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Bio-H_2 conversion of wastewater via hybrid dark/photo fermentation reactor

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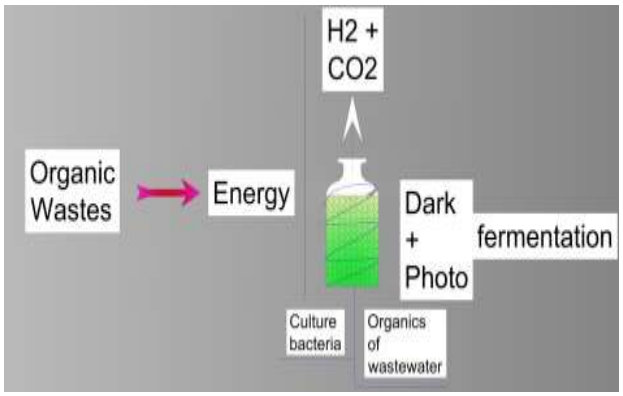
***Abstract*-Hydrogen energy is a clean source for liveliness better than fossil fuel that has hazardous effects on the environment and atmosphere. Food wastes and organics in the sewage sludge are a promising sustainable and renewable source for hydrogen production where amalgamation of waste treatment and energy production would be more than one benefit expressed in treatment of organic pollutants and energy generation. Discovering biohydrogen production from industrial wastewater by dark and photo fermentation was the main aim of this paper. The biogas produced was composed of H_2 and CO_2, and the maximum H_2 content was 25.94%. This ratio was achieved at batch configuration system and initial pH 6.2 with starch concentration 15 g/l. Cause of using dark fermentation effluent (DFE) was used as substrate for A *Rhodobacter capsulatus* strain and a clostridium culture were cultivated to produce hydrogen under different light-dark cycles. Acetic and butyric acids decreased due to first and second photo stages by 21.9% and 4.1 % respectively. Maximum hydrogen yield was 470.9 ml H_2/mol VFAs.**



KEYWORDS
Dark fermentation, photo fermentation, dark fermentation effluent and biohydrogen.

I. INTRODUCTION

Hydrogen is a new energy source that might be able to replace fossil fuels, more efficient and haven`t any environmental hazards. So, hydrogen is a promising fuel because it is clean, renewable and has a high energy density of 122 kJ/g. Organics in wastewater or other wastes that act viol problems became raw materials for biological H_2 production [1]. Hydrogen has a higher energy yield comparing to fusel fuel [2], [3]. From economic sideways, biological conversion of organics to hydrogen or including direct biophotolysis, photo & dark fermentation more economic than chemical and electrolysis due to complex operation requirement and production cost [4], [5]. The anaerobic fermentation process consists of three main stages for hydrogen production: hydrolysis, fermentation and acidogenesis. At the first phase, complex substrate rich in organic matters converted into more simple and monosaccharaides. This phase is considered the monitoring process for the consumption of the substrate and formation of hydrolysis end products. Then, these products which produced from hydrolysis phase are converted into volatile fatty acids (VFAs) such as acetic, propionic and butyric acids. Some of VFAs that formed are converted to H_2 and CO_2 in the last phase (acidogenesis). So, recycling of organics existing in wastewater for bio gas production, treatment of wastewater and birth of new sustainable source are considered an enormous movement in both environmental and energy fields. In addition, it is possible to produce H_2 from industrial wastewater according to type of organics in wastewater. Industrial wastewater containing residuals of wheat straws, beer lees, sugar beets, glucose, starch, fruits etc. Organic wastes rich in carbohydrates, lipids, protein and lignocellulose material [6]. Carbohydrate-rich substrate gifts higher hydrogen yields than other types.

As mentioned previously there are several methods for hydrogen production from sewage sludge, direct biophotolysis, indirect biophotolysis, dark fermentation and photo fermentation. Choosing suitable treatment method of organics for better revenue considered a vital matter. As Richa Kothari mentioned, indirect biophotolysis achieved higher rate production for hydrogen than direct biophotolysis by 507% [7]. While dark and photo fermentation achieved higher rates for hydrogen production than direct biophotolysis. Anaerobic treatment technology for the treatment of wastewater was developed by environmental engineers for over last two decades. *Clostridium sp.* has the ability to convert carbohydrates to CO_2, H_2 and VFAs [8], [3].

