Photocatalytic pretreatment for the redox conversion of waste activated sludge to enhance biohydrogen production

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Abstract

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Photocatalytic pretreatment of waste activated sludge (WAS) using a flat photocatalytic reactor was undertaken. Photocatalytic pretreatment enhanced the release of soluble substances from WAS, in which the soluble protein and soluble carbohydrate concentration increased by about 50% and 80%, respectively. Significant removal of heavy metal ions from the liquid phase of WAS was also achieved after photocatalytic pretreatment. In addition, the highest hydrogen yield and the highest concentration of volatile fatty acids (VFAs) were achieved from the photocatalysis pretreated WAS by batch anaerobic digestion (55 ℃). The cumulative hydrogen yield from photocatalysis pretreated WAS was 211.0 ml/l-sludge, much higher than those from UV pretreated WAS (111.0 ml/l-sludge) and from raw WAS (93.0 ml/l-sludge). The results indicate that photocatalysis is a promising WAS pretreatment method for the enhancement of biohydrogen production, probably due to the photo-oxidation of organics and simultaneous photo-reduction of heavy metal ions in WAS.

Keywords: Waste activated sludge; Photocatalytic pretreatment; Redox conversion; Anaerobic hydrogen production; Heavy metals

1. Introduction

Hydrogen is a promising alternative energy that produces high energy without greenhouse gases during the combustion process [1]. Hydrogen can be produced by both chemical and biological methods. Chemically, hydrogen can be produced by electrolysis and photocatalytic water splitting [2]. The latter is more energy-efficient than the former. Biologically, hydrogen can be generated by both photo-fermentation and dark fermentation [3] with the latter being more effective under present conditions. Some attempts have been tried to test hydrogen

production from easily biodegradable organics rich in glucose and sucrose [4, 5]. Recently, hydrogen production has also been explored on the wastes containing refractory materials such as cornstalk and waste activated sludge (WAS) [6, 7].

As for WAS, however, hydrolysis is the rate-limiting step in anaerobic digestion and its digestion inefficiency resulted from long hydraulic retention time (HRT) can be overcome under the condition of effective disintegration of microbial cells and hydrolysis of extracellular polymeric substances (EPS) in WAS [8]. Moreover, heavy metal ions (Cr, Pb, Cu, Zn, Ni and Cd) at concentrations above critical values in WAS will be toxic to microorganisms (hydrogenogens and methanogens) in anaerobic digestion process and to the natural ecosystem after being discharged into the environment [9]. Furthermore, the WAS can be easily converted to an agricultural fertilizer, if the heavy metal ions are removed or reduced to a non-toxic state by pretreatment. In order to improve the hydrolysis process as well as increase hydrogen yield, remove heavy metal ions and shorten the retention time, various pretreatment methods have been tested including alkaline pretreatment [10], acidification [11], ultrasonic treatment [12], microwave irradiation [13], enzyme [14], photocatalytic pretreatment [15, 16] and thermal hydrolysis [17-19]. However, it should be mentioned that all of the above methods increase the cost of sludge treatment when energy consumption and environmental benefits being taken into consideration. Photocatalysis, as an energy-saving and environment-friendly method, has been tested and used on wastewater treatment. The catalyst (TiO_2) can generate reducing conduction band electrons (e_{cb}^-) and oxidizing valence band holes (h_{vb}^+) in sufficient quantity with UV-light irradiation. However, few reports can be found on the photocatalytic method as a promising pretreatment to improve hydrogen production from WAS via anaerobic digestion [16].

The objective of this research is to evaluate the effect of photocatalytic pretreatment on biohydrogen production from WAS and the photo-reduction capacity for heavy metal ions in

WAS. For this purpose, the compositions of WAS and metabolites after anaerobic digestion were determined. In addition, the concentrations of soluble carbohydrate, protein and heavy metal ions (Cu, Zn, Cr, Ni, Pb, Cd) were also analyzed to disclose the changes of photo-oxidation capacity for organics and photo-reduction capacity for heavy metal ions in WAS after pretreatment.

