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Bio-hydrogen Production by Hydrolysis of Waste Active Sludge in Down Flow Packed Bed Reactor Using Photo-catalyst Nano-particles

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ABSTRACT

Biohydrogen was produced from biomass, two concentrations (2.5 and 5) % (v/v) of waste active sludge (WAS) were used in down flow packed bed reactor (DFPBR) by mesophilic mixed bacterial culture using different conditions included HRT (48, 24,12 and 8) h and pH between (5.5-7). Effects of advance oxidation (AOPs) on gas production by UV and TiO_2 in photo-reactor were studied. The results showed that the COD removal% of both WAS concentrations are coequal to (-0.898 and -3.58%) respectively in control pretreatment after 6 h, and the COD removal% in photo-reactor using TiO_2 photo-catalyst and UV light is equal to 70% and 40% respectively after 6 h. Also 5% of WAS was more efficient than 2.5% in gas production after using 4 M of HCl. HRT 8h and pH 5.5 were determined as the optimum condition for gas production; therefore, the H-volume and H_2/COD removal reached to 7.92 ml and 1.63 mL/gm L^{-1} respectively. These conditions were more efficient by UV light at 40 W in dark pretreatment that lead to reach H-volume to 22.5 ml and H_2/COD removal to 4.4mL/gm L^{-1} because of the ability of acidogenensis bacteria were tolerant this force of UV light, also the production by UV-Titanium nanoparticles was increased to 39.6 ml and H_2/COD removal reached to 10.8 mL/gm L^{-1} under the same optimum conditions.

Keywords: Biohydrogen, AOPs, Hydrolysis, WAS, Bioreactor, TiO_2 photo-catalysis.

1. INTRODUCTION

A Biofuel (biodiesel, bioethanol, and bio-methane etc.) is a fuel that is produced through contemporary biological processes, such as agriculture and anaerobic digestion, or that derived directly from plants, or indirectly from agricultural, commercial, domestic, and/or industrial wastes rather than a fuel produced by geological processes such as those involved in the formation of fossil fuels, such as coal and petroleum, from prehistoric biological matter [1]. Biohydrogen is considered as another form of biofuel. Biohydrogen is a type of biofuel which could be produced biologically from cultivation of the most commonly algae, bacteria and or from waste organic materials [2]. Bio-hydrogen has to be the alternative of petroleum fuel. It can be considered as a good potential future fuel in comparison with other biofuels because of the wide range of biomass that could be used as feedstock for its production, water that can only be produced during hydrogen consumption, finally biohydroden has the highest energy density compared with other fuels. Which, energy density of hydrogen (142 MJ/kg) is approximately three times that of gasoline (47 MJ/kg) or diesel (43 MJ/kg) [3]. According to the microorganisms used and the equipment involved, the biohydrogen produced can be divided based on dark fermentation, photo-fermentation, and electrochemical processes. Also the efficiency of the process is dependent on many factors such as type of microorganisms, temperature, PH, time and types of biomass used [4]. Another type of biomass is a Waste Active Sludge (WAS), it is the major biomass produced from the waste water treatment plane (settling tank),

and contains a complex organic material such as microbial flocks, and other polymeric in extracellular and intracellular substances. The cost of treating and disposing WAS was approximately 60% of operation cost of wastewater treatment plant [5]. WAS can be used as sources for biohydrogen production, because it is considered as a very important source of carbon and nitrogen to the microorganisms; therefore, it needs to be degraded before used to increase the efficiency of the process. Hydrolysis means the cleavage of chemical bonds by enzymes such as (proteases, glucosidases and lipases) and the addition of water molecules, especially in macromolecular components (proteins, polysaccharides and lipids). Therefore, the pretreatment methods as heat, acid, ultrasonic, microwave, advance oxidation (wet oxidation, ozonation, Ultraviolet (UV), and photo-catalysis) are used in the disintegration and solubilization of complex material into simple component and disrupt the cell walls of microbial flocks. These processes depend on the different factors like operating conditions, sludge composition and method of hydrolysis [6]. This pretreatment of the biocatalyst parent culture may be beneficial for shifting the metabolic pathways to increase acidogenesis, and inhibiting methanogenesis to improve the biohydrogen production yield with the prevention of competitive growth and coexistence of other biohydrogen consuming microorganisms [7]. UV-Photo-catalysis pretreatment can accelerate the anaerobic treatment of sludge, which finally increases biogas production, with low energy consumption. Advanced oxidation processes (AOPs), in a broad sense, are a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials in water and waste water by oxidation through reactions with hydroxyl radicals (·OH)[8]. AOPs has the potential to accelerate the hydrolysis of macromolecular components, such as (protein, fat, and lignin) by generating high reactive hydroxyl radicals (·OH and ·O). Heterogeneous photo-catalytic oxidation using TiO_2 is a promising alternative among AOPs for decomposing environmental contaminants, since it can be readily operated under ambient temperature and pressure and the possibility of using solar light as irradiation source [9]. TiO_2 has proven to be the most suitable photo-catalyst because of a high chemical stability, strong photo-catalytic activity, inexpensive and nontoxicity [10]. In additional, TiO_2 photo-catalysis has been widely used in wastewater treatment to decompose some recalcitrant contaminants such as methyl orange, rhodamine B, malachite green, and humic acids [11]. TiO_2 photo-catalysis seems to be a good pretreatment of WAS for enhancing its biodegradability by accelerating the hydrolysis of specific macromolecular components such as proteins [6]. Iraq uses unfavorable sources of fuel in gas turbine engines as a heavy fuel oil which is produced from refinery columns because of long years of suffering from the insufficient electricity production. The use of these fuels decreases the efficiency of gas turbine around 60-70%. But the use of biogas as a fuel of gas turbine increases the efficiency of engines, in addition, it can decrease the mass of pollutants produced from waste water treatment, and greenhouse gases. This study mainly focused on investigating the effected strategy to increase the biohydrogen production from effected microorganisms in WAS by loaded to DFPBR, and the effect of photo-catalysis (TiO_2) nano-particle as a photo-catalyst on the production.

