ACS ENGINEERING Au
AN OPEN ACCESS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Article

Multiobjective Optimization and Implementation of a Biorefinery Production Scheme for Sustainable Extraction of Pectin from Quince Biowaste

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Cite This: https://doi.org/10.1021/acsengineeringau.2c00018

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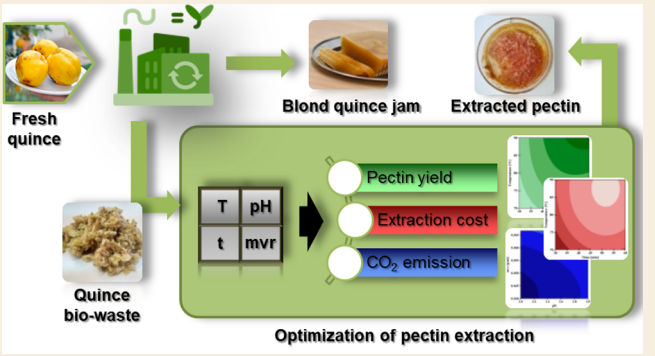
ABSTRACT: The objective of this study was to optimize the pectin extraction from industrial quince biowaste using citric acid as a hydrolytic agent and assisting the process with ultrasound technology. For this, the process was modeled using the Box–Behnken design (BBD) to find the factors' optimum values and their interactions. The quince pectin extraction was carried out by adding to the biowaste a citric acid solution at different pH values (2.0, 2.5, and 3.0) in mass volume ratios of 1/25, 1/20, and 1/15 g/mL and immersing it in an ultrasound bath for 30, 45, and 60 min at controlled temperatures of 70, 80, and 90 °C. Pectin yield, process cost, and CO_2 emission were calculated under different conditions according to the BBD model, and a polynomial function was adjusted for each dependent variable. A multiobjective optimization technique known as "Genetic algorithms" was used to find the proper extraction conditions that would maximize the pectin yield and minimize the process cost. The optimal extraction conditions obtained were as follows: pH = 2.12, mvr = 0.04 g/mL, time = 48.98 min, and temperature = 85.20 °C, with response variables of pectin yield = 12.78%, cost = 1.501 USD/kg of pectin, and calculated CO_2 emission = 0.565 kg of CO_2/kg of pectin.



KEYWORDS: *pectins, quince biowaste, optimization, response surface method, eco-friendly technology, biorefinery*

1. INTRODUCTION

Agro-industrial biowaste has great chemical potential to form valuable products, which can be obtained through sustainable processes. The agro-industrial biowaste presents issues such as the accumulation of large volumes, the proliferation of pests, and water and soil pollution. The application of integrated processes to biowaste from combined technologies constitutes a promising solution to these problems. These technologies based on biorefinery production schemes transform the biowaste into value-added products.[1]

In Argentina, approximately 28,500 tons of quince is produced annually,[2] positioning this country as the seventh larger producer of this fruit. According to the National Agricultural Census (2021), Mendoza and San Juan are the two Argentinian provinces with the largest productions: 1500 and 450 hectares, respectively.[3]

Quince (*Cydonia oblonga* Miller) belongs to the *Rosaceae* family, the same group to which pears and apples belong. It is a widely cultivated and processed fruit due to its culinary, nutritional, and therapeutic properties. The main nutritional components of quince are sugars, organic acids, and polysaccharides, followed by protein, lipids, and vitamins. It is important to highlight that quince has many functional properties because of its polyphenols content and antioxidant activity.

Fresh quinces are rarely consumed due to their pulp hardness, acidity, bitterness, and astringency, so fruit processing is essential before consumption.[4] Approximately 15% of the fruit is represented by the core, skins, and seeds, these portions being the main residue generated in the industrialization of quince for the production of paste and jam. In addition, 19.4% of the initial quince is lost during the production chain (production, harvest, and transport), generating 5500 tons of residue in Argentina per year, thus being a potential source for obtaining various byproducts.[5]

Pectin extraction is one of the most promising options to utilize the quince wastes generated at the production chain and

Received: April 4, 2022
Revised: June 9, 2022
Accepted: June 9, 2022

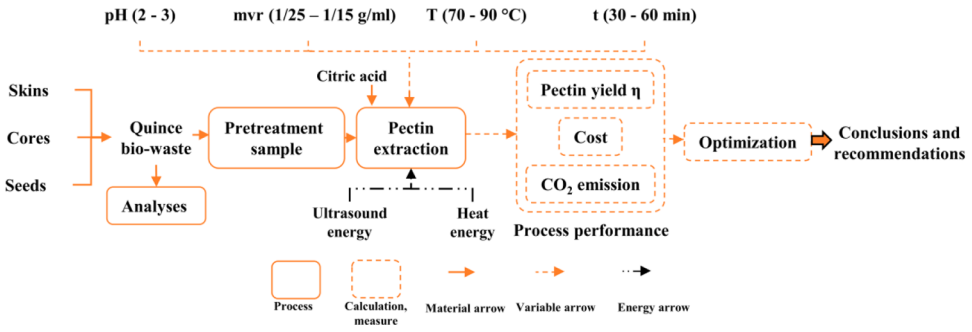


Figure 1. Logic diagram.

fruit processing.[6] Pectins own important gelling and absorption properties that make them interesting to be used in the food, pharmaceutical, and cosmetic industries. Pectins are complex polysaccharides formed mainly by D-galacturonic acid.[7−9] In fruits, most of the acid groups found in pectins are esterified by methanol and can be easily lost by acid or enzymatic hydrolysis. Acid hydrolysis is the least expensive and simplest technique used for pectin extraction.[10]

Many authors have used expensive and environmentally unfriendly acids such as hydrochloric, nitric, and sulfuric acids.[11−15] Other authors suggest the use of less pollutant acids such as acetic, citric, lactic, and tartaric acid for the hydrolytic process, gaining an acceptable process yield.[4,9,16−19] Ultrasound-assisted extraction is an efficient technology that uses acoustic energy to improve the diffusion of solvents through the cell walls washing out their content once the walls are broken.[20] This technique considerably reduces the extraction time and energy consumption compared with conventional methods and in combination with the use of organic acids leads to a cleaner, greener, and more proficient technology.[21] It has been proven that assisting the extraction process with ultrasound helps to improve the extraction yield; this behavior was reported in the extraction from tomato residues,[22] passion fruit,[23] mango peel,[24] orange peel,[21] sour orange peel,[25] and artichoke[26] among others.