2. Materials and Methods

2.1. WAS, digested sludge and catalyst

The WAS and digested sludge were collected from a sewage treatment plant in Shimodate, Ibaraki, Japan, then kept at 4°C. The characteristics of the WAS were shown in Table 1.The ratio (66.90%) of volatile solids (VS)/total solids (TS) indicates that the main components of the sludge were organic substances. The low ratio (9.60%) of soluble chemical oxygen demand (SCOD)/total chemical oxygen demand (TCOD) demonstrates that most COD is insoluble. Digested sludge was used as seeding sludge in the thermophilic anaerobic hydrogen fermentation experiment. The pH, TS, VS, TCOD and SCOD of the digested sludge were 7.1, 10.7 g/l, 7.3 g/l, 19.7 g/l and 0.5 g/l, respectively. Before used as seed inoculums, the digested sludge was heat-treated in a hot air oven at 120 ℃ for 30 minutes to inhibit methanogen [16]. The catalyst used in this study was a Degussa P-25 TiO_2 slurry (Degussa AG, Germany).

2.2. Pretreatment experiments

Photocatalysis was used as sludge pretreatment method in this study. As reported in our

previous study [16], the optimal pretreatment conditions were obtained as TiO_2 dosage of 3 g/l, circulating speed of 350 ml/min, UV-light intensity of 1.5 mW/cm^2, and duration of 6 h respectively in a circulating bed photocatalytic reactor. In this study, 180 ml raw WAS and 3 g/l TiO_2 were mixed completely, and then treated in a circulating bed photocatalytic reactor. In order to test the effect of photocatalysis with TiO_2 addition on WAS, UV-light pretreatment experiment (without TiO_2) was also conducted under the identical conditions.

2.3. Batch anaerobic digestion for bio-hydrogen production

The experiment of bio-hydrogen production from WAS was conducted in 30 ml serum bottles with a working volume of 25 ml containing 18% (v/v) of inoculum. The batch experiments were performed in duplicate under 55℃ for 5 days, using photocatalysis pretreated WAS, UV-light pretreated WAS and raw WAS (control) as substrate, respectively. The initial pH of the substrate was adjusted to 5.7 with 1 mol/l hydrochloric acid (HCl). The serum bottles were closed with rubber stoppers and caps. After replacement of the headspace with nitrogen to create anaerobic condition, the serum bottles were put into a temperature-controlled water-bath (55 ℃). The biogas production was measured every 12 h by water displacement method. The volatile fatty acids (VFAs) concentrations was determined every 12 h by HPLC. The fermentation medium was sampled at the initial and end of the hydrogen fermentation process for the measurement of pH, TS, VS, TCOD, SCOD, ammonia nitrogen, soluble protein, and soluble carbohydrate concentrations.

2.4. Analytical methods

COD, TS, and VS were detected in accordance with standard methods [22], and pH was

determined by a digital pH meter (Metter-Toledo Group). Liquid sample was centrifuged at 10,000 rpm for 10 minutes and the supernatant was used to determine SCOD, carbohydrate and protein concentrations. The concentration of ammonium nitrogen was determined by an Ion meter (Ti 9001, Toyo Chemical Laboratories Co., Ltd.). Phenol sulfuric method [23] with glucose as standard was used to determine carbohydrate concentration. Lowry method [24] with bovine serum albumin as standard was used to measure soluble protein. The concentrations of heavy metal ions (Cd, Zn, Pb, Gr, Cu, Ni) were analyzed by inductively coupled plasma mass spectrometry (ICP-MS: 2000 spectrometer Jobin-Yvon, Longjumeau, France). The liquid samples were centrifuged at 10,000 rpm for 10 minutes, and filtered through a 0.22 μm diameter filtration membrane before injection to ICP-MS. Biogas compositions including hydrogen, methane and carbon dioxide were determined by gas chromatography **(**GC-8A, SHIMAZU, JAPAN). VFAs including acetic (Ac), propionic (Pr), butyric (Bu) and Valeric (Va) acids were measured by a high performance liquid chromatography (HPLC, EcomLCP4100 Pump, LCD 2083 Detector, ECOM, Czech Rep.) with an ultraviolet (210 nm) detector (UV1000, Thermo Electron) and a Fast Acid Analysis column (Bio-Rad Lab.) using 0.005 M sulfuric acid as mobile phase at 1 ml/min. The liquid samples were centrifuged at 10,000 rpm for 10 minutes, and filtered through 0.45 mm cellulose acetate membrane before injection to HPLC.