Table 1: Characteristics of Raw, 2.5% and 5% (v/v) of WAS

Type	WAS (Raw)	WAS (2.5%)	WAS (5%)
VSS(g/L)	133	2.14	6.48
TSS(g/L)	265.8	4.3	13.29
COD(g/L)	32	0.44	1.52
Protein (g/L)	0.05	0.001	0.002
Ammonia (µmole/L)	25500	610	1300
Ash (g/L)	138	2.45	6.81

2. MATERIALS AND METHODS

About 5 liters of waste active sludge (WAS) sample was collected from a dry tank of Al-Rustumiah waste water treatment plant in south Baghdad / Iraq every week. The samples were stored in a refrigerator at 4°C. Its characteristics were analyzed before the experiments and are listed in (Table 1). Milk protein concentrate (MPC) obtained from Co. Cavan, Ireland. (Germany) was simulated as the protein of WAS, so that every gm of MPC85 contains 0.85 of milk protein. The TiO_2 photo-catalyst was provided by Cheng Du, LTD. China. Properties of the photo-catalyst are as follows: TiO_2 type Anatase, active surface area 60-80 m^2/gm with size 25nm), before using it as a photocatalyst, XRD test is used for ensuring its properties, then prepared as a solution by impregnation method by dissolving it with deionized water mixing it by ultrasonic probe (Q500 Sonictor, Qsonica-LTD, China).

2.1 Anaerobic Packed Bed Reactor

Two-cylinder packed bed reactor were constructed separately from plastic material and converted with thermostable teflon at each end off reactor, as show in fig. (2). Each reactor was with dimension (H = 60 cm, D_o = 8 cm, D_i= 7 cm), with total volume 2.3 L and working volume 1.25 L. It is filled with pours ceramic ball have a diameter 2 cm as a carrier material, the actual volume of liquid was about 1.25 L. The bottom of reactor had two points, first one which was divided into two parts, one for effluent exit and the other one for recycling to the reactor by peristaltic pump. The second point was for nitrogen gas flushing, and finally the top of reactor had one outlet for collection. The feeding and effluent pumped into two reactors by one intelligent flow peristaltic pump with pump head DG6-4(6 rolles-4 channels) with flow rate (0.00016-26 mL/min per channel) (Gold pump –China). The circulation of the reactor used two peristaltic pumps, the outlet gas from each bioreactor connects with trap column using as trapped for gasses, the outlet from trap column inters to washer gas column contain NaOH 0.2 M. The bubble gas outlet from washer column passes to measuring gas column. Finally, the reactor was surrounded by coil jacked and converted with aluminum paper protective layer.

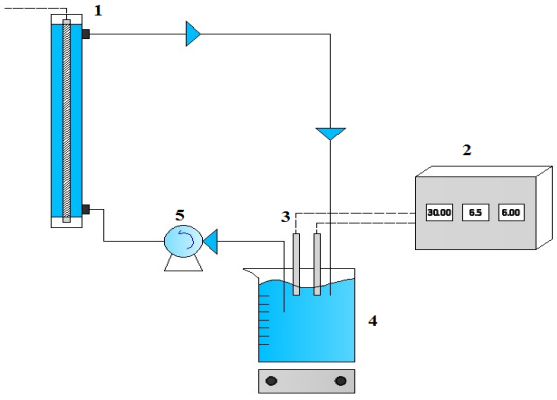

Figure 1: The Fluidized bed-photo-reactor
(1) Photo-reactor column, (2) control box, (3) temperature probe, (4) mixing tank, (5) stock pump

2.2 Anaerobic Production of Biohydrogen from Photo-catalysis Pretreated WAS using TiO_2

In order to accelerate the start-up process and achieve a stable hydrogen fermentation system, pretreatment of the seed sludge is required to enrich hydrogen-producing bacteria. Acidification, in comparison with other methods, is a simple, economic and effective pretreatment for enriching hydrogen-producing bacteria from WAS [15], [16]. To achieve that, the WAS was exposed to supply harsh conditions including (acidifying or heating) on solution. Firstly, hydrolyzed WAS from with no pre-treatment (control) with concentration (2.5 and 5) % (v/v) was added to fresh raw-WAS about 7.5% (v/v) as inoculum in tank and mixed with 4 M HCl solution for acidification. Secondly, the solution was stirred about 1-h then placed in the refrigerator at 4°C for 24 h. Finally, the hydrolyzed solution was completed to 1L of MSM and lactose with (1gm/L) as a carbon source then neutralized with 3M of sodium hydroxide (NaOH) [17].

