OPTIMIZATION OF HYDROGEN PRODUCTION FROM CITRUS PEEL WASTE IN BATCH REACTORS

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Abstract - In Brazil, approximately 8,825,276 t/year of citrus are produced, with 500t of waste being generated for every 1000t of processed fruit. This study aimed at optimizes H_2 obtainment from Citrus Peel Waste (CPW) by means of Rotational Central Composite Design. According to the surface response obtained, was regarded as optimum condition: 4 $gTVS.L^{-1}$ of inoculum, 29.8 $g.L^{-1}$ of substrate and pH 8.98. Based on the validation assay, it is possible to state that H_2 production was optimized, since the obtained P value for H_2 (48.47 $mmol.L^{-1}$) was 3.87 times higher than the value obtained before its optimization (12.54 $mmol.L^{-1}$).

Keywords - Lignocellulosic Biomass. Agro Industrial Waste. Bio-Hydrogen.

I. INTRODUCTION

Brazil is the world's leading producer of citrus, accounting for about 35% of orange production and 81.6% of exports of its concentrated juice [1,2]. After processing, between 50-60% of the volume of fruit produced becomes waste, including peels and bagasse [3]. Its composition is rich in carbohydrates, therefore, considered as a potential source of carbon and as a substrate for the biogas production. Besides inoculum composition, there are other relevant variables involved in H_2 obtainment in anaerobic reactors, such as temperature, initial pH, nutrient concentration and, mainly, the substrate used. Thus, the use of statistical tools becomes useful in establishing the optimal operating conditions for each fermentation process.The variation of a single factor at time is not fully representative, since this method does not allow the analysis of the influence between different factors [4,5]. The Central Rotational Composite Design (RCCD) provides a polynomial model that can be used to describe both the effect of each factor studied and the interaction between different factors in a response of interest[6], i.e H_2 production. Using the regression model, it is possible to obtain optimal operational conditions.

Since there is no consensus on the conditions to obtain biogas from these residues, such as inoculum concentration, substrate and pH, further studies are needed on these variables. The factorial design method is considered an efficient tool to evaluate optimal conditions in different processes [6]. In this scenario, the present study aimed at evaluating the significance of different variables, as well as the optimization of H_2 obtainment from Citrus Peel Waste (CPW).

II. MATERIAL AND METHODS

The CPW (Citrus sinensis L. Osbeck, var. Pera-Rio), a mixture of peel and bagasse, was collected and stored according to Calabrò et al. [1], at Laboratory of Biological Processes, University of São Paulo, campusSão Carlos. Pear oranges (Citrus sinensis L. Osbeck, var. Pera-Rio), fresh and ripe, were squeezed to remove juice and seeds, in order to obtain a residue similar to that produced in industrial plants. CPW was dehydrated in a drying oven at 50 °C for 24 hours, and ground in a knife mill (Wiley TE-650/1), to obtain particles ≤1mm. The autochthonous microbial consortium was obtained according to Haruta et al. [7] and Camargo et al. [8]. The allochthonous inoculum used was granulated sludge from an UASB reactor operated at 55 °C applied to the treatment of sugarcane vinasse, supplied by Usina São Martinho (Pradópolis, São Paulo, Brazil) and stored in plastic containers with a capacity of 30 L at 4 °C until use. The sludge underwent trituration using a household blender for 0.5 minutes for the destructuring of the granules. The reactors were submitted to N_2 atmosphere (100%) for 10 minutes, sealed with butyl cap and plastic screw, and incubated in an oven at 37 °C under static conditions. Headspace samples of 500 µL were collected for biogas composition analysis using gastight syringe equipped with latch.
The assays were performed to optimize the obtainment of H_2 from CPW by means of Rotational Central Composite Design (RCCD). Therefore, the influence of inoculum concentration (2.32-5.68 $gTVS.L^{-1}$), substrate (1.55-28.45 $g.L^{-1}$), and pH (4.32-7.68) was evaluated by a factorial design of 23, including 6 axial points and 3 repetitions at the central point, totaling 17 assays, which were

conducted in anaerobic batch reactors. Time to start H_2 production, maximum H_2 production rate and maximum H_2 production potential was determined by modified Gompertz model [9]. Kinetic parameters were calculated by Equation 1, via software OriginPro 9.0.

$$P_{ac} = P.\exp\{-\exp\left(\frac{Rm.e}{P}[\lambda - t] + 1\right)\} \quad (1)$$

where,
Pac= cumulative H_2 production ($mmol.L^{-1}$),
Rm= maximum H_2 production rate ($mmol.h^{-1}$),
e= Euler number (2.71828182),
λ= time to start the H_2 production (h^{-1}),
P= maximum H_2 production potential ($mmol.L^{-1}$).