Several authors have carried out an optimization of the pectin extraction process considering the influence of the operative variables on the performance of the process and on the pectins' quality. However, no work has been found in which a multiobjective optimization of the pectin extraction process has been carried out considering cost and some environmental impacts, such as the energy consumption and CO_2 emissions.[24,25,27−31] Moreover, no work found about the pectin extraction using citric acid and assisted by ultrasound has focused so far on quince biowaste, nor its pulp. It is of great importance to remark that, for each organic matrix, the yield and cost of the process are strongly affected by the technology and the used hydrolytic agent.

1.1. Objective of the Work

This work's objective was to optimize the pectin extraction from quince industrial biowaste from a paste and jam industry following an eco-friendly process (ultrasound-assisted extraction and citric acid solution as the hydrolyzing agent). For this purpose, the response surface methodology (RSM) was used, applying a Box−Behnken design (BBD) to obtain a mathematical model for pectin yield, cost, and CO_2 emission performances. The operating variables studied were as follows: extraction time (30−60 min), temperature (70−90 °C), pH (2−3), and mass/volume ratio (1/25−1/15). Thus, the acceptable solutions for extraction yield and cost were found using a multiple-objective optimization and the CO_2 emission was calculated under the optimal condition. Figure 1 shows a roadmap of this work.

2. EXPERIMENTAL METHODS

2.1. Sample Collection and Processing

The fresh quince (Figure 2a) is processed in an industry from San Juan, Argentina (Dulces Pizarro S.R.L.), that produces blond quince jam leaving a biowaste composed of seeds, skins, cores, and remains of pulp (Figure 2b). The residue, previously stored at 4 °C was dried at 50 °C in a convective oven for 24 h until moisture content was less than 15% and the dried residue was shredded using a crashing machine (TecnoDalvo brand, TDMC model) and sieved using a 25-mesh sieve to homogenize the particle size, discarding the coarse ones (Figure 2c). The fresh pectin extracted can be seen in Figure 2d, the pectin was dried at 50 °C for 24 h (Figure 2e), and it was bagged and stored until its characterization. From the pectin extraction process,

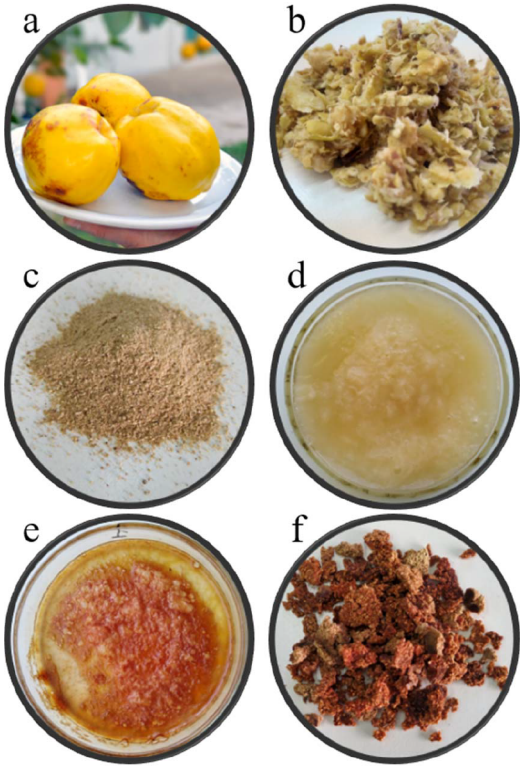


Figure 2. (a) Fresh quince. (b) Fresh quince biowaste. (c) Dried, shredded, and sieved samples. (d) Fresh pectin. (e) Dried pectin. (f) Remaining solid after process extraction.

https://doi.org/10.1021/acsengineeringau.2c00018
ACS Eng. Au XXXX, XXX, XXX−XXX

there is a remaining solid (Figure 2f) that also was dried and will be characterized in the near future to give it possible uses, thus achieving full use of the biowaste.

2.2. Biowaste Characterization

Quince biowaste samples (dried, shredded, and sieved) were chemically characterized by determining moisture (AOAC method 925.10),[32] lipids (AOAC method 920.39: Soxhlet extraction),[32] proteins (AOAC method 960.52: Kjeldahl method),[32] ashes (AOAC method 923.03: by calcination at 580 °C until obtaining white ashes),[32] and crude fiber (AOAC 962.09 method).[32] Also determined are as follows: Klason lignin (standard method ASTM D1106-56),[33] cellulose (standard method ASTM D1103-60),[34] holocellulose (Browning, 1967),[35] and hemicellulose (by difference between holocellulose and cellulose). From the fresh sample, the following physicochemical parameters were evaluated: pH (AOAC method 10.042),[32] titratable acidity (AOAC method 942.15),[32] and solid soluble content (AOAC method 932.12).[32] Furthermore, polyphenol content was determined using methanol:water extracts (80:20, HCl 0.1%) to measure the total concentration of phenolic compound (TP) following the Folin−Ciocalteu method, and the antioxidant activity was measured in vitro: radical trapping activity DPPH,[36] TEAC,[37] and FRAP.[37] Each determination was performed in triplicate (n = 3).

2.3. Pectin Characterization

The pectin extracted at the optimal condition was classified, and its properties such as gelling power, setting time, stability, and purity were determined to characterize it.[38] The most relevant properties measured in this study were the following: moisture content, ash content, equivalent weight (EW), methoxyl content (%Me), and degree of esterification (DE), as indicated by Tripathi et al. (2021),[38] Nguyen and Pirak (2019),[39] and Ezhil and Abilasha (2016).[40] Each determination was performed in triplicate (n = 3).

2.4. Experimental Design

The experimental design for pectin extraction consisted in mixing the dried and pulverized samples with a citric acid solution at pH 2.0, 2.5, and 3.0. The mass/volume ratios (mvr) used were 1/25, 1/20, and 1/15 g/mL. Afterward, they were subjected to ultrasound-assisted extraction and warming at specified temperatures of 70, 80, and 90 °C for 30, 45, and 60 min. Higher pH values are not convenient since various studies have shown that higher pH translates into poorer extraction yields.[15,25,29,30] On the other hand, lower pH values result in cost and citric acid solubility complications. Citric acid is a weak acid and requires very high concentrations to reach a pH below 2. In particular, 383 g of citric acid per liter of solution is required to reach pH 1.45 (the lowest possible considering acid solubility at 25 °C).