3. Results and discussion

3.1. Effect of photocatalytic pretreatment on WAS

As shown in Table 1, after photocatalytic pretreatment, the concentration of SCOD increased from 1752 to 3620 mg/l, and the soluble protein and carbohydrate concentrations

also increased approximately by 50% and 80%, respectively compared with the raw WAS. In addition, the decrease of TCOD and the increase of SCOD confirm the disruption of the floc structure of WAS and the release of extracellular and intracellular biopolymers from activated sludge flocs into the soluble phase [25, 26]. The large increase of soluble protein and carbohydrate concentration can be attributed to the release of extracellular polymeric substance (EPS) and cellular substances into the aqueous phase after photocatalytic pretreatment [27]. The increase of NH_4^+-N concentration in photocatalysis pretreated WAS was probably contributed by the degradation of some nitrogenous organics such as proteins and nucleic acid [12], which leaded to the pH increase of WAS after pretreatment. The results also indicate that UV-light had much less contribution to the disintegration of WAS and the release of soluble organics which was mainly brought about by the photocatalytic pretreatment. Restated, the changes of organics in WAS are owing to the oxidization of TiO_2 photocatalysis. When the refractory organics in WAS capture the valence band hole (h^+), they will be oxidized and release small molecule organics. Therefore, photocatalytic pretreatment can enhance the solubilization of sludge and eventually improve the bio-degradability of WAS [16, 28].

3.2 Effect of photocatalytic pretreatment on the removal of heavy metal ions

Oxidation by photo-generated holes takes place concurrently with reduction by the photo-generated electrons in a heterogeneous photocatalytic process [9]. In the photocatalysis process of WAS, the organic pollutants in WAS can capture the valence band hole and be oxidized, and heavy metal ions in WAS may trap the conduction band electrons and then be reduced.

The concentration changes in six heavy metal ions in the liquid phase of WAS are shown in Fig.1. The results indicate that the removal rate is different with respect to different metal

ions. Cr (VI) can be removed with the highest rate of 97.0%; the reason is probably that Cr (VI) was first photo-reduced to Cr (III) which then was removed by precipitation as $Cr(OH)_3$ [20, 29]. The removals of Cu (II) (92.0%) and Pb (II) (91.6%) follow, possibly due to that both heavy metal ions have more than +0.3 V of half-reaction standard reduction potentials and can be photo-reduced when using TiO_2 as catalyst [20, 21]. Generally, Zn (II), Cd (II) and Ni (II) can't be directly photo-reduced because their reduction potentials are more negative than those of photo-generated electrons [21]. However, WAS usually contains several organic hole scavengers (such as amino and carboxyl groups) which can enhance the removals of Zn (II), Cd (II) and Ni (II) [20, 30]. The removal rates of Cd (II), Ni (II) and Zn (II) were 83.7%, 82.3% and 81.0%, respectively in this study.

The results suggest that sufficient mixing or stirring could slightly (4.8%-10.6%) enhance the removal of heavy metal ions (Fig. 1). This observation might be brought about by the surface complexation of heavy metals with negatively charged polymers, ions exchange, precipitation, etc. during the stirring [17, 20]. UV-light pretreatment also has some slight improvement effect (24.2%-30.1%) on the removal of heavy metal ions. Obviously, photocatalytic pretreatment can significantly (81.0%-97.0%) enhance the removal of heavy metal ions probably by photo-reduction [9, 31] and/or by surface complexation with more soluble negatively charged functional groups [17] produced during the photocatalytic pretreatment process. The reason might be that heavy metal ions as electron acceptors could be photo-reduced, and the simultaneous photo-oxidation of organic molecules might accelerate this photo-reduction by offering electron donors [31], and vice versa. The oxidation-reduction synergistic reaction can add advantageous effect to sludge treatment under high concentration of heavy metal ions, which probably has improvement effect on hydrogen production.