2.3 Optimization for Bio-hydrogen production in DFPBR:

Firstly, Acidic treated WAS with two concentrations (2.5 and 5) % v/v was loaded into two DFPBR separately at the same time and condition, fig (2), to immobilize the WAS on packed materials along for 2 days to determine the optimum WAS concentration for biohydrogen producing. To evaluate the effect of HRT on biohydrogen production in DFPBR, different HRT including (48, 24, 12 and 8) h and different pH including (5.5-7) were conducted using WAS at concentration of 5%. Finally, the optimum condition of biohydrogen production was determined in DFPBR by using 5% WAS, which hydrolyzed by (UV and TiO_2+UV) at pH 5.5 and HRT 8 h along 44 days of operation as illustrated in table (3). In each operational condition of production COD, VSS, pH, hydrogen concentration and volume were measured.

2.4 Mineral Salt Medium (MSM) for Down Flow Packed Bed Reactor

This medium was prepared from the following components and contains (per liter of distilled water): Yeast Extract 0.5g, NH_4NO_3 0.1g, $CaCO_3$ 0.5g, $NaHPO_4.12H_2O$ 0.02g and $(NH_4)_2SO_4$ 0.002g [12].

2.5 Analytic Methods

Total Suspended Solid (TSS), Volatile Suspension Solid (VSS), Chemical Oxygen Demand (COD), and ammonia concentration (NH_4-N) in WAS and MPC were measured according to standard method [13]. Protein concentration was determined by the coomassie brilliant blue method with bovine serum albumin (BSA)

as standard method [14]. The pH value was measured using a pH meter (WTW Co., Germany, INOLAB 7110). Its soluble in WAS was defined as passing of liquid through a 0.45 µm glass microfiber filter. The filtrate was analyzed for COD and protein concentration. The gas composition H_2 was detected by a gas chromatography (GC-2014, SHIMADZU, Japan) using a machine equipped with TCD and molecular sieve column.

2.6 Photo-reactor

A lab scale fluidized bed photo-reactor was conducted for hydrolysis of WAS, where UV irradiate was used to energized Photo-catalysis. this photo-reactor contains 5-liter mixing tank, stock pump (12 liter/h) (Germany), UV reactor stainless steel cylinder 2.4 L with dimension (85cm×6.5 cm) fig.(1), irradiation of UV (40W, 254 nm) (Philips company).The Photo-reactor also contains temperature probe (China).

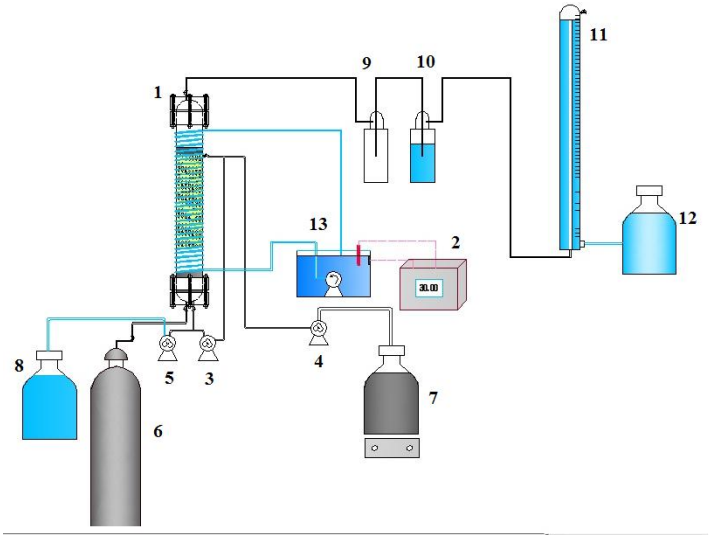

Figure 2: Anaerobic Down Flow Packed Bed Reactor
1: DFPBR, 2: Temp. Control Box, 3; 4; 5: Peristaltic Pump, 6: N_2 Gas Cylinder, 7: Feeding Tank, 8: Effluent Tank, 9: Trap Gas Column, 10: Washer Gas Column, 11: Measuring Gas Cylinder, 12: Storage Tank, 13: Water Bath

2.7 Hydrolysis WAS Simulated Protein by TiO_2 Photo-catalytic

To investigate the effect of TiO_2 photo-catalytic oxidation on the hydrolysis of macromolecular components of WAS, a series of semi-batch experiments were carried out using milk protein concentrate (MPC) as a protein model. MPC (1 gm-MPC85), diluted in 5L of distilled water was mixed for 1-h in the dark to achieve an adsorption/desorption equilibrium at pH=6.5, then loaded to photo-reactor. Then the UV lamp was switched on to initiate the photo-catalytic reaction. During irradiation, samples (5mL) were taken and filtrate every 1 h up to 6 h. The protein concentration was detected with a UV-vis spectrophotometer (UV1800, SHIMADZU, Japan) at 595 nm using coomassie brilliant blue method. Triplicate samples were conducted under the same condition, and the mean values were used for analyses. In order to optimize the operation parameters in this study, the photo-catalytic degradation of proteins MPC85 (0.85gm/L) at different TiO_2 dosage (0, 2.5, 5.0, and 7.5 mg L^{-1}) were studied in photo-reactor.