The experimental design focused on the extraction process factors to compare their relative importance. Thus, the parameters took the real values for the corresponding lowest (−1), central (0), and extreme levels (1) of coded variables. In this analysis, the Box−Behnken design (BBD) was used to model the process and find the optimum values of factors and their interactions.[41] The coded and real factors of the extraction process and their corresponding independent variables are shown in Table 1.

The variation of dependent variables was analyzed using multivariate regression.[41] Then, it was fitted into a mathematical second-order equation:

Table 1. Independent Variables and Their Coded Factor Levels

		coded factor levels		
independent variables	symbols	−1	0	1
extraction temperature, °C	T	70	80	90
extraction time, min	t	30	45	60
pH, dimensionless	pH	2	2.5	3
mass/volume ratio, g/mL	mvr	1/25	1/20	1/15

$$\hat{y} = b_0 + \sum b_i x_i + \sum b_{ij} x_i x_j + \sum b_{ii} x_i^2 \quad (1)$$

2.5. Extracted Pectin Yield

Pectin extractions were carried out applying the techniques proposed by Bayar et al.,[42] Grassino et al.,[22] and Ganesh et al.,[43] with some modifications. A sample weight of 0.5 ± 0.001 g was placed in 15 mL Falcon tubes previously filled with the citric acid solution. Falcon tubes have a double threaded cap designed to reduce leakage, preventing the escape of solvent vapors, especially when operating at higher temperatures. The tubes were immersed in the ultrasound bath (Arcano brand, PS-10A model, 2 L capacity) at the temperature and time established for the different tests; the ultrasound bath was pre-heated, and its temperature was controlled during the extractive process. Subsequently, they were centrifuged at 3000 rpm for 10 min to facilitate the subsequent filtering stage. Then, the samples were filtered to remove the remaining solids and the liquid extract was collected in 15 mL Falcon tubes. The pectin was precipitated by adding 5 mL of 96% ethanol and refrigerated at 4 °C for 24 h to improve the gelling of pectin. The pectin obtained was filtered using quantitative filters previously weighed and subsequently washed using 70% ethanol to eliminate impurities (monosaccharides, disaccharides, and polyphenols). Finally, the pectin was dried at 50 °C. The extraction yield (η) was calculated by eq 2. Each test was performed in triplicate for each condition defined by the experimental design described above.

$$\eta(\%) = \frac{\text{dried pectin} \times 100}{\text{dried sample}} \quad (2)$$

2.6. Cost Calculation: Electricity Demand and Materials Used

Costs were calculated considering the electricity demand and the materials used throughout the pectin extraction for each point defined by the experimental design (Section 2.4). Table 2 displays the cost values of electricity and materials used in the process.

Table 2. Cost Values of Electricity and Materials (Ortiz-Sánchez et al., 2021)[44]

material	symbol	price
citric acid	p_{ac}	0.19 USD/kg
ethanol	$p_{et\text{-}OH}$	0.98 USD/kg
energy	symbol	price
electricity	p_e	0.022 USD/MJ

In the Supporting Information section, Table S1 shows the consumption of energy and citric acid for each process condition per kg of pectin.

To calculate the energy cost, it is necessary to know the energy demand in the first place. Throughout the process, pectin extraction consumes two types of energy, one related to the use of ultrasound and the other related to heat exchange. Electricity is determined through the heater power (P_h) and ultrasound power (P_u) of the equipment used. The consumption of electricity made by the ultrasound equipment [kJ/kg of pectin] is

$$E_u = \frac{P_u \times t_u \times 100}{\eta \times w_{bw}} \quad (3)$$

where t_u is the time of extraction and w_{bw} is the mass of dry sample [kg].

Similarly, the consumption of electricity made by the heater [kJ/kg of pectin] is

$$E_h = \frac{P_h \times t_h \times 100}{\eta \times w_{bw}} \quad (4)$$

where t_h is the time in which the heater is on. This time was measured during the experiments.

https://doi.org/10.1021/acsengineeringau.2c00018
ACS Eng. Au XXXX, XXX, XXX−XXX

P_h and P_u are specified by the manufacturer, being 50 and 70 W, respectively.

Then, the total energy consumption is the sum of E_h and E_u:

$$E_t = E_h + E_u \tag{5}$$

Cost of energy [USD/kg of pectin] was determined in eq 6:

$$C_e = p_e \times E_t \tag{6}$$

Cost of the raw materials [USD/kg of pectin] was calculated considering the citric acid and the ethanol since the biowaste and water cost is zero. The cost of citric acid is

$$C_{ac} = p_{ac} \times M_{ac} \tag{7}$$

The mass of citric acid used for each experimental design condition to produce 1 kg of pectin is M_{ac}.

The volume of ethanol used is the same for each experimental design condition and is 1.578 kg of ethanol/kg of dried residue processed. The cost of ethanol is

$$C_{et-OH} = p_{et-OH} \times 1.578 \frac{\text{kg of ethanol}}{\text{kg of dried residue}} \times \left(\frac{100}{\eta}\right) \tag{8}$$

The total cost of pectin extraction considers the cost of energy, ethanol, and citric acid:

$$C_{total} = C_e + C_{et-OH} + C_{ac} \tag{9}$$

It is important to note that the electricity and heat consumption might be different at a large scale. However, this study is a first approximation for estimating their impact on the process cost carried out at the laboratory scale. Different authors demonstrated that process yield in ultrasound-assisted extractions is a function of (i) the geometry of the extractor, (ii) the energy dissipated per volume of a treated material, (iii) the ultrasound intensity, and (iv) the frequency of irradiation. Both dissipated energy and ultrasound intensity are independent of the scale, and thus the ultrasonic process can be scalable using these two parameters.[45,46]

In this work, it is assumed that, when the scaled-up process works under similar ultrasound-intensity and energy-dissipation conditions to that in a laboratory, comparable or better values for process yield can be obtained.

