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Optimization of furfural extraction from *Theobrama cacao* wastes using response surface methodology

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Abstract. Cacao farming in the Philippines is continually expanding due to an influx of government support and funding. Although a comprehensive development program was implemented, the large volume of cacao biomass waste generated annually remains underutilized. In an attempt to provide a means of reusing this waste, we test the extent to which furfural can be extracted from cacao pod wastes. A box-behnken experimental design was used to obtain the optimal conditions in the acid-catalyzed extraction of crude furfural. Extraction time (min), hydrochloric acid concentration (M), and amount of sodium chloride (g) were found to have a significant influence on the extraction yield of crude furfural. Actual values of these independent variables were chosen on the basis of preliminary experimental results. Optimum conditions using ridge analysis were found to be: extraction time 35.0 min, hydrochloric acid concentration 5.0 M, and amount of sodium chloride 7.0 g. Furfural extraction was also performed at optimum conditions to assess the validity of the empirical model. In conclusion, the high furfural extraction yield obtained in our experiments presents an opportunity to harness these unregulated wastes in producing high quality products.

1 Introduction

With the perceived decline in the global production of beans from the *Theobrama cacao* (cacao) tree, developing countries have been strongly encouraged to propagate cacao trees to fill the gap in the demand and supply of cocoa beans. For example, the Philippines took this opportunity and supported local cacao plantations with incentives to help this local industry to grow. The Philippine government further expressed its support to the expanding cacao industry by allowing its agencies to fully participate in the 2022 Cacao Challenge (that is to produce 100 000 MT of dried fermented cacao beans by 2022) [**1**]. This notion of providing incentives for developing countries therefore led to a fifty percent increase in the global production of cacao beans [**2**].

While the idea of using incentives to boost cacao bean production is beneficial to the local cacao industry, this also propagates the production of undesirable waste residues in cacao farms and plantations. It has been reported that about 52-76% of the whole cacao fruit are considered as undesirable solid residues in the form of cacao pods (CP) [**3-4**]. In fact, a ton of processed cocoa beans approximately generates 10 tons of CP solid residues [**5**]. Traditionally, CP residues are allowed to freely decompose in a secluded but open area within cacao plantations to mitigate possible environmental complications. However, untreated decomposing CP residues elevate the risk of spreading botanical diseases such as black pod rot [**5-6**]. The large volume of CP residues generated from the cacao fruit then presents a challenging waste management problem that must be immediately addressed.

Converting CP into furfuraldehyde (furfural) is an economical and promising way of reducing the volume of these waste residues into manageable levels. Furfural is a chemical with various applications in the field. For instance, furfural can be used as a selective solvent to refine petroleum, lubricating oils, diesel fuels, and vegetable oils [**7**]. Furfural can be also used as a starting chemical reagent to produce high value added products such as furfuryl alcohol and tetrahydrofurfuryl alcohol [**8**]. In the present work, we investigate the extent to which CP residues can be converted into furfural. To assess the suitability of CP residues as a precursor material for furfural production, we implemented a box-behnken experimental design to achieve an optimum yield of furfural derived from extracts of CP residues.

2 Materials and methods

2.1 Materials and reagents

Cacao (*Theobroma cacao L.*) pods used in this study were acquired from local markets in Barangay BinodegahanPio Duran Albay, Philippines. Fresh cacao pods were selected according to criteria described in Philippine National Standards for Cacao Beans [**9**]. The average particle size of the cacao pods was reduced to 1 cm. These smaller pods were then oven-dried for 5 hours at 110°C to remove excess moisture. After drying, the dried pods were ground to finer particles and sieved

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through a 1 mm screen. Analytical grade reagents (HCl and NaCl) used for acid hydrolysis were purchased from Belman Laboratories. Furfuraldehyde standard was purchased separately from Haihang Industry Co., Ltd. Distilled water was used in all experiments.

2.2 Determination of furfuraldehyde aqueous concentration

Furfural solutions with concentrations ranging from 50–300 ppm were prepared from the standard solution of furfuraldehdye. Aqueous concentrations of furfural were checked by performing a full wavelength scan using a Perkin Elmer Lambda 45 UV-Vis spectrophotometer. Highest absorbance was recorded at a wavelength of 276 nm. A calibration curve was then prepared to determine furfural concentrations from cacao pod extracts.

2.3 Acid hydrolysis experimental set-up

Procedure to hydrolyze cacao pods to furfuraldehydewas adopted from published literature[**7, 10**]. 10 g of dried pods and NaCl of known amount (6.0, 7.0, or 8.0 g) were mixed in the distilling flask. 100 mL of HCl solution (4.0, 4.5, or 5.0 M) was then carefully added into the flask (see **Fig. 1**). The resulting mixture was moderately agitated for 5 minutes to equally disperse the biomass in solution. The solution was heated to 160°C and agitation was continually induced to equally distribute heat in solution. Once the solution starts to boil, the distillate was condensed into liquid and collected in a receiving flask. The condensed distillate obtained was a clear yellow liquid. This set-up was conducted in a dark room to minimize furfural reactivity.