2.8 Photo-catalytic Pretreatment of WAS using (UV-TiO_2)

Due to the deep color and high-concentration of suspension solid (the characteristics in table (1) as raw WAS that may inhibit UV light transmission in the photo-catalytic pretreatment of WAS), it was diluted to (2.5, and 5) % (v/v) using distilled water before pretreatment. The characteristics of diluted WAS are shown in Table (1). The same suspension system was used as the experimental apparatus for TiO_2 photo-catalytic pretreatment of MPC and WAS.

Before irradiation, the suspension was magnetically stirred for 1 h in the dark for achieving equilibrium. Then the UV light irradiation with power lamp 40 W was conducted to initiate the photo-catalytic reaction. During the experiments, samples (5ml) were taken at a time interval of 2 h up to 6 h. The general characteristics of TiO_2 photo-catalysis pre-treated WAS were determined according to the standard methods.

3. RESULTS AND DISCUSSION

3.1 Protein degradation by UV Photolysis and TiO_2 Photo-catalysis

The degradation of protein was officiated under different conditions and the results are shown in table (2). With 1 h dark reaction, after 6 h UV irradiation, the result showed that the removal ratio of protein by TiO_2 photo-catalysis reached 57%, which was higher than those by UV photolysis (9%) or control (0). The results also indicated that TiO_2 photo-catalysis had improved

the non-enzymatic degradation of proteins. In the beginning, Proteins were hydrolyzed during the degradation to peptides and individual amino acids, which oxidative degraded to carboxylic acids and ammonia. Finally, Ammonia was converted to nitrite and nitrate [18]. This could be validated by the decreased pH level. Constant with zero concentration of ammonia in TiO_2 photo-catalysis. During 6 h UV irradiation, which agrees with [19] examining the effect of TiO_2 on dinitrogen photo-reduction to ammonia by nano-partical with 73 m^2 / gm and with UV with power lamp 160 W. While pH levels of the suspensions with TiO_2 photo-catalysis and UV photolysis continuously decreased from 5.3 to 5.8 and 6.51, respectively. Photo-catalytic oxidation changes the conformation of proteins and causes peptide hydrolysis [20].

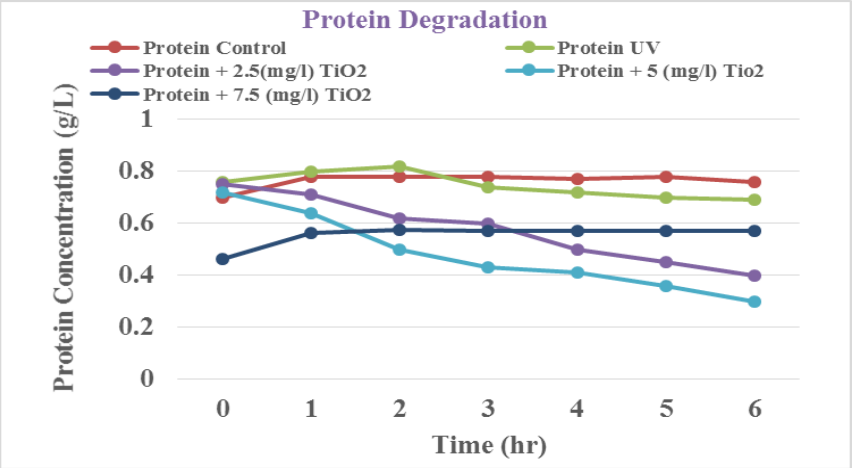

Figure 3: Photo-catalytic Degradation of Protein in Photo-catalysis reactor at different TiO_2 concentrations after 6 h of operation

3.2 Effect of TiO_2 Dosage on the Photo-catalytic Degradation of Protein

The photo-catalytic degradation efficiency of protein with various TiO_2 dosages is described in fig. (3)**.** Both the degradation ratio and apparent rate constant (*K*) increase up to a maximum value with increasing TiO_2 dosage, and then decrease as further increasing the dosage. As shown in fig. (3), increasing the TiO_2 dosage up to 5.0 mg L^{-1} obviously increases the protein degradation, where an increase in TiO_2 dosage would provide more available active sites on the photo-catalyst surface where proteins can be adsorbed. In addition, the increased amount of TiO_2 photo-catalyst produces more oxidative radicals under UV irradiation, which are sufficient and readily accessible for the degradation of nearby protein molecules. However, increasing the TiO_2 dosage from 5.0 to 7.5mg/L could be decreased the hydrolyzed of protein due to the reduction of active surface area available for protein adsorption and UV photons absorption caused by the agglomerating of TiO_2 nano-particles with high concentration. On the other hand, higher concentration of TiO_2 nano-particles lowered the passing intensity of UV light due to the scattering effect [21].

