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Maximization of hydrogen fermentative process from delignified *water hyacinth* using sodium chlorite

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ABSTRACT

This study investigated the direct supplementation of sodium chlorite ($NaClO_2$) in acidic fermentation process rather than using $NaClO_2$ as a pretreatment agent. This approach targets saving both of the cost of external acetic acid that needs to be added in pretreatment and the loss of polysaccharide, which simultaneously occurs during pretreatment process. Whereas, fermentation of water hyacinth (WH) provided quite low H_2 yield (HY) of 39.7 ± 2.5 mL/g_{TVS} and lignin destruction of 2.6 ± 0.2%. Cellulase and xylanase enzymes amounted to 2.15 ± 0.18 and 1.81 ± 0.14 U/mL, respectively. *Enterobacter and Clostridium* sp. accounted for 2.41 ± 0.15 × 10^5 and 4.02 ± 0.27 × 10^4 cfu/mL, respectively. However, $NaClO_2$ addition significantly augmented HY, cellulase and xylanase enzymes to 119.6 ± 7.8 mL/g_{TVS}, 3.46 ± 0.21 and 2.09 ± 0.23 U/mL at dosage of 8.0 mg/L, respectively. Moreover, cellulose, hemicellulose and lignin degradation efficiencies were maximized to 57.8 ± 3.1, 46.3 ± 3.8 and 31.6 ± 1.6%, respectively. *Enterobacter and Clostridium* sp. counts were 4.23 ± 0.28 × 10^5 and 9.75 ± 0.52 × 10^4 cfu/mL, respectively in the batches supplemented with $NaClO_2$. Nevertheless, at a dosage exceeding 8.0 mg/L, the HY (26.1 ± 2.0 mL/g_{TVS}) and bacterial count was highly deteriorated due to the excessive production of inhibitory phenolic compounds of 1.61 ± 0.12 g/L in the medium where the destruction of lignin was quite high (38.8 ± 2.4%).

1. Introduction

Water hyacinth (*Eichhornia Crassipes*) accumulation in Nile River reveals serious environmental issues, because of waterways clogging and air-water interface blocking, which in turn, deteriorates water quality and reduces dissolved oxygen content in water [1]. Fortunately, WH contains nutrients and biodegradable organics, which can be easily converted into bioenergy in term of hydrogen [2]. H_2 is considered as an ideal gas that can substitute fossil fuels due to its high energy potential (2.75-folds higher than hydrocarbon fuels) and producing water as a sole product from combustion [3,4]. Thermochemical processes are effective for H_2 production from lignocellulosic wastes, but a huge amount of energy is consumed for operation [5]. On contrast, biological hydrogen fermentative process is the most effective technology of low cost [6,7]. However, the main obstacle for fermentation process of lignocellulosic wastes is the presence of lignin fraction that needs to be eliminated in order to give a chance for harvesting higher H_2 potential [8,9].

The presence of lignin (3.5%) in WH creates a barrier for degradation of organic constituents, particularly cellulose (20%) and hemicellulose (48%) [10–12]. Previous studies examined lignin destruction using various pretreatment methods such as chemical and/or mechanical, microwave irradiation, steam explosion, hot water, ionic liquid and enzymatic pretreatment processes [13–16]. A comparison between different mechanisms used in previous studies for lignin elimination was stated at Table 1. Whereas, Feng et al. [17] showed that the maximum reducing sugar yield was achieved by microwave-assisted dilute H_2SO_4 pretreatment of WH and the H_2 yield was optimized using the subsequent dark fermentation step. Acid pre-treatment in combination with dark-fermentation process of WH achieved a maximum hydrogen yield (HY) of 127.6 mmol H_2/L [18]. A higher HY of 134.9 mL/g_{TVS} was obtained from pretreated WH using microwave-assisted dilute H_2SO_4 (1% v/v) at a temperature of 35 °C [19]. The lowest HY of 38.2 mmol H_2/L/d and 51.7 mL/g_{TVS} was registered from fermentation process of raw and alkali pretreatment of WH at a temperature of 45 °C [20,21]. However, all the aforementioned approaches depended on using highly consuming energy methods which make them economically uncompetitive [22].