While *Rhodopseudomonas sp.* has the ability of converting residual VFAs to H_2. In this process, organic pollutants and wastes are finally converted into hydrogen through a sequence of chain reactions by distinct groups of anaerobic microorganisms [9]. Production of hydrogen

applying needs of industries such synthesis of ammonia, alcohols and aldehydes. In addition, hydrogen is preferred than other fuels as an energy source cause combustion production is only water. At this effort, this paper will discuss different effects of parameter`s values changing on hydrogen production.

II. MATERIALS AND METHODS

1-Substrate: Starch wastewater collected from starch manufacturing company situated in Tanta city, Egypt. Starch solution used as substrate and adapted in concentration 15 g/l for all reactors. Solution screened carefully and completely mixed.

2- Seed inoculum: The seed sludge was collected from sewage sludge from aeration tank of wastewater treatment plant (WWTP) located in Tanta, Egypt. After 2 months of anaerobic cultivation using starch as the substrate in a continuous stirred-tank reactor (CSTR) reactor, acclimated seed sludge was inoculated in batch reactor. Bottles filled up to 100 ml with 50 ml of pretreated sludge and 50 ml from substrate solution. Sludge was pretreated by heating at (90° C for 30 mins) to inhibit the activity of hydrogen consumers (methanogens) [10], [11]. pH of sewage sludge was controlled at 5.5±0.1 in the CSTR.

3-Experimental work: Experiment was performed in four bottles as batch system. Each reactor has a working volume 125 ml and was operated at a consistent temperature value 41± 1 °C. Light-emitting diode (LED) was used as a light source and surrounded bottles for photo fermentation creating light intensity 8600 Lux about (290 W/m^2). Cycles of dark and photo replicated twice during two days as follows:

First six hours were dark followed by photo state for eighteen hours then, the same cycle replicated again. Bottle no. 1 measured after expiration of first dark stage, bottle no. 2 measured after expiration of first photo stage, bottle no. 3 measured after second dark stage, and finally bottle no. 4 measured after second photo stage as shown in Fig. 1. Each reactor was sealed to assure anaerobic condition.

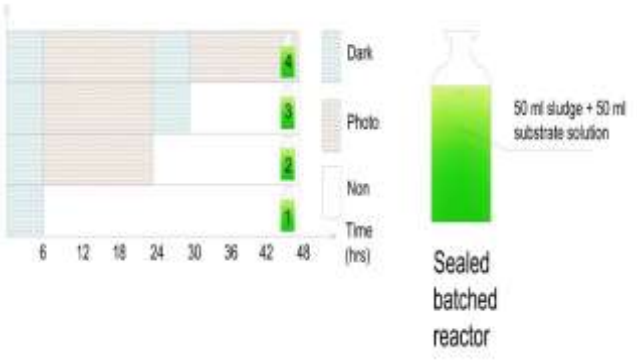


Fig.1: Durations of dark and photo cycles operated at batch system.

III. ANALYTICAL METHOD

Volatile suspended solids (VSS) were measured using filter paper of 0.45 µm pore size according to standard methods. The cumulative volume of biogas was calculated from the volumes of gases in the headspace of the bottles and the total volumes of both gases collected in the gas containers at each time.

Volatile fatty acids (VFAs) profile was monitored using high performance liquid chromatography [HPLC; UV detector; using Apollo C8 with 4.6 mm diameter × 150mm length and 5 µm As particle size; flow rate-0.8 ml/min; wavelength-210 nm; mobile phase-ethanol (40%) with distilled water (60%) at temperature 50 °C]. Samples were centrifuged (8,000 rpm for 10 min) and one drop from pure H_2SO_4 was added to the sample then mix filtered using syringe filter with size 0.22µm. Adding H2SO4 removes complex hydrocarbons and reactive pesticides that cause baseline.

Biogas was sampled after the pressure release using a gas-tight syringe and analyzed for H_2, CH_4, and CO_2 content using a gas chromatograph (HP6890, Agilent Technologies) equipped with a thermal conductivity detector (TCD) and a stainless steel column (121.9 _ 3.18 _ 2.16 mm) packed with HayeSep DB at 100/120 mesh (Alltech Associates, Inc.). Argon was used as the carrier gas at 30 mL/min and the temperatures of the injector, oven, and detector were 120, 100, and 120 _C, respectively. A biogas standard (Scott Specialty Gases, Plumsteadville, PA) composed of CH_4 (30 ± 2%, v/v), H_2 (30 ± 2%), and CO_2 (40 ± 2%) was used for calibration.