III. RESULTS AND DISCUSSION

According to the conditions established for each assay, the maximum production of H_2 (P) ranged from 0.01 to 29.26 mmol $H_2.L^{-1}$, the velocity (Rm) ranged from 0.01 to 2.48 $mmol.h^{-1}$ and the time required to start the H_2 production (λ) ranged from 3.74 to 20 hours (Table 1). The central points presented a small variation, indicating a good repeatability of the process. The regression model obtained for P at the significance level of 10% relies only on the statistically significant terms ($p \leq 0.1$), being two linear terms (x_2 and x_3), a quadratic term (x_2^2) and an interaction ($x_2.x_3$), concerning the pH variable (x_2) and substrate concentration + pH (x_3) (Equation 2). The inoculum concentration variable (x1) was not considered significant (p=0.9972) within the 10% confidence interval (Figure 1).

$$Y_1 = 15.29 + 7.35x_2 - 1.97x_2^2 + 1.38x_3 + 4.70x_2x_3 \quad (2)$$

Where,
Y_1 = P, maximum predicted H_2 production;
x_2 = pH, linear effect;
x_2^2 = pH, quadratic effect;
x_3 = substrate concentration ($g.L^{-1}$), linear effect;
$x_2.x_3$ = interaction between x_2 and x_3.

Assay	x_1	x_2	x_3	Y_1
E1	3.0	7.0	4.5	7.44
E2	5.0	7.0	4.5	6.17
E3	3.0	23.0	4.5	11.24
E4	5.0	23.0	4.5	16.29
E5	3.0	7.0	7.5	2.35
E6	5.0	7.0	7.5	2.75
E7	3.0	23.0	7.5	27.39
E8	5.0	23.0	7.5	29.26
E9	2.3	15.0	6.0	15.66
E10	5.7	15.0	6.0	12.10
E11	4.0	1.5	6.0	0.01
E12	4.0	28.5	6.0	20.75
E13	4.0	15.0	3.5	14.90
E14	4.0	15.0	8.5	13.85
E15	4.0	15.0	6.0	19.69
E16	4.0	15.0	6.0	17.51
E17	4.0	15.0	6.0	15.69

Table 1: Results related to the accumulated hydrogen production for the variables studied in the RCCD. x_1= Inoculum concentration ($gTVS.L^{-1}$); x_2= Substrate concentration ($g.L^{-1}$); x_3= pH; Y_1= P; Y_2= Rm; Y_3= λ. H_2 production (P), maximum H_2 production rate (Rm), start time of H_2 production (λ) and R^2 obtained from the Gompertz equation.

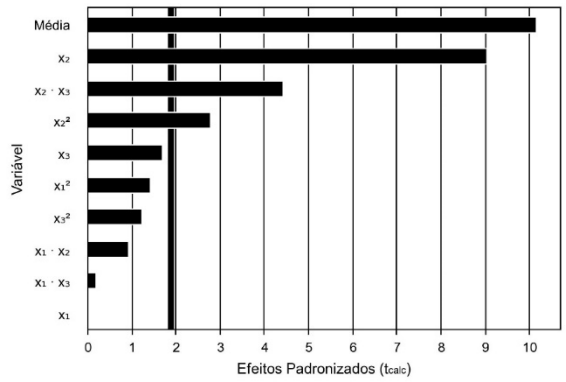

Figure 1: Pareto diagram- Significance for P response (90% confidence interval). x_1= Inoculum concentration ($gTVS.L^{-1}$); x_2= Substrate concentration ($g.L^{-1}$); x_3= pH; Y_1= P; Y_2= Rm; Y_3= λ. H_2 production (P), maximum H_2 production rate (Rm), start time of H_2 production (λ) and R^2 obtained from the Gompertz equation.