3.3 Effect of photocatalytic pretreatment on hydrogen production

Fig. 2a indicates the hydrogen production from raw WAS, UV-light pretreated WAS and photocatalysis pretreated WAS. The cumulative hydrogen production increased rapidly during the first 12 h till day 3 with the increasing trend leveling off after 3.5 day's fermentation. The three kinds of sludge did not produce any more hydrogen after day 5 with the order of cumulative hydrogen yields as follows: photocatalysis pretreated WAS > UV-light pretreated WAS > raw WAS, which was 211.0, 111.0 and 93.0 ml/l-sludge, respectively. That means that photocatalytic pretreatment could remarkably promote hydrogen production from sludge. Meanwhile, no methane was detected from the photocatalysis pretreated WAS (Fig. 2b). Conversely, methane was produced from the anaerobic digestion of UV-light pretreated WAS and the raw WAS from day 2 on, and their cumulative methane productions were 19.9 and 60.3 ml/l-sludge, respectively. The results indicate that utilizing the photocatalytic pretreated WAS as substrate is most effective for anaerobic hydrogen production in comparison with the raw WAS and UV-light pretreated WAS. By comparison with other pretreatment methods, hydrogen production from photocatalysis pretreated WAS via thermophilic fermentation (55℃) is more effective with the hydrogen yield of 211.0 ml/l-sludge. In our previous study, the hydrogen yield was 53.2 ml/l-sludge [16] from photocatalysis pretreated WAS via mesophilic fermentation (35℃). Guo et al. [33] achieved 43 ml/l-sludge of hydrogen from ultrasonic pretreated WAS via mesophilic fermentation (35℃). Restated, photocatalytic technology could be a promising pretreatment for the degradation of refractory organics for biohydrogen production.

3.4. Effect of pretreatment on metabolites and pH value

The gas phase analysis showed that only H_2 and CO_2 were detected in the biogas from the photocatalysis pretreated WAS during the process of hydrogen production. A similar result was also reported by Guo et al. [33] who treated waste sludge by sterilization, microwave and ultrasonication. Conversely, in the controls (raw WAS), CH_4 was not only detected but also increased with time in the later stage of hydrogen production.

Liquid product analysis showed that after fermentation the metabolites were mainly acetate, propionate and butyrate. The major difference in VFAs among the three kinds of sludge lay in the changes of Ac acid concentration. The cumulative concentrations were 528, 643 and 1020 mg/l for Ac, 365,326 and 296 mg/l for Pr, 420, 451 and 620 mg/l for Bu acids in the raw, UV pretreated and photocatalysis pretreated WAS, respectively. During the entire fermentation process, Pr and Bu acids concentration increased continuously in the three sludge reactors, while the Ac acid concentration changed differently in the three reactors. Ac acid increased continuously in the photocatalysis pretreated WAS (Fig. 3c), but first increased then decreased from day 3 in the UV-light pretreated WAS (Fig. 3b) and raw WAS (Fig. 3a) reactors. Moreover, the decrease rate in the raw WAS reactor was higher than that in the UV-light pretreated WAS reactor. This result is in accordance with the change of methane in these two reactors shown in Fig. 2b**.** This phenomenon implies that Ac acid might be consumed for methane production [34]. The fact that Ac acid concentration was the highest among the three major VFAs, indicates that biohydrogen production from WAS is still an Ac acid type fermentation [35], *i.e.* the photocatalysis pretreatment does not change the fermentation type of WAS.

Although the concentrations of VFAs increased disproportionately, the pH values did not decrease but increased from the same initial value of 5.7 to 5.9, 5.9 and 6.1, respectively (Fig. 4). This observation could be largely attributed to the increase in NH_4^+-N concentration in three sludge reactors (Fig. 4).

