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A two-stage modelling and optimization of biohydrogen production from a mixture of agro-municipal waste

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A B S T R A C T

A two-stage modelling and optimization of biohydrogen production is reported. A mixture design was used to determine the optimum proportions of bean husk (BH), corn stalk (CS), and organic fraction of solid municipal waste (OFSMW). The optimum operational setpoints for substrate concentration, pH, temperature and hydraulic retention time (HRT) were further investigated using the box-behnken design. The quadratic polynomial model from the mixture design had a coefficient of determination (R^2) of 0.9427 and the optimized mixtures were in the ratio of OFSMW:BH:CS = 30:0:0 and OFSMW:BH:CS = 15:15:0 with yields of 56.47 ml H_2/g TVS and 41.16 ml H_2/g TVS respectively. Optimization on physicochemical process parameters on the improved substrate gave the setpoints of 40.45 g/l, 7.9, 30.29 °C, 86.28 h for substrate concentration, pH, temperature and HRT respectively having a predicted H_2 yield of 57.73 ml H_2/g TVS. Model validation gave 58.62 ml H_2/g TVS, thus an improvement of 3.8% on the optimized mixture. Biohydrogen production can be significantly enhanced by a suitable mixture of agro-municipal waste and operational optimal setpoints.

1. Introduction

The dependence on fossil fuels poses great challenges to both the climatic and environmental systems, thus prompts an urgent need for the development of non-polluting and renewable energy sources. Biohydrogen is an excellent alternative energy since its combustion produces only water. It has a high energy yield (122 kJ/g) which is 2.75 times greater than its equivalent of hydrocarbon fuels [1,2]. Its production via the fermentative route is more environmentally friendly, less energy intensive compared to the chemical hydrogen production methods [3]. Despite its many benefits, progress towards a biohydrogen economy has been hindered by a low yield on costly substrates.

Agricultural and organic municipal waste substrates are abundant, costless, renewable and can potentially be used as substrates for bioenergy production. An estimated annual yield of 118 × 10^9 tons of dry biomass is generated worldwide [4], the energy equivalent of 60–70 billion tons of crude oil. South Africa generated 59 million tons of general waste in 2011. The agricultural and municipal fractions were estimated at 2.95 and 7.88 million tons respectively, and only 35% of these, mainly of municipal types, were recycled [5]. The rest were burnt or disposed of in landfills. Biohydrogen production

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using these substrates will not only alleviate environmental hazards but also save the energy demands needed to treat them. This work investigates the optimum proportion of bean husk (BH), corn stalk (CS) and organic fraction of solid municipal waste (OFSMW) for biohydrogen production using a mixture design. Furthermore, the effects of input parameters of substrate concentration, pH, temperature and hydraulic retention time (HRT) on hydrogen response, using the mixed substrate, are modelled and optimized.

2. Materials and methods

2.1. Determination of optimum substrate composition using a mixture design

2.1.1. Mixture design and substrate pre-treatment

A mixture design was used to determine the optimum proportion of co-substrates of BH, CS and OFSMW for biohydrogen production. Fourteen different mixtures were generated with varying proportions of these substrates to a total concentration of 30 g/l (Table 1). The agricultural waste of BH and CS were collected from the Ukulinga Research Farm, University of KwaZulu-Natal, Pietermaritzburg, South Africa. They were dried at room temperature, reduced in particle size to 2.00–2.80 mm, and kept for further use. OFSMW was simulated according to Gomez et al. [6], and was made up of 10% apple, 10% orange, 35% cabbage, 35% potato, 8% bread, and 2% paper. The total volatile solids (TVS) content of experimental mixed crop residues was determined according to Equation (1).

$$\mathrm{TVS} = \frac{\text{Weight of dried waste} - \text{Weight of ash}}{\text{Weight of dried waste}} \times 100\% \quad (1)$$

2.1.2. Inoculum development

Hydrogen-producing mixed consortia used in the study was obtained from the anaerobic sludge collected from the Darvill waste water treatment plant, Pietermaritzburg, South Africa. Previous studies with this inoculum showed the presence of endospore forming clostridia (unpublished results). The sludge was heated at 100 °C for 30 min to deactivate the hydrogen consuming methanogenic bacteria, thus enabling the survival of hydrogen producing endospore forming bacteria.