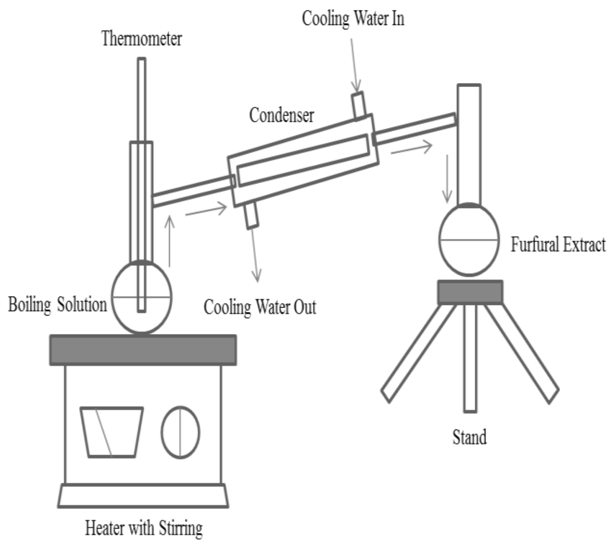

Fig. 1. Cacao Pod Acid Hydrolysis Experimental Set-up

2.4 Experimental design

A box-behnken experimental design (see **Table 1** and **Table 2**) generated using Stat-Ease design expert software was implemented to investigate the influence of independent variables (HCl concentration M; amount of NaCl g; residence time min) in optimizing the desired response (furfural yield mg/L). All experimental runs were performed in duplicates.

Table 1. Independent Variables Influencing Furfural Yield

Factor	Unit	Factor level	
		Low	High
HCl Cocentration	M	4.0	5.0
Amount of NaCl	g	6	8
Residence Time	min	35	45

Table 2. Box-Behnken Design Experimental Runs

Run	Factor 1 A: HCl Concentration (M)	Factor 2 B: Amount of NaCl (g)	Factor 3 C: Residence Time (min)
1	4	6	40
2	5	7	45
3	5	7	35
4	4.5	8	35
5	4.5	6	45
6	4.5	8	45
7	5	6	40
8	4	8	40
9	4.5	7	40
10	4.5	6	35
11	4	7	35
12	4.5	7	40
13	5	8	40
14	4	7	45
15	4.5	7	40
16	4.5	7	40
17	4.5	7	40

3 Results and discussion

3.1 Preliminary experiments

To determine the possible factor levels that would be used for optimization, preliminary experiments were conducted. Working levels for HCl concentration, amount of NaCl, and residence time were investigated by implementing a one-factor-at-a-time (OFAT) methodology. The possible ranges identified where furfural extracted from CP residues would be maximized are summarized in **Table 3**. Based on the results of these experiments (data not shown), furfural yields were found to be high (between 180 and 220 ppm) within the following working range: HCl Concentration = 4-5 M; amount of NaCl = 6-8 g; and residence time = 35-45 min. Hence, these were used as the working factor levels for the response surface methodology applied in this study.

Table 3. Levels Tested in Preliminary Experiments

Factor	Range	Unit
HCl concentration	1–5	M
Amount of NaCl	2-8	g
Residence Time	15–45	min

3.2 Statistical tests and mathematical model building

To maximize the amount of furfural that can be extracted from the CP, a response surface methodology was implemented in this study. A box-behnken design with three-factors and 12 experimental runs was adopted. Using Design Expert 11 Software® (Stat-Ease, USA), 5 center points were also added to measure the degree of variability and stability of the response variable (furfural yield). A second-order mathematical model was then generated by the software used. The model (p-value<0.0001) with the actual factors is given in **Eq. 1**.

$$Furfural\,Yield = Intercept + C_1A + C_2B + C_3C + C_4AB + C_5AC + C_6BC + C_7A^2 + C_8B^2 + C_9C^2 \quad (1)$$

where A corresponds to the factor HCl concentration (M), B is the amount of NaCl (g), C is the residence time (min), and C_1 to C_9 are coefficients with values summarized in **Table 4**.

Table 4. Values of Coefficients in the Empirical Model

Term	Coefficient Value	p-value	Remarks
Intercept	-511.92	-	-
A	-653.52	0.002511	Significant
B	927.12	0.003465	Significant
C	-47.23	0.2986	Not Significant
AB	-64.80	0.001833	Significant
AC	-6.92	0.07378	Not Significant
BC	0.97	0.6055	Not Significant
A^2	158.66	0.0002	Significant
B^2	-49.68	<0.0001	Significant
C^2	0.91	0.01841	Significant

Table 5 summarizes the predicted and observed values for the furfural yield. It was noted that the predicted values are in good agreement with the observed values. To further examine whether the predicted values were valid, the software was used to assess the goodness of fit of the empirical model.