3.5 Comparison with other pretreatments

WAS pretreatment has positive effects on the solubilization of organic materials [36]. However, not all of these pretreated WAS are appropriate for anaerobic hydrogen production. The advantages and disadvantages of these pretreatments are listed in Table 2. Acid and alkaline pretreatment without heating have less effect on hydrogen production and might cause secondary pollution to the environment due to chemical addition [7, 10, 11, 36]. Microwave and heating can efficiently enhance hydrogen production but consume large amount of energy at the same time [1, 17, 33, 36]. Guo et al. [33] noted that ultrasonic pretreatment would inhibit hydrogen production due to the production of some inhibitors and extraction of heavy metal ions during the pretreatment process. Wang et al. [5] reported that enzyme pretreatment was an expensive method and had some problems related to adsorption and desorption from substrate surfaces. Although there are some problems like low efficiency of supported catalyst resulting in the requirement of some special photocatalytic reactor, photocatalysis has been proved to be a more low-cost and eco-friendly pretreatment method than others. During this process, organic pollutants can be photo-oxidized with heavy metal ions being photo-reduced and eventually hydrogen production being improved. In addition, this process can make use of solar energy directly, and the catalyst is nontoxic and sometimes reusable. For example, after the photocatalytic pretreatment of WAS, the mixture of suspended TiO_2 and WAS can be used for synthesis of adsorbent [29]. Therefore, photocatalysis is expected to be widely applied in the pretreatment of WAS in the near future.

4. Conclusions

Photocatalytic pretreatment of WAS is an alternative method to promote the release of soluble organics and the uptake of heavy metal ions. In the meantime, the increase of soluble organics, especially soluble carbohydrate and soluble protein, and the decrease of heavy metal ions in the liquid phase further enhanced the hydrogen production from WAS by dark anaerobic digestion. The maximum cumulative hydrogen yields of 211.0, 111.0 and 93.0 ml/l-sludge were achieved from photocatalysis pretreated WAS, UV-light pretreated WAS and raw WAS, respectively. Moreover, CH_4 was not detected in the gas phase during hydrogen production from the photocatalysis pretreated WAS. In contrast, CH_4 was not only present but also increased over time during the later stages of hydrogen production from raw sludge. The main liquid metabolite was acetic acid, suggesting that dark anaerobic hydrogen fermentation of photocatalysis pretreated WAS was still an acetic acid type fermentation.

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Table 1 The characteristics of waste activated sludge (WAS) before and after pretreatment by UV-light and photocatalysis

Items	Raw WAS	UV-light pretreated WAS	Photocatalysis pretreated WAS
TCOD (total chemical oxygen demand, mg/l)	18249	17981	17210
SCOD (soluble chemical oxygen demand, mg/l)	1752	1893	3620
TS (total solids, mg/l)	7483	7302	6870
VS (volatile solids, mg/l)	5006	5119	5980
Soluble protein (mg/l)	1293	1386	1946
Soluble carbohydrate (mg/l)	486	504	879
NH_4^+-N (mg/l)	106	130	320
pH	6.7	7.3	7.6

Table 2 Main advantages and disadvantages of various pretreatment methods for waste activated sludge (WAS)

Treatment method	Experimental conditions	Advantages	Disadvantages	References
Heating	121-180℃, 20min-60min，600-2500kbar	Improve the solids hydrolysis rate, reduce sludge volume, no chemical addition, adsorb toxic metals, increase hydrogen yield.	Increase final effluent color and ammonia inhibition, high energy consumption.	[17, 33, 36]
Acid	Adjust solution to pH=2 using 37% HCl, 24 h, then to pH=7 using NaOH/$Ca(OH)_2$	Low-cost, easy to operate, high metal-binding capacities.	Low selectivity, produce waste products and inhibitors, time consuming.	[7, 11]
Alkaline	8 g NaOH/100 g TS-sludge, 20min-60min	Low-cost, easy to operate, high metal-binding capacities, increase hydrogen yield.	Low selectivity, produce waste products, time consuming, higher concentration inhibition.	[10, 36]
Microwave	560 w × 2 min; 850W × 3min	Significantly reduce sludge volume and processing time, ease of control, compactness, no chemical addition, no harmful by-products, increase hydrogen yield.	Destruct microorganisms non-selectively, higher energy consumption, extract heavy metal ions from sludge.	[1, 33]
Ultrasonic	2 w/ml × 5 min; 5000 kJ/kg TSS×5 min	Effectively improve organics solubilization and sludge disintegration, less retention time, reduce sludge volume, less harmful by-products.	Fail to reduce VS, frequently replace the ultrasound probes, extract heavy metal ions from sludge, reduce hydrogen yield	[18,33]
Enzyme	0.6% (w/w, enzyme/TS-sludge), 40-50℃, 4 h	Easy to control, no harmful by-products; enhance solid reduction, increase hydrogen yield.	Limitation of accessible surface area and enzyme adsorption, pretreatment needed to remove lignin and hemicellulose.	[5,14,]
Photocatalysis	20W lamp, TiO_2 of 20 mg/l, and 96 h ; 15 W lamp, TiO_2 of 3 g/l, and 6h	Remove heavy metals and organic pollutant simultaneously, no harmful by-products, increase hydrogen yield, energy-saving and environmentally-friendly.	Time consuming, low efficiency of supported photocatalyst.	[9,16, 20]