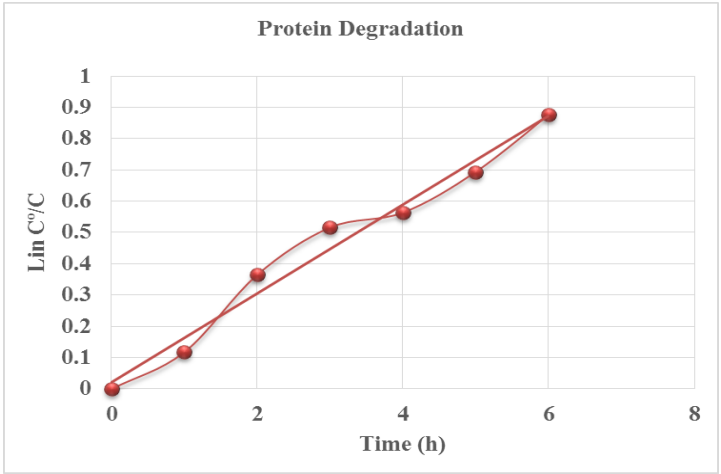

Figure 4: Equation of Protein Degradation

3.3 Modeling of photo-reactor

A semi-empirical model has been adopted for characterizing the performance of the heterogeneous photo-catalyst system for protein. The chapping of peptide bond that occurs by AOPs constitute free carboxylic acids and NH_3 in WAS, where reaction rate constant was calculated using reaction for each experiment according to pseudo-first-order model [22]. This model can be shown as follows

$$\mathbf{Ln}\left(\frac{\mathbf{Co}}{\mathbf{C}}\right) = \mathbf{K} * \mathbf{t}$$

Where:

$\mathbf{C_o}$: is the initial concentration of pollutants and protein, **C**: is the concentration at irradiation time **t** (t in min) and $\mathbf{K}$ is the pseudo-first-order rate constants in min^{-1}. $\mathbf{K}$ is dependent on $[TiO_2]$

A plot of $\mathbf{ln}(\frac{Co}{C})$ versus time for each experiment leads to a straight line whose slope is $\mathbf{K}$ as shown in fig. (4). The *K* value (8.426×10^{-3} min^{-1}) was achieved with 5.0 mg L^{-1} TiO_2 dosage.

The aim of this model is to evaluate the rate progress of protein degradation and organic material, which summarizes their efficiency. Predicted results are shown in fig (4). The predicted values are in a good agreement with the experimental results, and high intensity (40 W) of UV irradiation lamp, which leads to oxidizing ammonia to nitrite and nitrate by free radical agent ($OH\cdot$ and $O\cdot$). This sequence of reaction agreed with Lihuang *etal*. [23], who studied the effect of radical agent ($OH\cdot$) on ammonia concentration using TiO_2 p25 with UV irradiation 253 nm, and UV lamp intensity (20 w/m^2), and proved that ammonia converted to nitrate and nitrate in the final of experiment. Also the results were approximately similar to the work of Xingong *etal*. [24], who used TiO_2 p25 irradiated by UV lamp with power 450 w/m^2.

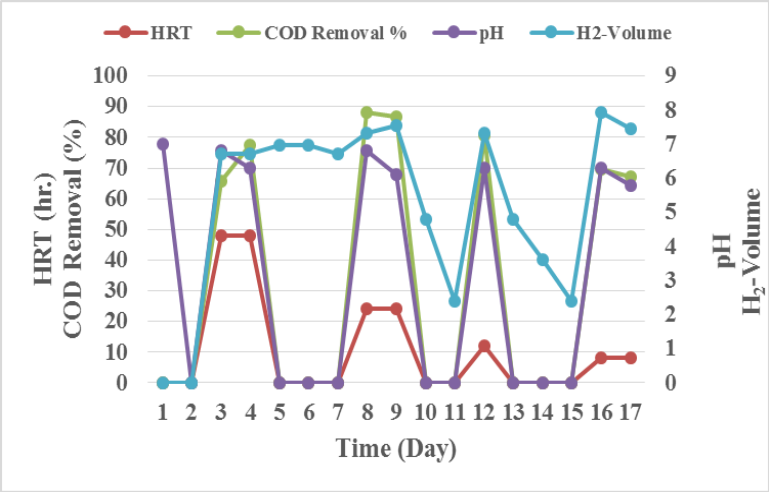

Figure 5: Relationship between HRT, pH with COD removal %, and H_2 volume Production in DFPBR using 5% (v/v) WAS