IV. RESULTS AND DISCUSSION

1-Effect of sludge pretreatment: After each cycle for all reactors, samples of biogas that produced were analyzed by gas chromatograph (GC) at lab in Tanta University. There was no any methane in the biogas detected by GC. That means destruction of methanogens by heating. Methanogens mainly consume hydrogen that produced in fermentation process.

2-Buffering pH behavior: It is apparent from Fig. 2 that the pH values of starch fermentation decreased with increasing time due to acetic or butyric acid production. Finally, it reached an almost constant value of 5.65 due to the same type of fermentation reaction. While the corresponding cumulative biogas increased with increasing time. Nonetheless decreasing in pH value doesn`t mean increasing in production of biogas with the same level of pH decreasing.

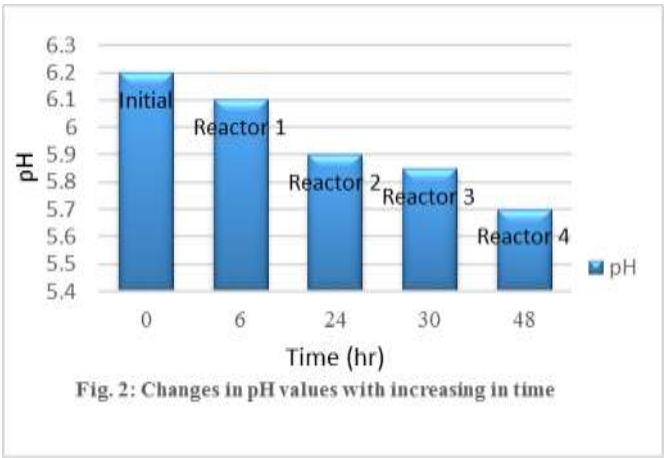


Fig. 2: Changes in pH values with increasing in time

3- H_2 production in start-up process: H_2 production increased rapidly as shown in Fig.3. Production in each stage is not regular cause of differ condition for each one. For instance, clostridium species has a different behavior in the pass way of hydrolysis. Hydrogenase is the main key catalyzes H_2 molecules. Also, heterotrophic bacteria have the ability to ferment sugars under anaerobic conditions to produce H_2, CH_4 gases and volatile fatty acids (VFAs). Dark fermentation has higher yield and production than photo fermentation, but it leave high concentrations from VFAs that can be used as a fuel source for Rhodopseudomonas sp. [12].

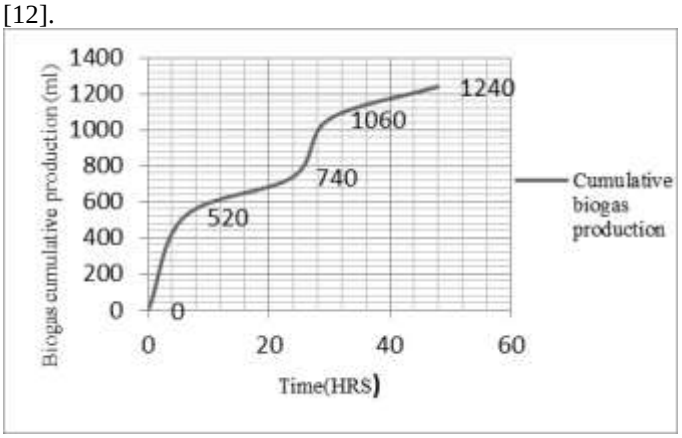


Fig.3: Cumulative biogas production during batch fermentation

Making light intensity in range 6000-10000 Lux (W/m^2) made reproduction of photo bacteria haste which made volatile suspended solids VSS varied than excepted as shown in Fig.4. Decreasing in VSS after dark fermentation stage was realistic according to consuming substrate by clostridium sp. Carbohydrates that existed in organics was finally converted to H_2 and CO_2. Biogas was analyzed by GC detector and H_2 content shown in table (1).

Table (1): pH, VSS, cumulative biogas, H2 content and carbon dioxide content results in each phase.