The ultrasound-assisted extraction was performed at 70 W. Similar power has been reported to be appropriate for reaching high pectin yields.[31,47−49] The energy effectively taken up by the samples was considered equal to 0.80.[45,50]

2.7. CO_2 Emission

Climate Transparency (2019)[51] recommends that the estimations of indirect CO_2 emission can be calculated through the CO_2 emission factor. In Argentina, this factor is equal to 0.3583 kg CO_2/kWh. The values of energy consumption (Section 2.6) are multiplied by the CO_2 emission factor to obtain the indirect emission of CO_2 for each experimental design condition.

$$CO_2 \text{ emission} = 0.3583 \frac{\text{kg}}{\text{kWh}} \times E_t \tag{10}$$

2.8. Multiobjective Optimization

The approach of this study toward the circular economy is based on optimization techniques using mathematical models and multivariate multiobjective optimization. These tools are of great use to carry out sustainability analyses in biorefinery processes. Optimization allows revealing the operating conditions that provide better performance. On the other hand, it allows the minimization of production costs. The mathematical functions that represent process performance and costs are known as objective functions. The multiobjective optimization problem can be defined as a method for determining the values of a decision variables vector that satisfy a set of constraints and optimize a vector function. The elements of these vector functions represent the objective functions, which can be used simultaneously to find an acceptable solution for decision-making.

The performance in the extraction of pectin and the cost associated with the process (to achieve an optimal design according to the objectives of the circular economy) were considered objective functions. The multiobjective optimization problem can be expressed as follows:

$$\min(100 - \hat{y}_{\text{pectin yield}}[\%], \hat{y}_{\text{cost}}[\text{USD/kg of pectin}] = f(x_1, x_2, x_3, x_4) \tag{11}$$

Pareto's optimization considers a general expression

$$\min(\hat{y}_1(x), \hat{y}_2(x), ..., \hat{y}_n(x)) \tag{12}$$

subject to $x \in X$ with $k \geq 2$ as the number of objective functions f_i. Optimization aims to find optimal solutions $x^* \in X$, in which case, the elements cannot be improved without worsening, at least, one other element.[52] The established constraint was chosen according to the market price of pectin (3−11 USD/kg of pectin).[44,53] Considering 10% of the profit margin to compete in the international worldwide trade, the set of feasible solutions can be represented on the Pareto front.

Matlab R2017b software has the built-in multiobjective Genetic Algorithm (gamultiobj),[54] which is the Non-Dominated Classification Genetic Algorithm − II,[55] and has been applied by several authors.[56−58]

3. RESULTS AND DISCUSSION

3.1. Biowaste Characterization

In Table 3, the physicochemical characterization results of fresh residue are shown.

Table 3. Fresh Sample Physicochemical Characterization

parameter	content
moisture content [%]	72.0 ± 2.0
pH	3.82 ± 0.03
titratable acidity [g malic acid/L]	0.57 ± 0.02
soluble solid [° Brix]	7.2 ± 0.1

Acidity and pH are important parameters since they favor the hydrolytic process to carry out the pectin extraction. The acidity and pH obtained were similar to the reported values by Raji et al. (2017)[4] for quince pulp. The content of soluble solid is lower than that obtained by Sharma et al. (2011)[59] for quince pulp, as a consequence of the type of residue used in this work, which contains only remains of pulp (the phase where the free sugars are concentrated).

In Table 4, the biowaste proximal composition on a dry basis (db) can be observed.

Lipid and protein contents are low for this residue. The major components of the waste correspond to the lignocellulosic material and fiber, values similar to those reported for quince pulp[14,60] and a quince residue composed of

Table 4. Biowaste Proximal Composition on a Dry Basis

component	content [%]
lipid	0.48 ± 0.03
protein	0.28 ± 0.02
ash	0.46 ± 0.02
crude fiber	7.02 ± 1.06
lignin	6.68 ± 0.22
holocellulose	19.37 ± 0.14
cellulose	16.15 ± 1.58
hemicellulose	3.22 ± 1.01

https://doi.org/10.1021/acsengineeringau.2c00018
ACS Eng. Au XXXX, XXX, XXX−XXX

seeds, cores, and skins.[61] The ash content, related to the mineral content (K, Ca, Na, and Mn), is low.[60]

Furthermore, the total phenolic content (TPC) and the antioxidant activity (AA) were determined for the fresh samples (Figure 2b) and the dried residue (Figure 2c) to evaluate how the drying process affects the content of the antioxidant compound (Table 5).

Table 5. Fresh and Dried Biowaste Polyphenolic Content on a Dry Basis

determination	fresh sample	dried Sample
TPC [mg AG/100 g sample]	1396 ± 60	741 ± 53
AA/DPPH [mg Trolox/g sample]	5.4 ± 0.1	2.5 ± 0.1
FRAP [mg Trolox/g sample]	5.0 ± 0.3	2.7 ± 0.2
TEAC [mg Trolox/g sample]	5.77 ± 0.1	4.0 ± 0.1

TPC, DPPH (2,2-diphenyl-1-picrylhydrazyl radical), FRAP (ferric reducing antioxidant power), and TEAC (Trolox equivalent antioxidant capacity) in the dried residue showed lower values than the one in the fresh residue. It was observed that at the DPP and the AA form, the wet waste concerning the dried one presented a loss of approximately 50%. It is important to highlight that the residue provides significant antioxidant and bioactive components that contribute to the high nutritional value of the residue.[60,62,63]

3.2. Pectin Characterization

The quality parameters measured in the pectin extracted at the process optimal condition were as follows: moisture content, ash content, equivalent weight (EW), methoxyl content (% Me), and degree of esterification (DE); these parameter results can be appreciated in Table 6.

Table 6. Quality Parameters of Quince Biowaste Pectin

parameter	content
moisture content [%]	3.11 ± 0.14
ash content [%]	1.63 ± 0.08
equivalent weight [g/mL]	110.30 ± 1.20
methoxyl content [%]	12.85 ± 0.45
degree of esterification [%]	31.37 ± 0.52

The pectin moisture content is low (3.11 ± 0.14), which increases the shelf life of the product and prevents microbial degradation.[38] The ash content can be a parameter that determines the purity of pectin; when ash is lower than 9−10%, it is considered good-quality pectin for gel formation.[64] A high equivalent weight may be explained as a consequence of higher partial degradation of pectin,[38] and since quince biowaste pectin has a low equivalent weight compared with pectin from other samples, this indicates that there was no degradation during the extraction process. The methoxyl content of pectin is important to control the gel strength, the setting time, and the sensitivity to metal ions and to determine the functional properties of pectin solutions and abilities.[65] Normally, methoxyl content varies from 0.2% to 12% depending on the source and extraction procedure, with the results of this study being close to that range. Finally, the degree of esterification can be used to classify pectin into two groups: low methoxyl pectin (LMP) with a DE < 50% and high methoxyl content pectin (HMP); the pectin here obtained can be classified as LMP.[42,65,66] In this work, the quality parameters of quince biowaste pectin are similar to the values reported by Bayar et al. (2017)[42] with similar samples.