Table 5. Observed and Predicted Values from the Box-Behnken Experimental Design

Run	A	B	C	Observed	Predicted	% Error
1	-1	-1	0	340.80	327.50	-3.90
2	1	-1	0	454.11	436.44	-3.89
3	-1	1	0	332.21	349.87	5.32
4	1	1	0	315.93	329.23	4.21
5	-1	0	-1	386.34	386.92	0.15
6	1	0	-1	460.71	465.66	1.07
7	-1	0	1	440.37	435.42	-1.12
8	1	0	1	445.56	444.97	-0.13
9	0	-1	-1	350.29	363.00	3.63
10	0	1	-1	329.15	310.90	-5.55
11	0	-1	1	348.97	367.22	5.23
12	0	1	1	347.20	334.48	-3.66
13	0	0	0	387.64	370.77	-4.35
14	0	0	0	392.23	370.77	-5.47
15	0	0	0	389.00	370.77	-4.68
16	0	0	0	343.07	370.77	8.08
17	0	0	0	341.93	370.77	8.44

As summarized in **Table 6**, R^2 values were very close to unity and strongly indicate that the second-order response model has a good fit. Furthermore, the adjusted and predicted R^2 are also in good agreement with each other. These results highlight that there is a strong correlation between the predicted and observed outcomes.

Table 6. Statistical Fit of the Empirical Model

Fit Statistics			
Std. Dev.	26.17	**R^2**	0.7939
Mean	376.79	**Adjusted R^2**	0.7167
C.V. %	6.94	**Predicted R^2**	0.6337

3.3 Optimization of pectin recovery

The furfural extraction process employed in this study was optimized by using the validated mathematical model. The suitable conditions for achieving a maximum furfural yield are presented in **Fig. 2**. These represented the factor combination with the highest desirability. Essentially, based on the verified model, desirability close to unity would give a response close to the experimental value. Furthermore, as shown in **Fig. 3**, the 3D response surface gave an estimated furfural yield of 465.66 ppm. To test whether this predicted value would be in close agreement to the observed value, confirmatory runs were also done. It was noted that an error between 8-19% was incurred. The high variability obtained may be due high reactivity of furfural with the environment. Nevertheless, the validated model has still a good potential to predict furfural yields within the working ranges specified in this study.

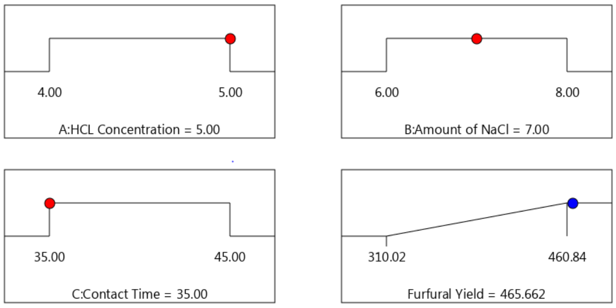

Fig. 2. Factor Level Combination to Maximize Furfural Yield

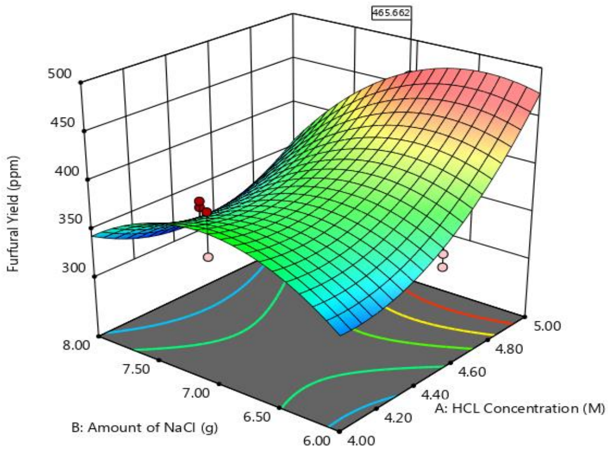

Fig. 3. 3D Response Surface for Furfural Yield

4 Conclusion

The use of CP wastes as raw materials for furfural production is an economical way of managing the increasing volume of CP annually. In the present work, we have provided evidences that CP can effectively be converted into furfural. We have also noted that a relatively high furfural yield (460.71 ppm) was achieved experimentally. This obtained response was replicated by using the empirical model generated. Optimum conditions were found to be: HCl concentration = 5.0 M; amount of NaCl = 7.0 g; residence time = 35.0 min.

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