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Table 1
Hydrogen yield harvested from WH using different mechanisms for lignin destruction.

Substrate	Lignin destruction mechanisms	H_2 yield (mL/g_{TVS})	Reference
Water hyacinth	Microwave-assisted dilute H_2SO_4 treatment and AC detoxification	134.9	[19]
Water hyacinth	Microwave coupled with dilute H_2SO_4 (1% v/v)	112.3	[1]
Water hyacinth	Microwave-heated alkali pretreatment	63.9	[41]
Water hyacinth	Adding 8 mg $NaClO_2$/L to the fermentation process	119.6 ± 7.8	This study

One of the most prevalent and well-established method for the lignin elimination from lignocellulosic biomass is acid-chlorite delignification using an aqueous solution of acetic acid and sodium chlorite at moderate temperatures [23]. Formerly, Hubbell and Ragauskas [24] performed a delignification process using the acetic acid with sodium chlorite at different lignin contents subjected to a reaction time of 6 h, at temperature of 70 °C. After pretreatment, lignin contents were reduced from of 1%, 5%, 10%, 15%, 20% and 30% to be 0.09%, 0.53%, 0.53%, 0.53%, 1.0% and 1.6%, respectively. In addition, Abdel-Fattah and Abdel-Naby [25] pretreated WH with 0.1% sodium chlorite ($NaClO_2$) for 1 h at 100 °C coupled with peracetic acid at 100 °C for 15 min. Such pretreatment exhibited recovered lignin, cellulose and hemicellulose of 2.56%, 96.69%, and 81.38%, respectively. Furthermore, delignification of sugarcane bagasse using sodium chlorite/acetic acid reduced its lignin content from 22.8 to 6.8% after 4 h [26]. Recently, Kim et al. [27] harvested ethanol yield of 0.266 g/g from coffee residue after enzymatic hydrolysis of pretreated coffee residue with sodium chlorite and acetic acid at 80 °C for 1 h with three times repetition. However, this process had a detrimental effect on cellulose degree of polymerization due to acid hydrolysis and/or oxidative cleavage of the cellulose chain. Acid-chlorite primarily acts on lignin in biomass, but it can also affect the polysaccharides. Whereas, when more lignin is removed, the polysaccharide fraction is partially degraded, possibly due to removal of lignin–carbohydrate complexes [28].

Therefore, the proposed method in this study is based on the exploiting sodium chlorite ($NaClO_2$) through its direct addition to the fermentation of WH without prior pretreatment process. Since, acetic acid is routinely produced via fermentation process, then reacts with $NaClO_2$ to produce chlorine dioxide (ClO_2), which is a strong delignifing agent [29]. In addition, Na^+ that is released into the fermentation media, enhances H_2 producing bacteria performance [30]. Using sodium chlorite in this manner will surely save acetic acid cost and will led to avoiding polysaccharides loss, whereas, their degradation will internally occur in the fermenter itself. However, chlorine dioxide (ClO_2) has a toxic effect on bacterial growth at low concentration [31], hence, the tested $NaClO_2$ concentrations have to be in small levels. Consequently, the aim of this research is to evaluate the effect of adding trace concentrations of sodium chlorite on H_2 harvested from WH. Moreover, addressing the influence of supplemented sodium chlorite onto substrate degradation, liberated phenolic compound, enzymatic activities, bacterial count and metabolic pathways are carried out. Finally, the study identifies the net gain energy and articulates an economic analysis for the proposed methodology.

2. Materials and methods

2.1. Substrate and H_2 producing bacteria

Water hyacinth (WH) plants were harvested from Al-Mahmudiyah Canal, Alexandria, Egypt. The collected samples were naturally dried using sunlight for a period of 7 days to simulate the existing situation.