3.3. Experimental Design

The three-level BBD design for each factor (temperature, time, pH, and mvr) of the process extraction yield, cost, and CO_2 emission are shown in the Supporting Information in Table S2.

3.3.1. Effect of Simultaneous Variables on Pectin Yield, Cost, and CO_2 Emission. The maximum extraction yield was obtained in the following ranges of the conditions studied: pH = 2−2.2, mvr = 0.040−0.045 g/mL, t = 50−60 min, and T = 85−90 °C (Figure 3). In coincidence with other authors, as can be seen in Figure 3, the extraction yield tends to grow when T and t increase and mvr and pH decrease.[38,40,42,67] Increasing the temperature favors the pectin solubility while a longer time causes higher contact between solvent and cell walls. Additionally, high acidic solvents have the potential to make contact straightforwardly with insoluble forms of pectin and hydrolyze them into soluble forms by reducing their molecular weight without any degradation and improving the discharge of pectin into the surrounding extraction medium.[21] On the other hand, lower mvr leads to greater spatial availability among solvent molecules that move pectin outward from plant matrices. Pectin extraction from quince was also studied by Hadi et al. (2020)[68] obtaining a pectin yield of 10.25% but using hydrochloric acid, which may produce negative environmental impacts and is more expensive than citric acid.[69,70] The highest yields were achieved by Acikgoz (2011),[11] Sharma et al. (2011),[59] and Rop et al. (2011)[14] with 1.83, 1.80, and 3.50%, respectively, employing the conventional method of extraction (mixing), and citric acid as a hydrolytic agent. These yields were lower than those obtained in this work, what allows to affirm that assisting the process with ultrasound considerably favors the extraction. Furthermore, other authors reported comparable pectin yields using a similar (ultrasound-assisted) extraction process: Raji et al. (2017)[4] obtained a yield of 14.3% with melon waste, Güzel and Akpinar (2019)[9] reached 13.3% with apple peels, and Grassino et al. (2016)[22] achieved a maximum yield of 18.5% with tomato peel waste.

No cost and CO_2 emission reports of the pectin extraction process from quince biowaste were found. In Figure 4, the cost of the pectin extraction process versus the independent variables in pairs can be observed. It would be expected that the cost of the process would increase at higher values of t and T and lower mvr and pH since it translates into higher consumption of energy and citric acid; nevertheless, the opposite situation was observed as a consequence of a large increase in the extraction yields, obtaining the minimum costs at the following ranges: pH = 2−2.1, mvr = 1/20−1/25 g/mL, t = 45−55 min, and T = 85−90 °C. In Figure 5, the CO_2 emission versus the independent variables was analyzed in pairs. The CO_2 emission is the minimum at lower values of T and t as expected, and it is not significantly affected by the pH and mvr values. CO_2 emissions were indirectly calculated from energy consumption; therefore, the higher the temperature and time, the higher are CO_2 emissions.

The optimal ranges for pectin yield and cost are not the same, which is the reason why a multiobjective optimization is more appropriate for this study (Section 3.4). CO_2 emission was not considered an objective function because it was not measured experimentally but calculated indirectly.

https://doi.org/10.1021/acsengineeringau.2c00018
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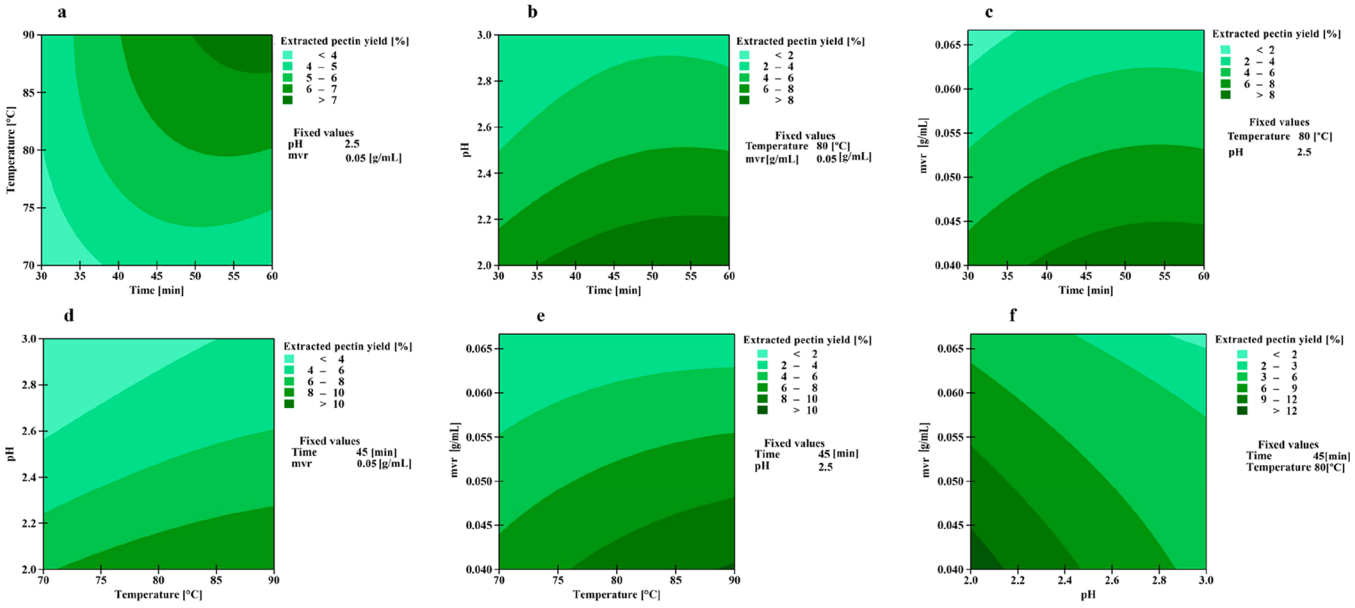

Figure 3. Pectin yield vs (a) T and t, (b) pH and t, (c) mvr and t, (d) pH and T, (e) mvr and T, and (f) mvr and pH.

