic feasibility of the SWH, it is essential to consider that the treatment itself requires relatively high energy inputs.

Still, the process may be coupled to other activities and use waste heat from boilers already available in the industry. In addition, it is possible to adopt a regeneration system. This way, the hot fluid that leaves the reactor can exchange heat with the liquid flowing into the reactor, reducing thermal energy requirements [32]. The literature demonstrates that SWH is a feasible option to produce sugars from brewer's spent grains [56] and flavanones from orange peel [57]. However, scale-up and economic studies for amino acids production from pouty feathers should be further investigated for industrial implementation.

3.4. Statistical modeling and optimization of SWH

The effects of temperature and water flow were investigated by a 2^2 central composite design. Statistical model incorporating the second order function was evaluated for all the amino acids produced from SWH (Table S1) and analyzed by ANOVA (Table S2). The lack of fit was significant ($p < 0.05$) for most of the independent variables considered in the study, with the exceptions of aspartic acid, serine, isoleucine, and methionine. Similarly, aspartic acid ($R^2_{adj.} = 0.941$), serine ($R^2_{adj.} = 0.831$), and isoleucine ($R^2_{adj.} = 0.831$) presented R^2 value higher than 0.8, an admittedly arbitrary value but one that has been recommended as an indication of a good fit [58].

The equations for the adjusted regression model for the statistically valid variables in the second order function (Eq. 1) were the following:

$$Aspartic\ acid\ \left(\frac{mg}{L}\right) = 2258.67 - 20.35T + 0.05T^2 + 70.23Q - 0.12Q^2 - 0.30TQ$$

$$Serine\ \left(\frac{mg}{L}\right) = 936.15 - 5.10T - 0.01T^2 + 0.24Q + 0.83Q^2 - 0.03TQ$$

$$Isoleucine\ \left(\frac{mg}{L}\right) = 3191.02 - 38.90T + 0.11T^2 - 153.85Q - 2.02Q^2 - 0.61TQ$$

$$Methionine\ \left(\frac{mg}{L}\right) = 650.38 - 5.72T + 0.02T^2 + 20.27Q - 1.26Q^2 - 0.18TQ$$

where, T represents the reaction temperature (°C), and Q represents the flow of water (mL min^{-1}) used for the SWH process.

Three-dimensional response surfaces were generated for the statistically valid variables (Fig. 4**)**. Aspartic acid and serine concentrations were maximized at high flow (around 10 mL min^{-1}) and low temperature (around 210 °C). Isoleucine and methionine presented the opposite behavior, with the highest concentrations obtained at low water flow (5 mL min^{-1}) and high temperature (250 °C). Beyond, Fig. 5 illustrates the temperature and flow rate effect, which resulted in the recovery of the mentioned amino acids. These results indicate that conditions can be optimized for the recovery of the desired amino acid. It shows that it is possible to obtain specific amino acids at the expense of others.

4. Conclusions

SWH technology was evaluated as a chemical-free technology to obtain amino acids from poultry feathers. The effects of reaction temperature (210, 230, 250 °C) and water flow rate (5, 7.5, and 10 mL min^{-1}) on the amino acid content of the hydrolysate were investigated. Aspartic acid and serine concentrations were maximized at the highest flow rate (10 mL min^{-1}) and the lowest temperature (210 °C). In comparison, isoleucine and methionine were maximized at the opposite extreme (250 °C and 5 mL min^{-1}). These observations are broadly consistent with peptide bond hydrolysis to produce water-soluble polypeptides and/or amino acids, followed by extraction of the resulting amino acids. Amino acid content broadly followed trends expected from their natural abundance in the poultry feathers and their expected solubility in water at different temperatures. Finally, SWH has the potential for chemical-free obtaining of amino acids from protein-rich waste.

Declaration of Competing Interest

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.