Since ANOVA analysis (Table 2) indicated that the regression model is significant (Figure 2), it was possible to obtain the surface response (Figure 1), where the conditions of 4 $g.L^{-1}$ of inoculum, initial pH of the reaction medium of 8.98 and 29.8 $g.L^{-1}$ of CPW as substrate were considered for the experimental validation as an optimal condition for biogas production (P). Based on the experimental validation assay, it is possible to state that H_2 production was optimized, since the obtained P value (48.47 $mmol.L^{-1}$) was 3.87 times higher than the P value obtained before its optimization (12.54 $mmol.L^{-1}$). The results obtained showed that the RCCD strategy used was effective in the optimization of H_2 obtainment from CPW.

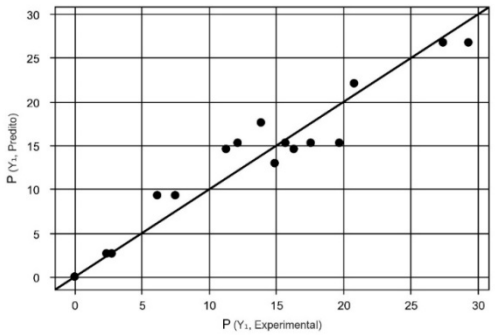

Figure 2: Experimental values and predicted values obtained for P response.

SV	SQ	DF	MQ	Calculated F	p-value
Regression	990.7	4	247.7	31.1	0.00
Residues	95.5	12	8.0		
Lack of fit	87.5	10	8.7	2.2	0.35
Pure error	8.0	2	4.0		
Total	1086.2	16	246.8	30.9	

Table 2: Statistical data (ANOVA) obtained after performing the RCCD assays, for the response P in 90% confidence interval. The R2 obtained was 91.21%.

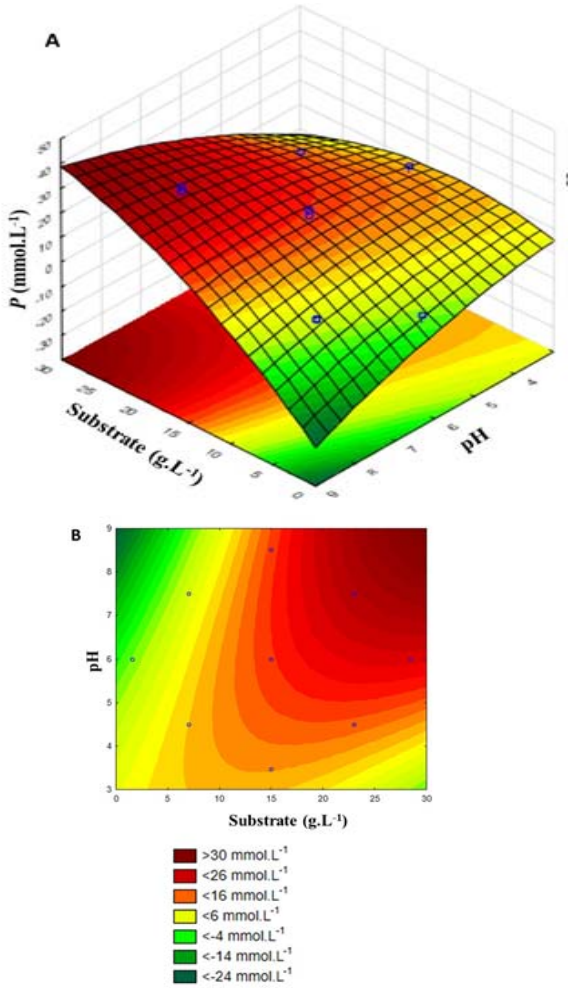

Figure 2: Response surface obtained for the interaction between substrate (g.L-1) and pH. P= H2 production potential.

CONCLUSION

The maximum H_2 production potential was optimized using the Rotational Central Composite Design (RCCD) statistical method, and the optimal conditions for the process were 4 $gSTV.L^{-1}$ of inoculum (granulated sludge from an UASB reactor operated at 55 °C applied to the treatment of sugarcane vinasse), 29.8 $g.L^{-1}$ of Citrus Peel Waste as substrate and initial pH of the reaction medium of 8.98. The maximum H_2 production potential (P) obtained (48.47 mmol $H_2.L^{-1}$) was 3.87 times higher than the P value obtained before its optimization (12.54 mmol $H_2.L^{-1}$).

ACKNOWLEDGEMENTS

This work was funded by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (processes 2017/01722-0 and 2015/06246-7) and was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

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