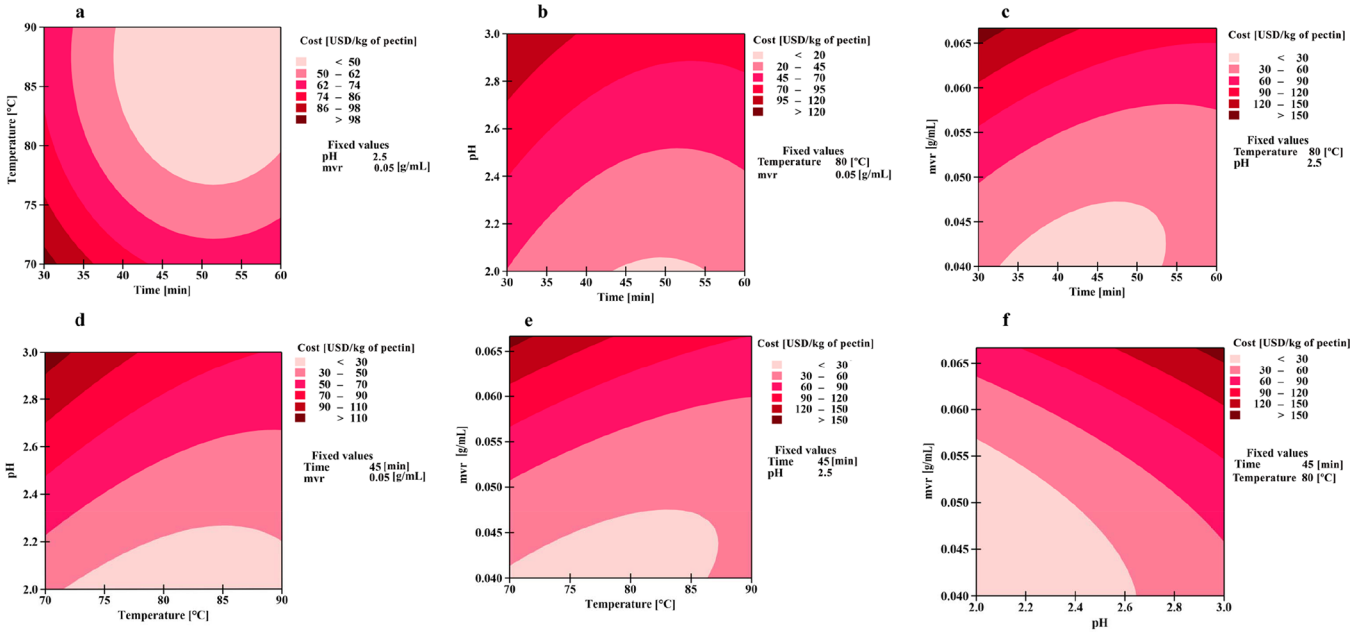

Figure 4. Pectin cost vs (a) T and t, (b) pH and t, (c) mvr and t, (d) pH and T, (e) mvr and T, and (f) mvr and pH.

Furthermore, although no scaling-up method has been published so far for ultrasound-assisted pectin extraction, there are some reports of similar tasks for other organic compounds:

- For antioxidants, comparable[71] or better[72] yields have been recorded for a larger than laboratory scale.
- For polysaccharides—under the same ultrasonic power dissipation—yields are higher for scales larger than laboratory.[73]

These results support the validity of the approximation as a way of establishing a yield threshold for ultrasound-assisted pectin extraction, which would work even on a larger scale than laboratory-scale.

A more exhaustive cost calculation could be done if some other factors were considered. A deeper analysis of the energy consumption for ultrasound-assisted pectin extraction and the design of appropriate ultrasound equipment to simulate the entire process on an industrial scale could be included in future work.

3.3.2. Model Validation and Canonical Analysis for Extracted Pectin Yield, Cost, and CO_2 Emission. The extracted pectin yield, cost, and CO_2 emission from quince biowaste at the conditions under study—codified time (x_1), temperature (x_2), pH (x_3), and mass volume ratio (x_4)—were fitted into polynomial functions. The complete model, including the non-significant terms, for pectin yield (eq S1), cost (eq S2), and CO_2 emission (eq S3) can be appreciated in the Supporting Information. A multivariable regression was performed to determine eqs S1−S3 coefficients.

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ACS Eng. Au XXXX, XXX, XXX−XXX