3.4 Optimization for Bio-hydrogen production in DFPBR

The hydrolyzed WAS (6.5) at concentration (2.5 and 5) % v/v were loaded in two-cylinder packed bed reactor separately, to determine the best concentration of WAS that produces biohydrogen from mixed culture. According to the results illustrated in fig. (5), the COD removal value and hydrogen production reached to 69.55% and 7.92 mL in HRT 8h and pH 5.8 respectively, while COD removal% value reached to 69.5%, compared with hydrogen volume reaching to 6.72 mL in batch operation at 48h and pH 6.8, COD removal% value equal to 77%, hydrogen volume 7.56 mL in semi-continuous operation at 24 h in pH 6.1 whereas COD removal% value 86%, hydrogen volume equal to 7.32 mL in semi-continuous operation at 12 h and pH 6.2, therefore the optimum HRT and pH for production biohydrogen from mixed culture were of 8 h. and 5.5 respectively comparison with concentration of 2.5%, that insufficient to produce biohydrogen gas due to low COD loaded in the DFPBR (Table 1). However, high hydrogen yield was obtained at initial pH range from pH 5.5 - 7.0. Based on this phenomenon, many studies have tried to enhance the hydrogen yield through fixing pH of a reactor at around pH 5.5 [25]. O-Thong with coworkers found that the initial pH of 5.5 was optimized for anaerobic microflora which gave a maximum hydrogen production of 4820 mL H_2/l-POME corresponding to hydrogen yield of 243 mL H_2/g-sugar. Changes in pH influence the metabolic activity of

bacteria producing H_2 and the fermentative process in general because pH affects the activity of the hydrogenase enzyme as well as the metabolic routes. The metabolic pathways for the production of H_2 cause a decrease in pH during the exponential growth phase of the bacteria, Rossi *et al*. [26] clearly indicates the acidogenic nature of microbiological activity. This drop in pH is important because the low pH helps in the reduction of methanogenesis.

The effect of HRT on hydrogen production that is shown in fig (5), hydrogen yield was found by increasing OLR with decreased in HRT. Hydrogenic activity also increased with the decrease of HRT [27]. HRT is considered an important factor in the selection of microorganisms because microorganisms are required with growth rates that can withstand the mechanical dilution caused by continuous volumetric circulation. An extended fermentation time was unfavorable for H_2 production because of the metabolic shift from acidogenesis to methanogenesis. Preferably, a shorter HRT would restrict the growth rate of methanogenic microorganisms. For satisfactory H_2 yields, the optimum HRTs were between 8 and 14 h for a wide variety of substrates [28]. By maintaining short HRTs (2–10 h), the methanogenesis was effectively suppressed [29].

3.5 Protein degradation in WAS by using UV-photolysis, and TiO_2 catalysis

The major obstacle in TiO_2 photo-catalytic pretreatment of WAS was the inhibited UV light transmission caused by its deep color and high-concentration suspension solid characteristics [15]. For that reason, dilution WAS (2.5, and 5) %(v/v) with TiO_2 dosage of 5mg/L, and UV irradiation lamp 40 W by a series of semi-batch experiments were used to give high efficiency of reaction in this study. The main characteristics of using (5%) v/v diluted WAS after 6-h pretreatment are listed in table (2). The ratio of COD removal % of WAS pretreated by TiO_2 in photo-catalysis, photolysis and control were equal to (0, 41 and 73) %, respectively. The results exhibited that photo-catalysis in comparison with other pretreatments evidently accelerate hydrolysis of WAS, as shown in decreased level of pH from 6.7 to 5.8 by TiO_2 photo-catalysis, while the decrease in photolysis and control were 6.3, and 6.4 respectively. This indicates that pretreatment of WAS by TiO_2 ameliorated hydrolyzed of macromolecular components such as proteins to carboxylic acids. On the other hand, photo-catalysis showed increased in ratio of soluble protein to 40% that shows the effect of photo-catalysis on the microorganism contained in WAS. This increased because collapsed in cell wall by free radical agent (·OH) that excepted with Angela and Cesar [30], when studied the effect of TiO_2 photo-catalyst with solar irradiation on *E.coli* K12, TiO_2 decrease the number of *E.coli* to 99% with decrease of pH 7-4 during 2 h of irradiation. While VSS decreased to become 91%. Generally, protein degradation of WAS pre-treated by photo-catalysis was converted to Ammonia which is the main product of protein degradation increased to the maximum concentration NH_3 in the end of experiment which accepted with [31]. In the end, pretreatment of WAS by using TiO_2 photo-catalytic would be accelerated by degradation it into smaller molecular weight hydrolysates, that would become more smoothly consumed by microorganisms in vassal anaerobic digestion.

Table 2: Degradation of MPC and WAS 5% (v/v) in photo-reactor.