Acknowledgments

The authors thank Dr. Sioji Kuana of Três Fronteiras (Seara, SC, Brazil) Company. The authors acknowledge the financial support from the Brazilian Science and Research Foundation (CNPq) and Higher-Level Personnel Improvement Coordination (CAPES) – Brazil – Finance code 001. The financial support from the São Paulo Research Foundation – FAPESP (2018/05999-0; 2018/14938-4). W.G. Sganzerla thanks FAPESP for the doctorate scholarship (2019/26925-7). T. Forster-Carneiro thanks CNPq for the productivity grant (302473/2019-0). Solange I. Mussatto thanks the Novo Nordisk Foundation (NNF, Denmark – grant number NNF20SA0066233). The author's thank Donna Murillo, who collaborated in some of the initial experiments that established the methodology. MTT thanks the U.S. National Science Foundation (ENG #1554283).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.supflu.2021.105492.

References

[1] M. Adrian, T. Elizabeth, Poverty, politics and plastic: organic waste sorting in Blantyre's public markets, J. Urban Manag. 10 (3) (2021) 192–204.
[2] P. Centobelli, R. Cerchione, D. Chiaroni, P. Del Vecchio, A. Urbinati, Designing business models in circular economy: a systematic literature review and research agenda, Bus. Strategy Environ. 29 (2020) 1734–1749.
[3] A.T. Ubando, C.B. Felix, W.-H. Chen, Biorefineries in circular bioeconomy: a comprehensive review, Bioresour. Technol. 299 (2020), 122585.
[4] J.A. Bergendahl, J. Sarkis, M.T. Timko, Transdisciplinarity and the food energy and water nexus: ecological modernization and supply chain sustainability perspectives, Resour., Conserv. Recycl. 133 (2018) 309–319.
[5] G. Velvizhi, S. Shanthakumar, B. Das, A. Pugazhendhi, T.S. Priya, B. Ashok, K. Nanthagopal, R. Vignesh, C. Karthick, Biodegradable and non-biodegradable fraction of municipal solid waste for multifaceted applications through a closed loop integrated refinery platform: paving a path towards circular economy, Sci. Total Environ. 731 (2020), 138049.
[6] S. Wainaina, M.K. Awasthi, S. Sarsaiya, H. Chen, E. Singh, A. Kumar, B. Ravindran, S.K. Awasthi, T. Liu, Y. Duan, Resource recovery and circular economy from organic solid waste using aerobic and anaerobic digestion technologies, Bioresour. Technol. 301 (2020), 122778.
[7] I. Campos, L.M.P. Valente, E. Matos, P. Marques, F. Freire, Life-cycle assessment of animal feed ingredients: poultry fat, poultry by-product meal and hydrolyzed feather meal, J. Clean. Prod. 252 (2020), 119845.
[8] N. Reddy, M. Santosh, Chapter 14 – recovery and applications of feather proteins, in: Protein Byproducts – Transformation from Environmental Burden Into Value-Added Products 2016, Elsevier Science, 2016, pp. 255–274.
[9] J.C. Santana, R.B. Gardim, P.F. Almeida, G.B. Borini, A.P. Quispe, S.A. Llanos, J. A. Heredia, S. Zamuner, F. Gamarra, T. Farias, Valorization of chicken feet by-product of the poultry industry: high qualities of gelatin and biofilm from extraction of collagen, Polymers 12 (2020) 529.
[10] Z. Peng, X. Mao, J. Zhang, G. Du, J. Chen, Biotransformation of keratin waste to amino acids and active peptides based on cell-free catalysis, Biotechnol. Biofuels 13 (2020) 1–12.
[11] M. Khumalo, B. Sithole, T. Tesfaye, Valorisation of waste chicken feathers: optimisation of keratin extraction from waste chicken feathers by sodium bisulphite, sodium dodecyl sulphate and urea, J. Environ. Manag. 262 (2020), 110329.
[12] T. Tesfaye, B. Sithole, D. Ramjugernath, V. Chunilall, Valorisation of chicken feathers: characterisation of chemical properties, Waste Manag. 68 (2017) 626–635.
[13] J.A. Stingone, S. Wing, Poultry litter incineration as a source of energy: reviewing the potential for impacts on environmental health and justice, N. Solut.: J. Environ. Occup. Health Policy 21 (2011) 27–42.
[14] O.D. Fagbemi, B. Sithole, T. Tesfaye, Optimization of keratin protein extraction from waste chicken feathers using hybrid pre-treatment techniques, Sustain. Chem. Pharm. 17 (2020), 100267.
[15] H.D.D. Ziero, L.S. Buller, A. Mudhoo, L.C. Ampese, S.I. Mussatto, T.F. Carneiro, An overview of subcritical and supercritical water treatment of different biomasses for