Parameter	pH	VSS (g/l)	Biogas production (ml/l)	H_2 %	CO_2 %
Initial	6.2	196	-	-	-
After first dark stage	6.1	190	520	25.08	37.06
After first photo stage	5.9	203	740	24.16	37.85
After second dark stage	5.85	184	1060	25.94	36.93
After second photo stage	5.7	196.6	1240	24.5	37.72

But VSS increased again due to growing up in bacterial count of Rhodobacter after 24 hrs. Then the same result replicated at the second recycle from 24 to 48 hrs. Sequencing between dark and photo fermentation reduce strict operation conditions for production of sustainable biogas whether CH_4, H_2 or both [13].

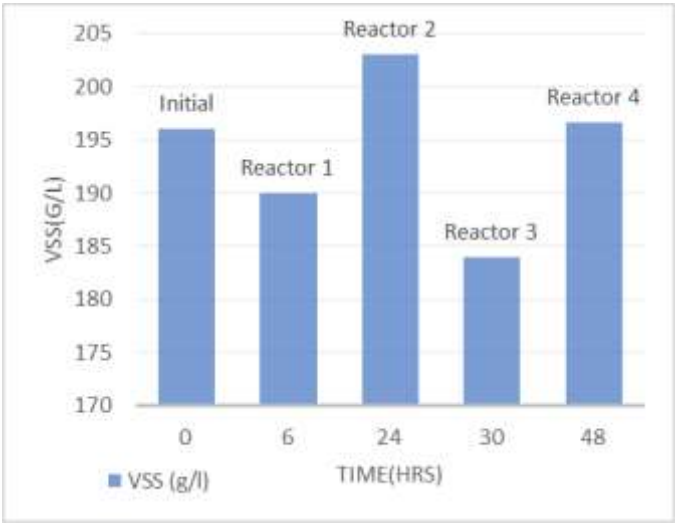
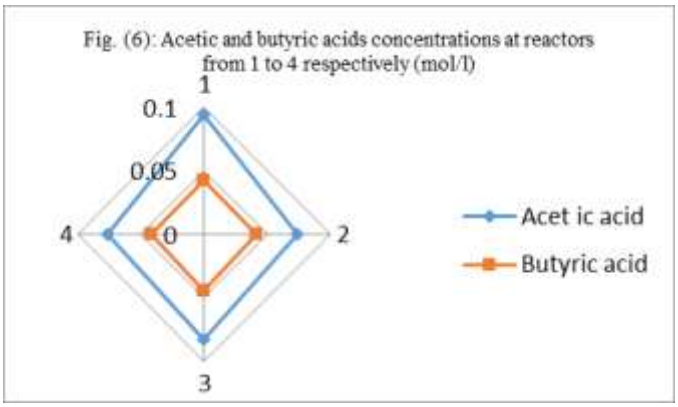


Fig.4: VSS values at each dark and photo stage

Converting of organic pollutants that existed in substrate was clear after treatment by digestion as shown in filter paper in Fig.5.

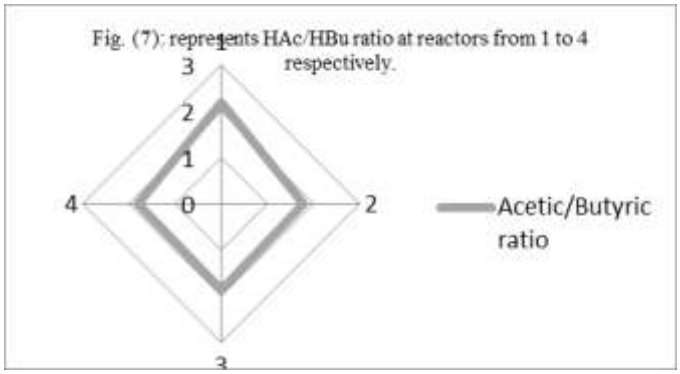
Fig.5: shows decreasing in organics in substrate after each fermentation cycle: 1)after first dark cycle, 2) after first photo cycle, 3)after second dark cycle and 4)after second photo cycle.