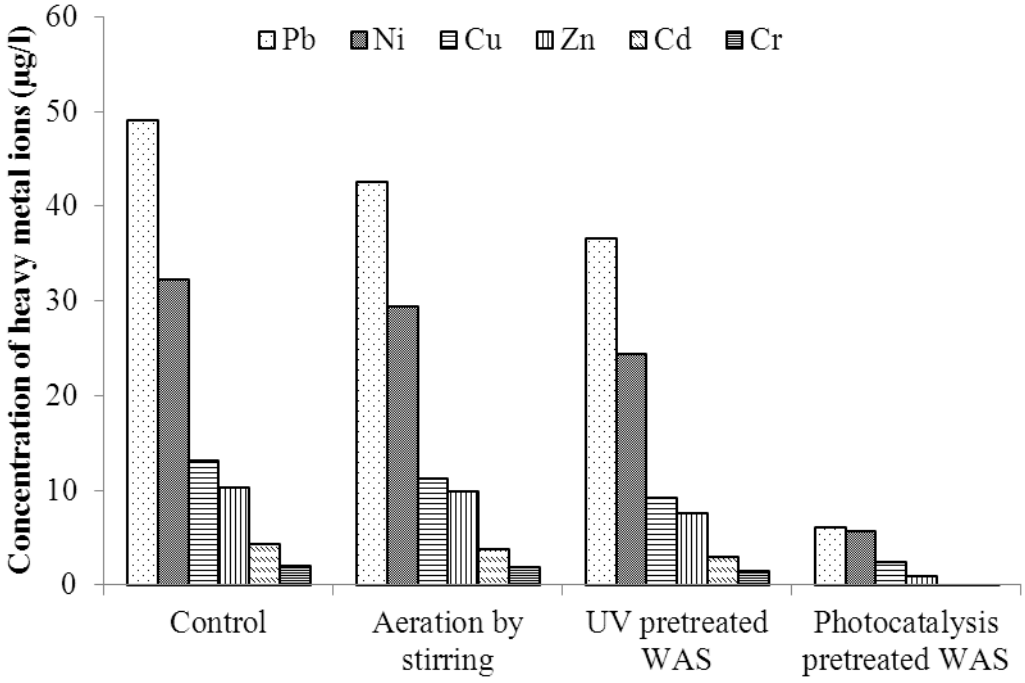
Figure captions

Fig.1. Concentration changes of heavy metal ions in control (raw WAS), Aeration WAS (stirring by magnetic stirrers, 6 h), UV-light pretreated WAS, photocatalysis pretreated WAS

Fig.2. Effect of photocatalytic pretreatment on (a) hydrogen production; (b) methane production

Fig.3. VFA variations during hydrogen fermentation (a) in raw WAS; (b) UV-light pretreated WAS; (c) photocatalysis pretreated WAS

Fig.4. Changes of pH and NH_4^+-N before and after hydrogen fermentation in three kinds WAS