protein and amino acids production and recovery, J. Environ. Chem. Eng. 8 (2020), 104406.
[16] K. Ivanov, S. Ivanova, M. Georgieva, P. Atanasov, Production and regulatory analytical control of amino acids include in food additives, Pharmacia 61 (2014) 48–54.
[17] Q. Yang, X. Cai, Z. Liu, S. Wang, Antioxidant assessment of schizochytrium meal protein enzymatic hydrolysate and its potential application, J. Aquat. Food Prod. Technol. 28 (2019) 413–426.
[18] C. Alvarez, M. Rendueles, M. Diaz, The yield of peptides and amino acids following acid hydrolysis of haemoglobin from porcine blood, Anim. Prod. Sci. 52 (2012) 313–320.
[19] D.G. Pereira, A. Justus, H.G. Falcão, Td.S. Rocha, E.I. Ida, L.E. Kurozawa, Enzymatic hydrolysis of okara protein concentrate by mixture of endo and exopeptidase, J. Food Process. Preserv. 43 (2019), e14134.
[20] G. Brunner, Supercritical fluids: technology and application to food processing, J. Food Eng. 67 (2005) 21–33.
[21] P.S. Saravana, A. Tilahun, C. Gerenew, V.D. Tri, N.H. Kim, G.-D. Kim, H.-C. Woo, B.-S. Chun, Subcritical water extraction of fucoidan from Saccharina japonica: optimization, characterization and biological studies, J. Appl. Phycol. 30 (2018) 579–590.
[22] S. Gbashi, O.A. Adebo, L. Piater, N.E. Madala, P.B. Njobeh, Subcritical water extraction of biological materials, Sep. Purif. Rev. 46 (2017) 21–34.
[23] M.V. Kiamahalleh, G. Najafpour-Darzi, M. Rahimnejad, A.A. Moghadamnia, M. V. Kiamahalleh, High performance curcumin subcritical water extraction from turmeric (Curcuma longa L.), J. Chromatogr. B 1022 (2016) 191–198.
[24] I. Okajima, T. Sako, Energy conversion of biomass with supercritical and subcritical water using large-scale plants, J. Biosci. Bioeng. 117 (2014) 1–9.
[25] B. Motavaf, P.E. Savage, Effect of process variables on food waste valorization via hydrothermal liquefaction, ACS EST Eng. 1 (2021) 363–374.
[26] A.D. Espinoza, R.O. Morawicki, T. Hager, Hydrolysis of whey protein isolate using subcritical water, J. Food Sci. 77 (2012) C20–C26.
[27] J.-S. Park, Y.-R. Jeong, B.-S. Chun, Physiological activities and bioactive compound from laver (Pyropia yezoensis) hydrolysates by using subcritical water hydrolysis, J. Supercrit. Fluids 148 (2019) 130–136.
[28] R. Ahmed, B.-S. Chun, Subcritical water hydrolysis for the production of bioactive peptides from tuna skin collagen, J. Supercrit. Fluids 141 (2018) 88–96.
[29] H.-J. Lee, V.C. Roy, T.C. Ho, J.-S. Park, Y.-R. Jeong, S.-C. Lee, S.-Y. Kim, B.-S. Chun, Amino acid profiles and biopotentiality of hydrolysates obtained from comb penshell (Atrina pectinata) viscera using subcritical water hydrolysis, Mar. Drugs 19 (3) (2021) 137.
[30] W.A.S. Chamika, T.C. Ho, V.C. Roy, A.T. Kiddane, J.-S. Park, G.-D. Kim, B.-S. Chun, In vitro characterization of bioactive compounds extracted from sea urchin (Stomopneustes variolaris) using green and conventional techniques, Food Chem. 361 (2021), 129866.
[31] F.W. Maciel-Silva, S.I. Mussatto, T. Forster-Carneiro, Integration of subcritical water pretreatment and anaerobic digestion technologies for valorization of açai processing industries residues, J. Clean. Prod. 228 (2019) 1131–1142.