Exp	Type	pH	COD_i gm/L	COD_o gm/L	COD rem. %	VSS_i gm/L	VSS_o gm/L	VSS remo. %	$Protein_i$ gm/L	$Protein_o$ gm/L	NH_{3i} µmole /L	NH_{3o} µmole /L	NH_3 increa. %
1	MPC- control	6.5	-	-	-	-	-	-	0.85	0.76	0	0	-
2	MPC-UV	5.8	-	-	-	-	-	-	0.85	0.69	0	60	-
3	MPC-TiO_2+UV(2.5 mg/l)	5.8	-	-	-	-	-	-	0.85	0.4	0	0	-
4	MPC-TiO_2+UV (5mg/l)	5.3	-	-	-	-	-	-	0.85	0.31	0	0	-
5	MPC-TiO_2+UV (7.5mg/l)	6.3	-	-	-	-	-	-	0.85	0.57	0	0	-
6	WAS-Control	6.4	1.52	1.8	0	6.48	4.2	35%	0..002	0.072	1300	1360	4.6%
7	WAS-UV	6.3	7.57	4.36	41%	3.47	3.35	3.5%	0.13	0.08	1310	1430	9.1%
8	WAS-TiO_2+UV	5.8	4.42	1.18	73%	8.2	0.67	91%	0.092	0.129	1250	1430	14.4%

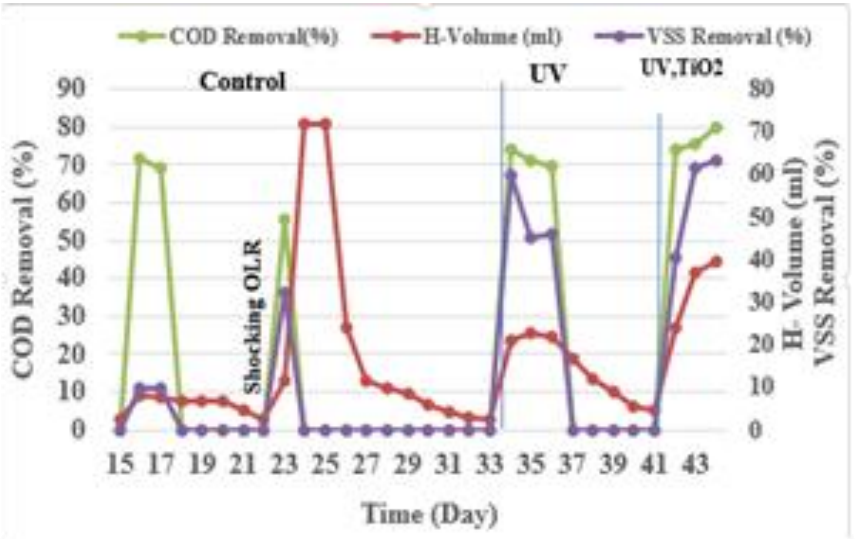

Figure 6: Relationship between Pretreatments of WAS and COD, VSS Removal (%) and Bio-hydrogen Production.

Effect of using (UV+TiO_2) photo-catalyst on Biohydrogen production in DFPBR

The effect of WAS with a concentration (5%) v/v by using TiO_2 photo-catalysis for biohydrogen production was conducted in DFPBR in a continuous operation during 72 h in the optimum condition of HRT(8 h), and optimum pH (5.5) in mesophilic condition ranged (30±2). The results in the fig. (6) display that photo-catalysis pretreatment of WAS showed higher rate of biohydrogen production reaching to 39.6 mL of H_2/day in comparison with photolysis and control pretreatment were decreased biohydrogen volume to 22.5, and 7.9 mL H_2/day, respectively.

On the other hand, higher COD removal efficiency was observed with TiO_2 photo-catalyst reached 80% in comparison with 71% and 69% for photolysis and control respectively fig (6), and (7). While, higher VSS removal efficiency (63%) was achieved with pretreatment of WAS by photo-catalysis, in comparison to lower removal efficiency with photolysis, and control reached to 45%, and 9.7% respectably. However, hydrogen production rate HPR which referred to the activity of microorganism to produced biohydrogen (H_2/COD day) was higher in photo-catalysis pretreatment (10.8 H_2/COD removed day) compared with photolysis and control 4 and1.57 respectably. Accordingly, the biohydrogen production as (H_2/VSS removed. day) value were 31.18, 10.32, and 12 (H_2/VSS Day) respectively. Finally, from the result obtained, TiO_2 photo-catalysis of WAS would increase the biohydrogen volume by degradation the micro-molecule of WAS into simpler molecule for that the microorganisms in DFPBR could consume the organic material faster than that of WAS pretreated with photolysis and control. For that reason, using of photo-catalyst pretreatment of WAS will be beneficial to the increase of the biohydrogen production. In addition, the effect of organic loading rate (OLR) shock and starvation strategies on biohydrogen production in DFPBR was tested. The result in fig (6) shows that exposing of microorganisms to OLR shock led to maximum production of biohydrogen volume (11.64 mL/day) when COD_i concentration supplanted with 3 g/l of lactose at day 23 of operation, in which the COD_i in the reactor raised to 14 gm/L. But the maximum of biohydrogen produced in the sample taken after 24 h of the end operation with (72 mL) the result illustrated in (table 3).