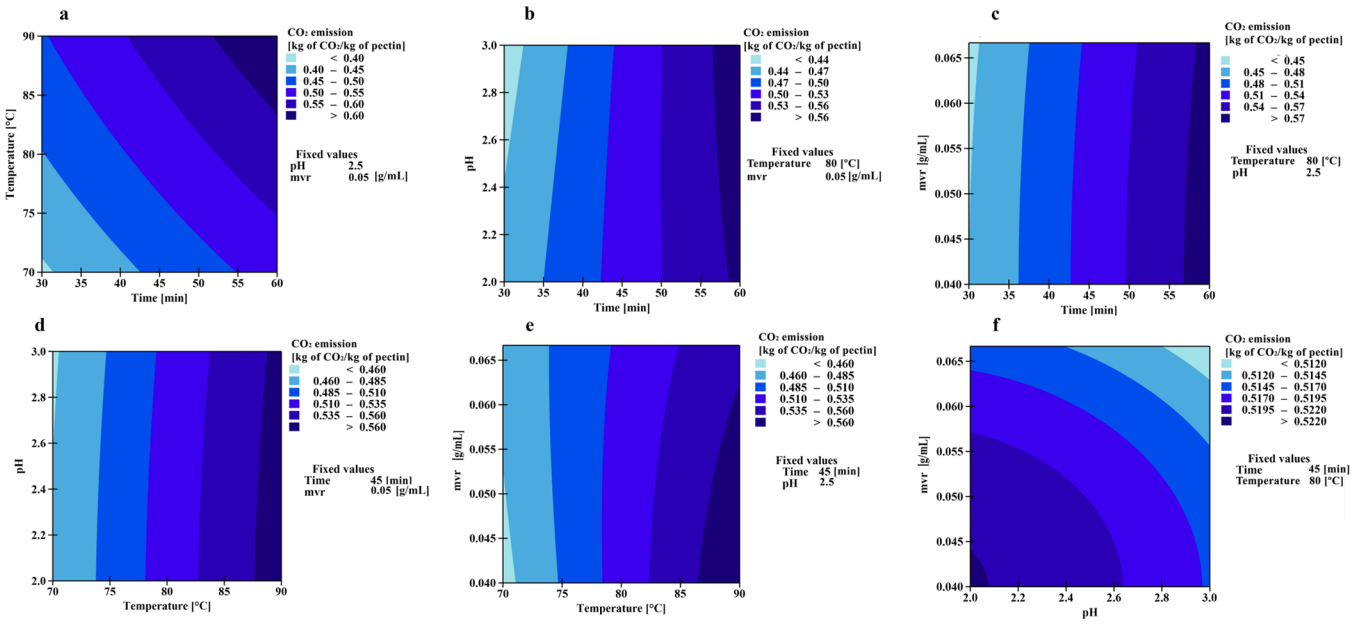

Figure 5. CO_2 emission vs (a) T and t, (b) pH and t, (c) mvr and t, (d) pH and T, (e) mvr and T, and (f) mvr and pH.

Table 7. ANOVA of Pectin Yield, Cost, and CO_2 Emission Regression Models

response variable	variation source	sum of squares	degrees of freedom	mean square	calculated F value	tabulated F value, F (14,66,0.05)
pectin yield	regression	753.358	14	53.811	96.670	1.845
	residues	36.737	66	0.557		"significant"
	total	790.045	80			
	R^2	0.953				
	adjusted R^2	0.944				
cost	regression	153,487	14	10,963	27.710	1.845
	residues	26,115	66	395.7		"significant"
	total	179,602	80			
	R^2	0.855				
	adjusted R^2	0.824				
CO_2 emission	regression	0.269	14	0.019	65.79	1.845
	residues	0.019	66	0.000		"significant"
	total	0.288	80			
	R^2	0.933				
	adjusted R^2	0.919				

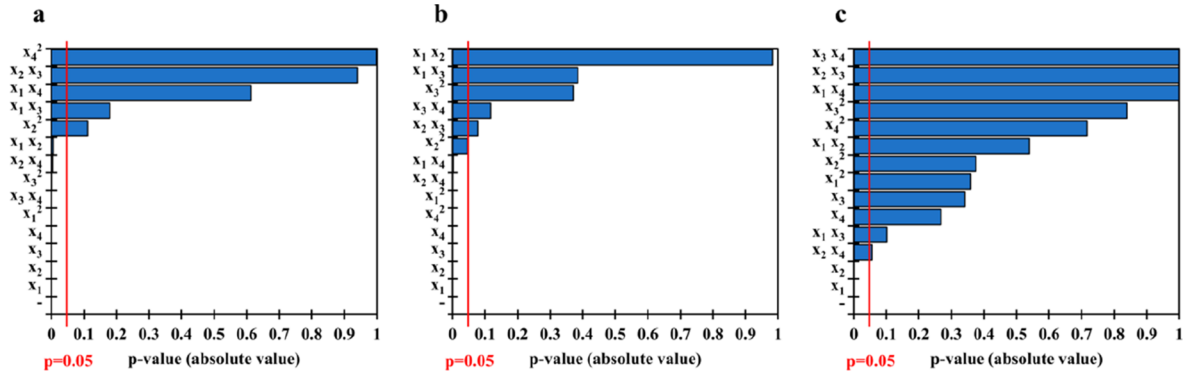

Figure 6. Pareto chart with p values of the statistical contribution of the model terms for (a) pectin yield, (b) cost, and (c) CO_2 emission.

To confirm the good data adjustment, statistical tests were carried out. In this sense, ANOVA was performed using Fisher's test.

Table 7 displays the ANOVA results. Generally, Fisher's test calculates the data variance considering the ratio of the mean square of group variance error-related. The calculated F value must be higher than the tabulated value to be considered a good predictor model. The results of Table 7 show that the value of F calculated for the pectin yield model is higher than the tabulated value, (F (14,66,0.05) = 1.87). Thus, these values

https://doi.org/10.1021/acsengineeringau.2c00018
ACS Eng. Au XXXX, XXX, XXX−XXX

show that the null hypothesis must be rejected. Therefore, the regression model represents a good predictor of the pectin yield response. Moreover, the coefficient of determination (R^2) is 0.953, 0.855, and 0.933 for pectin yield, cost, and CO_2 emission, respectively. In all three cases, R^2 values are higher than 0.75 were obtained, which implies that the models are good fits.[74]

The p values associated with Student's t test are shown in Figure 6. The single factors, b_1, b_2, b_3, and b_4 for variables x_1, x_2, x_3, and x_4, respectively, are the linear effects, while factors b_{12}, b_{13}, b_{23}, b_{14}, b_{24}, and b_{34} for x_1x_2, x_1x_3, x_2x_3, x_1x_4, x_2x_4, and x_3x_4, respectively, are the interaction terms. The second-order terms are the quadratic effect on the response variable, which are b_{11}, b_{22}, b_{33}, and b_{44} for x_1^2, x_2^2, x_3^2, and x_4^2, respectively.

The p value allows validating the significance of each coefficient at a specified significance level.[41] The significance level for this case is 95%. When a p value is less than 0.05, the effect of this coefficient is "significant" and contributes principally to the dependent variable. The variance inflation factor (VIF) explains the collinearity between variables. Results (value of 1) of the VIF shown in Table S3 indicate, for interaction terms, that there is no correlation between predictor variables in the model.

Figure 6 shows the results of the p value for each of the linear and quadratic coded variables and their interactions. All the statistical parameters can be seen in Table S3.