[32] L.C. Ampese, L.S. Buller, J. Myers, M.T. Timko, G. Martins, T. Forster-Carneiro, Valorization of Macaúba husks from biodiesel production using subcritical water hydrolysis pretreatment followed by anaerobic digestion, J. Environ. Chem. Eng. 9 (2021), 105656.
[33] J.M. Prado, L.A. Follegatti-Romero, T. Forster-Carneiro, M.A. Rostagno, F. Maugeri Filho, M.A.A. Meireles, Hydrolysis of sugarcane bagasse in subcritical water, J. Supercrit. Fluids 86 (2014) 15–22.
[34] J.M. Prado, D. Lachos-Perez, T. Forster-Carneiro, M.A. Rostagno, Sub- and supercritical water hydrolysis of agricultural and food industry residues for the production of fermentable sugars: a review, Food Bioprod. Process. 98 (2016) 95–123.
[35] W.G. Sganzerla, G.L. Zabot, P.C. Torres-Mayanga, L.S. Buller, S.I. Mussatto, T. Forster-Carneiro, Techno-economic assessment of subcritical water hydrolysis process for sugars production from brewer's spent grains, Ind. Crops Prod. 171 (2021), 113836.
[36] D. Lachos-Perez, A.M. Baseggio, P. Mayanga-Torres, M.R.M. Junior, M. Rostagno, J. Martínez, T. Forster-Carneiro, Subcritical water extraction of flavanones from defatted orange peel, J. Supercrit. Fluids 138 (2018) 7–16.
[37] P.C. Torres-Mayanga, D. Lachos-Perez, A. Mudhoo, S. Kumar, A.B. Brown, M. Tyufekchiev, G. Dragone, S.I. Mussatto, M.A. Rostagno, M. Timko, Production of biofuel precursors and value-added chemicals from hydrolysates resulting from hydrothermal processing of biomass: a review, Biomass Bioenergy 130 (2019), 105397.
[38] A.K.M. Asaduzzaman, A.T. Getachew, Y.-J. Cho, J.-S. Park, M. Haq, B.-S. Chun, Characterization of pepsin-solubilised collagen recovered from mackerel (Scomber japonicus) bone and skin using subcritical water hydrolysis, Int. J. Biol. Macromol. 148 (2020) 1290–1297.
[39] I. Marcet, C. Álvarez, B. Paredes, M. Díaz, The use of sub-critical water hydrolysis for the recovery of peptides and free amino acids from food processing wastes, Rev. Sources Main. Parameters, Waste Manag. 49 (2016) 364–371.
[40] AOAC. Official Methods of Analysis of the Association of Official Analytical Chemistry, seventeenth ed., Association of Official Analytical Chemistry, Washington, 2006.
[41] APHA – American Public Health Association. Standard Methods for the Examination of Water and Wastewater, twenty-third ed., American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, 2017.
[42] APHA – American Public Health Association. Method 5220 Chemical Oxygen Demand (COD). Standard Methods for the Examination of Water and Wastewater, twenty-third ed., American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, 2017.
[43] D. Lachos-Perez, G. Tompsett, P. Guerra, M. Timko, M. Rostagno, J. Martínez, T. Forster-Carneiro, Sugars and char formation on subcritical water hydrolysis of sugarcane straw, Bioresour. Technol. 243 (2017) 1069–1077.