Table 1 – Biohydrogen production from mixture design.

Batch	A: OFSMW (g/l)	B: bean husk (g/l)	C: corn stalk (g/l)	H_2 yield (ml/g TVS)
1	30	0	0	56.47
2	5	5	20	11.57
3	0	30	0	17.67
4	0	15	15	12.73
5	20	5	5	40.54
6	15	15	0	33.4
7	15	15	0	23.75
8	30	0	0	54.22
9	0	0	30	3.9
10	10	10	10	16.37
11	15	0	15	24.05
12	0	0	30	3.68
13	5	20	5	14.56
14	0	30	0	31.04

2.1.3. Fermentation process

The fermentation processes were carried out in parallel bioreactors of 250 ml modified Erlenmeyer flasks. Reactors were fed with co-substrates at concentrations as stated in the mixture design to a total value of 30 g/L, supplemented with inorganic salts (all in g/L): NH_4Cl 0.5, KH_2PO_4 0.25, K_2HPO_4 0.25, $MgCl_2.6H_2O$ 0.3, $FeCl_3$ 0.025, $ZnCl_2$ 0.0115, $CuCl_2$ 0.0105, $CaCl_2$ 0.005 and $MnCl_2$ 0.015. They were inoculated with 10 ml of pretreated sludge and made up to a working volume of 100 ml with distilled water. Anaerobiosis was created by flushing the reactors with nitrogen gas for 1 min. The initial pH was adjusted to 6.5. Fermentations were carried out in duplicate in a water bath shaker with operational setpoints of 60 rpm, 35 °C and 72 h for agitation, temperature and HRT respectively.

2.1.4. Analytical procedure

The evolving biogas volume was measured using the water displacement method [7]. This method is reliable and offers the possibility of being interfaced with a computer module. The hydrogen fraction of mixed biogas was determined using the hydrogen sensor BCP-H_2 (Bluesens, Germany) with a range of 0–100% and a measuring principle based on thermal conductivity detector. The cumulative volume of biohydrogen produced was computed regularly according to Equation (2).

$$V_{H,i} = V_{H,i-1} + C_{H,i}\left(V_{G,i} - V_{G,i-1}\right) + V_H\left(C_{H,i} - C_{H,i-1}\right) \quad (2)$$

$V_{H,i}$ and $V_{H,i-1}$ are cumulative hydrogen gas volumes at the current (i) and previous (i−1) time intervals, $V_{G,i}$ and $V_{G,i-1}$ the total biogas volumes in the current and previous time intervals, $C_{H,i}$ and $C_{H,i-1}$ the fraction of hydrogen gas in the headspace of the reactor in the current and previous time intervals, and V_H the total volume of headspace in the reactor [8].

2.1.5. Modelling and optimization of mixtures

The experimental data were used in multiple regression analysis to develop a quadratic model that relates hydrogen production to the proportions of BH, CS and OFSMW in the mixture, according to Equation (3).

$$Y = \alpha_0 + \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 + \alpha_{11} x_1^2 + \alpha_{22} x_2^2 + \alpha_{33} x_3^2 + \alpha_{12} x_1 x_2 + \alpha_{13} x_1 x_3 + \alpha_{23} x_2 x_3 \quad (3)$$

where Y is the hydrogen response, α_0 is the intercept, $\alpha_1 x_1$ to $\alpha_3 x_3$ represents the linear blending portion, $\alpha_{11} x_1^2$ to $\alpha_{33} x_3^2$ are quadratic coefficients and $\alpha_{12} x_1 x_2$ to $\alpha_{23} x_2 x_3$ are the interaction coefficients.

The significance of the model was assessed by the Analysis of Variance (ANOVA) using Design Expert software (Stat Ease, Inc, USA). The optimum proportion of the co-substrates in the mixture was obtained by solving the quadratic equation. The optimum substrate concentration and other physico-