The terms that present $p \geq 0.05$ are not significant at a 95% confidence level of significance. Thus, the mathematical expressions for the prediction of pectin yield (eq 13), cost (eq 14), and CO_2 emission (eq 15) are as follows:

$$\hat{y}_{\text{pectin yield}}[\%] = 5.769 + 1.002\,x_1 + 1.118\,x_2 - 2.867\,x_3 - 2.987\,x_4 - 0.801\,x_1^2 + 0.595\,x_3^2 + 1.281\,x_3x_4 \quad (13)$$

$$\hat{y}_{\text{cost}}[\text{USD/kg of pectin}] = 46.970 - 14.280\,x_1 - 18.180\,x_2 + 32.850\,x_3 + 46.330\,x_4 + 16.540\,x_1^2 + 21.980\,x_4^2 - 19.020\,x_1x_4 - 20.420\,x_2\,x_4 \quad (14)$$

$$\hat{y}_{CO_2\ \text{emission}}\ [\text{kg of } CO_2\text{/kg of pectin}] = 0.519 + 0.066\,x_1 + 0.055\,x_2 - 0.010\,x_2\,x_4 \quad (15)$$

The increase in temperature and time and the decrease in mvr and pH cause an increase in the pectin extraction yield as can be seen in Figure 3. The effect of these independent variables on the response variable was also found by Tripathi et al. (2021),[38] Bayar et al. (2017),[42] Ezhil and Abilasha (2016),[40] and Kavak (2017).[67] Moreover, by lowering the pH and mvr, the cost decreases as shown in Figure 4 despite a higher consumption of citric acid. Similar behavior is observed for the energy when t and T are increased, although CO_2 emission goes up as shown in Figure 5.[41]

The quadratic and interaction terms between the coded variables are associated with the model, where the interactions would indicate that there could be a synergistic effect between these variables.

3.4. Multiobjective Optimization

Multiobjective optimization was used to find acceptable solutions for decision-making. The results are shown at the Pareto front (Figure 7). Table S4 in the Supporting Information shows detailed data of the optimal process conditions related to its acceptable solutions.

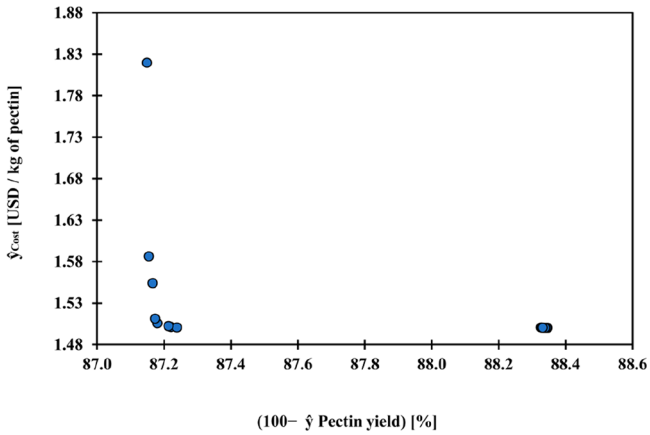

Figure 7. Pareto front obtained by the multiobjective optimization considering the pectin extraction yield and cost.

The recommended extraction conditions to obtain the most acceptable compromise between the process variables correspond to run 4 (Table S4). For this, the recommended pectin extraction conditions are the following: t = 48.98 min, T = 85.20 °C, pH = 2.12, and mvr = 0.04 g/mL, obtaining a high pectin yield = 12.78%, for a cost = 1.501 USD/kg of pectin. The CO_2 emission calculated for the mentioned condition is 0.565 kg of CO_2/kg of pectin.

4. CONCLUSIONS

The influence of time and temperature for the ultrasound-assisted extraction of pectin, in combination with other operating parameters, such as pH of the solution and the mvr, as well as the multiobjective optimization, was studied. The experiments under different conditions based on the Box–Behnken experimental design allowed performing models of prediction to determine the process performance, pectin extraction yield, cost, and indirect CO_2 emission.

The extraction yield increased when temperature and time increased and mvr and pH decreased. The pectin yield obtained in this study by assisted ultrasound combined with citric acid produced a higher value than those reported in the literature.

The process cost decreased while time and temperature increased and mvr and pH decreased as a consequence of higher pectin yields.

The CO_2 emission takes lower values at lower temperatures and time, and CO_2 emission is not significantly affected by the pH or mvr values.

The results of statistical analysis showed that these three models are good predictors, with their coefficients of determination equal to 0.953, 0.855, and 0.933 for pectin yield extraction, cost, and indirect CO_2 emission, respectively.

The multiobjective optimization allowed knowing the recommended extraction conditions to obtain the most acceptable compromise relationship among cost and pectin extraction variables. The recommended operating conditions

https://doi.org/10.1021/acsengineeringau.2c00018
ACS Eng. Au XXXX, XXX, XXX−XXX

are 48.98 min for time, 85.20 °C for temperature, 2.12 for pH, and 0.04 g/mL for mvr. Under those conditions, the pectin yield was 12.78% and the cost resulted in 1.501 USD/kg of pectin. The indirect CO_2 emission calculated for the mentioned conditions corresponds to 0.565 kg of CO_2/kg of pectin.

The performance of the prediction model in this study for extracted pectin yield and process cost and their optimization satisfies the efforts focused on circular economy and biorefinery to carry out sustainability analyses.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsengineeringau.2c00018.

Energy and citric acid consumption per kilogram of pectin obtained for each operation condition (Table S1); three-level BBD design for each factor (temperature, time, pH, and mvr) of the process extraction yield, cost, and CO_2 (Table S2); statistical parameters of regression coefficients and their effect on the sorted significance for the pectin yield, cost, and CO_2 emission models (Table S3); acceptable solutions and their codified process variables values (Table S4); and mathematical model of multiple regression analysis (eqs S1−S3) (PDF)

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Author Contributions

#M.R.-G. and D.Z.-G. have equal contributions.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank DULCES PIZARRO S.R.L. for providing the quince waste samples (husk and seeds). The authors wish to express their gratitude to the following Argentine institutions: the University of San Juan (PDTS Res. 1054/18); the University of Comahue (PIN 2017-04/I223); CONICET - National Scientific and Technical Research Council (PUE PROBIEN 22920150100067 and PIP 11220200100950CO); IDEA (Res. 0279/2019); ANPCYT-FONCYT (PICT JI 2017-2047 and PICT-2019-01810). M.R.-G., I.M., and R.T.-S. have doctoral fellowships from CONICET. D.Z.-G. has a post-doctoral fellowship from CONICET. M.P.F., R.R., and G.M. are Research Members of CONICET, Argentina.

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https://doi.org/10.1021/acsengineeringau.2c00018
ACS Eng. Au XXXX, XXX, XXX−XXX