[44] D. Lachos-Perez, F. Martinez-Jimenez, C. Rezende, G. Tompsett, M. Timko, T. Forster-Carneiro, Subcritical water hydrolysis of sugarcane bagasse: an approach on solid residues characterization, J. Supercrit. Fluids 108 (2016) 69–78.
[45] C.O. Tuck, E. Pérez, I.T. Horváth, R.A. Sheldon, M. Poliakoff, Valorization of biomass: deriving more value from waste, Science 337 (2012) 695.
[46] I. Sereewatthanawut, S. Prapintip, K. Watchiraruji, M. Goto, M. Sasaki, A. Shotipruk, Extraction of protein and amino acids from deoiled rice bran by subcritical water hydrolysis, Bioresour. Technol. 99 (2008) 555–561.
[47] G. Zhu, X. Zhu, Q. Fan, X. Wan, Recovery of biomass wastes by hydrolysis in sub-critical water, Resour., Conserv. Recycl. 55 (2011) 409–416.
[48] S. Ueno, H. Ichinoi, J. Zhao, T. Fujii, Degradation of fish gelatin using hot-compressed water and the properties of the degradation products, High. Press. Res. 35 (2015) 203–213.
[49] M.B. Esteban, A.J. García, P. Ramos, M.C. Márquez, Sub-critical water hydrolysis of hog hair for amino acid production, Bioresour. Technol. 101 (2010) 2472–2476.
[50] V.A. Schommer, B.M. Wenzel, D.J. Daroit, Anaerobic co-digestion of swine manure and chicken feathers: effects of manure maturation and microbial pretreatment of feathers on methane production, Renew. Energy 152 (2020) 1284–1291.
[51] N. Sato, A.T. Quitain, K. Kang, H. Daimon, K. Fujie, Reaction kinetics of amino acid decomposition in high-temperature and high-pressure water, Ind. Eng. Chem. Res. 43 (2004) 3217–3222.
[52] J. Cherry, C. Young, A. Shewfelt, Characterization of protein isolates from keratinous material of poultry feathers, J. Food Sci. 40 (1975) 331–335.
[53] A.K.M. Asaduzzaman, B.-S. Chun, Recovery of functional materials with thermally stable antioxidative properties in squid muscle hydrolyzates by subcritical water, J. Food Sci. Technol. 52 (2015) 793–802.
[54] H. Stiborova, B. Branska, T. Vesela, P. Lovecka, M. Stranska, J. Hajslova, M. Jiru, P. Patakova, K. Demnerova, Transformation of raw feather waste into digestible peptides and amino acids, J. Chem. Technol. Biotechnol. 91 (2016) 1629–1637.
[55] G. Coward-Kelly, F.K. Agbogbo, M.T. Holtzapple, Lime treatment of keratinous materials for the generation of highly digestible animal feed: 2. Animal hair, Bioresour. Technol. 97 (2006) 1344–1352.
[56] P.C. Torres-Mayanga, S.P.H. Azambuja, M. Tyufekchiev, G.A. Tompsett, M. T. Timko, R. Goldbeck, M.A. Rostagno, T. Forster-Carneiro, Subcritical water hydrolysis of brewer's spent grains: Selective production of hemicellulosic sugars (C-5 sugars), J. Supercrit. Fluids 145 (2019) 19–30.
[57] D. Lachos-Perez, L.S. Buller, W.G. Sganzerla, L.P. Ody, G.L. Zabot, T. Forster-Carneiro, Sequential hydrothermal process for production of flavanones and sugars from orange peel: an economic assessment, Biofuels, Bioprod. Bioref. 15 (2021) 202–217.
[58] J. Chen, X. Wang, B. Zhang, Y. Yang, Y. Song, F. Zhang, B. Liu, Y. Zhou, Y. Yi, Y. Shan, X. Lü, Integrating enzymatic hydrolysis into subcritical water pretreatment optimization for bioethanol production from wheat straw, Sci. Total Environ. 770 (2021), 145321.