Table 2
Characteristics of the pulverized water hyacinth (WH).

Parameters	Unit	Water hyacinth
Density	kg/m^3	365.6 ± 13.0
Total solids (TS)	g/kg	975.4 ± 10.5
Volatile solids (VS)	g/kg	730.8 ± 8.2
Cellulose	% TS	29.1 ± 1.4
Hemicellulose	% TS	31.8 ± 2.5
Lignin	% TS	5.2 ± 0.8
Carbohydrates[a]	g/L	0.58 ± 0.03
Protein	% TS	18.5 ± 2.1
Ash	% TS	12.7 ± 1.4

[a] Measured using solution of 1 g dried water hyacinth in 1 L distilled water.

The dried WH were crushed, crumbled (> 20-mesh size) and further dried at a temperature of 105 °C for 24 h. Afterwards, the samples were finally disintegrated using a strong crusher resulting an average size of 0.2 mm in order to be easily digested in fermentation process. The crushed WH was stored for later experiments. The characteristics of WH are presented in Table 2.

The seed sludge was harvested from the thickener tank of a full scale wastewater treatment plant situated in Alexandria city, Egypt. Seed sludge was allowed to be settled for 24 h for harvesting the desired active bacteria. The settled sludge was fed into the continuous stirred-tank reactor (CSTR) (5L) for acquiring well acclimatization and maximizing both of activity and bacterial growth. The reactor was daily fed with glucose concentration of 5.0 g/L and operated at an HRT of 2.0 h with temperature of 35 °C and pH value of 5.5 for two consecutive months in order to washout methanogens and enrich the H_2-producing bacteria (HPB) [32]. Average H_2 production rate (HPR) acquired from CSTR was 39.7 L/day. HPB were pre-heated at 70 °C for 30 min to ensure the complete inhibition of the bioactivity of hydrogen consumers. The characteristics of inoculum sludge were 5.5 ± 0.2 for pH, 0.93 ± 0.1 g/L as $CaCO_3$ for alkalinity, 30.6 ± 2.9 g/L for total solids (TS) and 25.3 ± 2.1 g/L for volatile solids (VS). In addition, *Enterobacter* and *Clostridium* sp. were amounted of $2.81 \pm 0.16 \times 10^3$ and $1.73 \pm 0.09 \times 10^4$ cfu/mL, respectively in the raw inoculum sludge used in this experiment.

2.2. Batch fermentation experiments

Batch experiments were conducted using 150 mL serum bottles with working volumes of 100 mL under anaerobic conditions. One liter of the nutrient stock solution was prepared using 500 g $NaHCO_3$, 250 g of K_2HPO_4, 100 g of $MgSO_4{\cdot}7H_2O$, 10 g of $CaCl_2{\cdot}2H_2O$, 2 g of $FeCl_3{\cdot}6H_2O$, 0.05 g of H_3BO_3, 0.05 g of $ZnSO_4$, 0.03 g of $CuSO_4{\cdot}5H_2O$, 0.5 g of $MnCl_2{\cdot}4H_2O$, 0.05 g of NH_4Cl, and 0.05 g of $NiSO_4$. Thirteen batch reactors were filled with 50 mL of HPB, 1 mL of nutrient stock solution, and 20 g/L WH. Sodium chlorite was supplemented to the batches with doses of 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 15.0 and 20.0 mg/L. The initial pH values inside all batch reactors were 6.0 ± 0.05. The headspaces of the batches were purged with N_2 gas for a period of 3 min. to remove the oxygen and sustain the anaerobic environment, and then bottles were capped with rubber stoppers and aluminum caps. The batches were incubated in a reciprocal shaker operating at 150 rpm and maintained at a temperature of 35 °C. All experimental tests were conducted in triplicate

2.3. Kinetic model

Cumulative hydrogen production was modeled using modified Gompertz equation as described earlier by Elsamadony et al. [33] to assess the effect of different dosages of $NaClO_2$ on the hydrogen potential and maximum hydrogen rate.