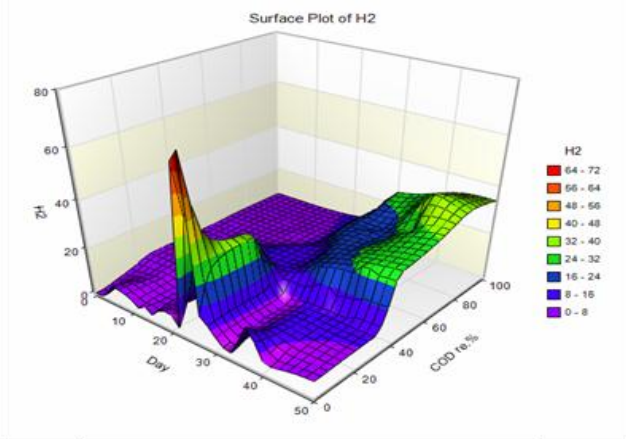

Figure (7): COD Removal (%) of Three Pretreatment Methods

Table 3: DFPBR Operation Stages

Exp. No.	Type	HRT h	pH	COD_i gm/L	COD_o gm/L	COD Re%	VSS_i gm/L	VSS_o gm/L	VSS Re.%	H%	H-vol. mL	H_2/COD mL/gm/L	H_2/VSS mL/gm/L
1	*1 Imm	IMM	7	4.04	-	-	9.43	-	-	0	0	-	-
2	*1 Imm	IMM	-	-	-	-	-	-	-	0	0	-	-
3	Control	48	6.8	2.24	1.44	35.7	4.2	0.63	85	0.56	6.72	8.4	1.88
4	Control	48	6.3	2.66	1.22	54.1	5.39	8.48	-57.33	0.56	6.72	4.66	-2.17
8	Control	24	6.8	6.57	1.25	81	10.47	4.25	59.40	0.61	7.32	1.37	1.17
9	Control	24	6.1	6.57	1.4	78.7	10.47	5.46	47.85	0.63	7.56	1.46	1.5
12	Control	12	6.3	6.54	1.6	75.5	8.27	4.7	43.17	0.61	7.32	1.48	2.05
16	Control	8	6.1	6.79	1.94	71.4	6.37	5.75	9.761	0.66	7.92	1.63	12.73
17	Control	8	5.8	6.81	2.1	69.1	6.37	5.75	9.733	0.62	7.44	1.57	12
23	*2Control	8(3gm lactose)	5.5	14	6.23	55.5	6.54	4.43	32.26	0.97	11.64	1.49	5.51
34	UV pre.	8 UV pre	5.5	7.14	1.84	74	8.07	3.23	59.97	1.4	21	3.9	4.33
35	UV pre.	8 UV pre	5.5	8.45	2.42	71	4.84	2.66	45.04	1.5	22.5	4.4	10.32
36	UV pre.	8 UV pre	5.5	7.76	2.34	69.8	4.39	2.37	46.01	1.45	21.75	4.9	10.76
42	TiO_2 pre.	8 TiO_2 pre	5.5	6.81	1.77	74	3.14	1.87	40.44	1.2	24	4.7	10
43	TiO_2 pre.	8 TiO_2	5.5	4.88	1.44	75.4	3.42	1.32	61.40	1.68	36.96	10	17.6
44	TiO_2 pre.	8 TiO_2	5.5	4.9	1.26	80	3.79	1.39	63.32	1.8	39.6	10.1	31.18

*1 Immobilization

*2 Increasing concentration of lactose from 1 to 3 gm/L to shown the effect of shocking OLR strategy.

*3 No feed (circulation only) shown the effect of starvation strategy.

*4 Exp. No. (5, 6, 7, 10, 11, 13, 14, 15, 18, 19, 20, 21, 22, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 37, 38, 39, 40 and 41) represented with o feeding and the H-Volume (mL) of each one equal to (6.96, 6.96, 6.727, 4.8, 2.4, 4.8, 3.6, 2.4, 6.96, 6.72, 6.72, 4.8, 2.4, 72, 72, 24, 11.4, 9.6, 8.4, 6,4.2, 3, 2.4, 16.5, 12, 9, 5.25 and 4.5) respectively

4. CONCLUSION

The objective of the current study was to investigate the strategies to increase bio-hydrogen production in DFPBR from WAS, which included selected carbon source (lactose), decreasing HRT with increasing OLR, shocking OLR, starvation microorganism by cutoff feeding after 24-72 h of dosage, and hydrolysis of macro-material (protein) in WAS by using TiO_2 photo-catalysis. Optimal conditions for photo-catalytic degradation of proteins were observed at TiO_2 dosage of 5.0 mg L^{-1} under 40 w m^{-2} UV light irradiation. Optimum conditions of biohydrogen production in DFPBR were observed at WAS (5) %(v/v), HRT 8 h, pH=5.5 and TiO_2 (5mg/L). Finally, exposing of microorganism to OLR shuck increased the biohydrogen production in DFPBR. Another forthcoming study by the researcher about the identification of microorganism in photo-reactor and DFPBR. Which help to identify the micro-organism that selected by these strategies.

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