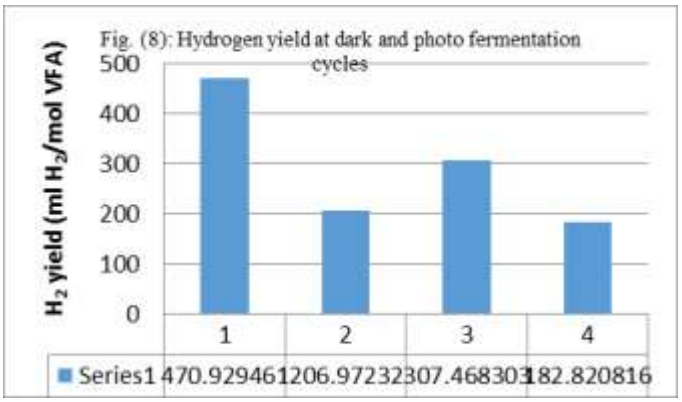
VFAs measuring give an important indication for metabolic pathway especially acetic acid/ butyric acid (HAc/HBu) ratio that expresses H_2 production. In general, accumulation of VFAs causes inhibition for H_2 production or let us to say it imbalance in the process not inhibition. VFAs reflect the balance between produced and consumed acids that express the performance of fermentation process as revealed in Fig. (7), (8). So, CSTR is favored for better performance. Propionic acid is one from inhibitor acids that should be in

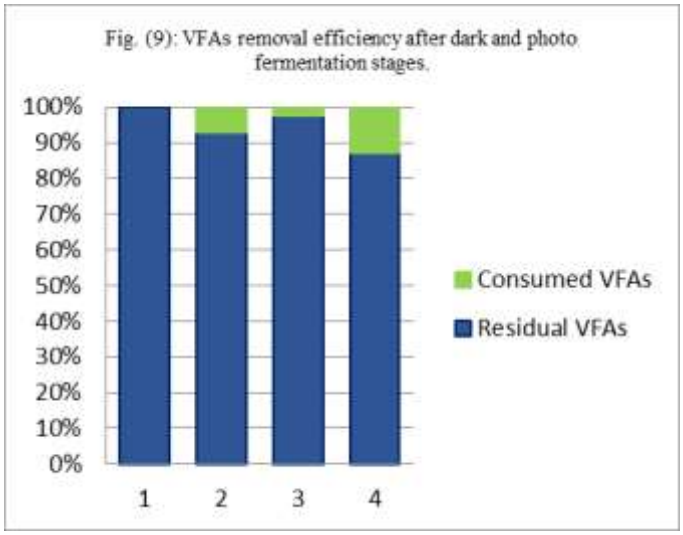
balance with acetic acid which main factor for H_2 production [14]. Also it has previously been reported that the butyric and propionic acids ratios are the best indicators of process instability. Furthermore, total concentration of volatile fatty acids should not exceed 2500 mg/l for efficient hydrogen production [12], [15].

4- VFAs removal: It is remarkable that concentration of



acetic acid decreases from 0.094 mol/l at first reactor to 0.073 mol/l at second reactor which means using photo fermentation combined with dark decreases or consumes VFAs that produced from dark fermentation (DF). Accumulation of VFAs was as a result of hydrolysis of substrate when H_2 yield was 470.9 ml H_2/mol VFAs. This value yield value was the maximum and remarkable in highest H_2 production in first dark fermentation stage (1). Subsequence, VFAs concentrations increased in the third reactor by 12.2 % due to second dark fermentation stage. To end with, reduction in VFAs concentration in the second photo fermentation stage at reactor (4) as shown in Fig. (6). Also Fig. (7) shows priority for dark fermentation for high H_2 production than photo fermentation. This result suggests that H_2 production depends not only on the initial VFAs coming from dark fermentation effluent (DFE) as shown in Fig. (8), but also on the remaining organic matter present in DFE. Nonetheless at last, photo fermentation is recommended for VFAs consumption and for conservation of hydrogen production in moderate rate till end of process.





V. CONCLUSION

It was demonstrated that sequential dark and photo fermentation was effective to maximize H_2 production from WW. pH controlling may act an important parameter which could improve H_2 content. Using heating as sludge pretreatment was active as resulted in methane content (0.00 %) by GC. High concentration of photo bacteria needs to be optimized by light intensity to inhibit increasing resulted VSS. Monitoring VFAs variation leads to:

1) No need for external pH strict control as acidification due to production of VFAs during dark-fermentation can be balanced by the utilization of VFAs (alkalization) in photo-fermentation.

2) Substrate toxicity and production inhibition can be minimized since the products of dark-fermentation are consumed in photo-fermentation soon they are produced.

3) By way of the process is carried out in single stage; time of fermentation process is reduced.

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