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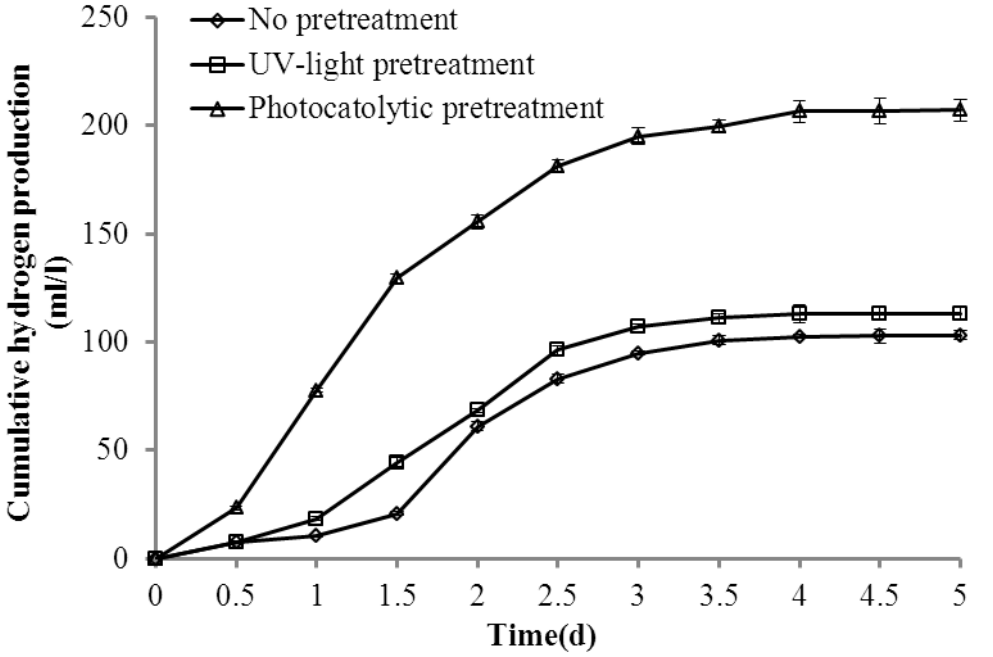

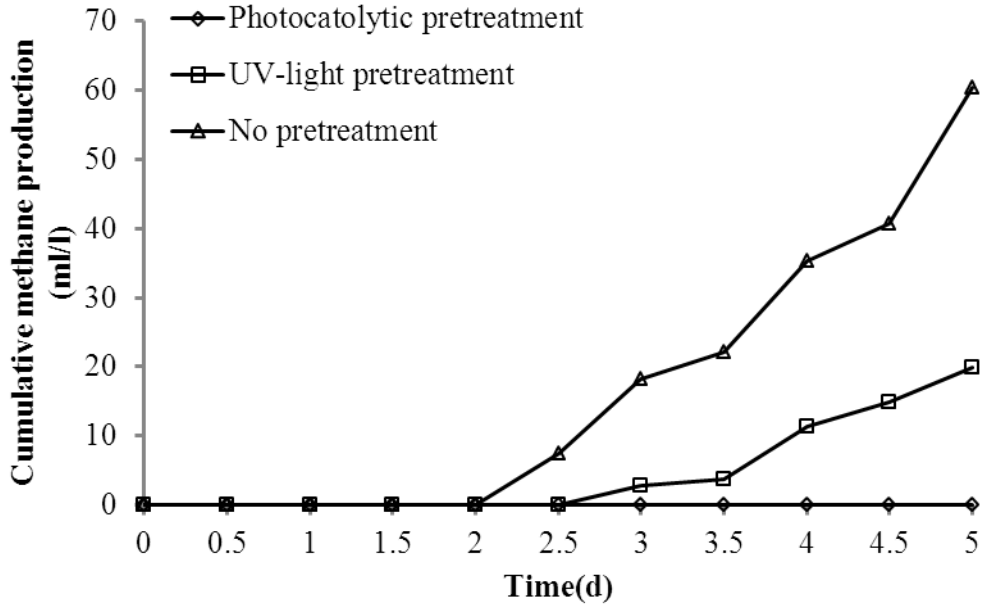

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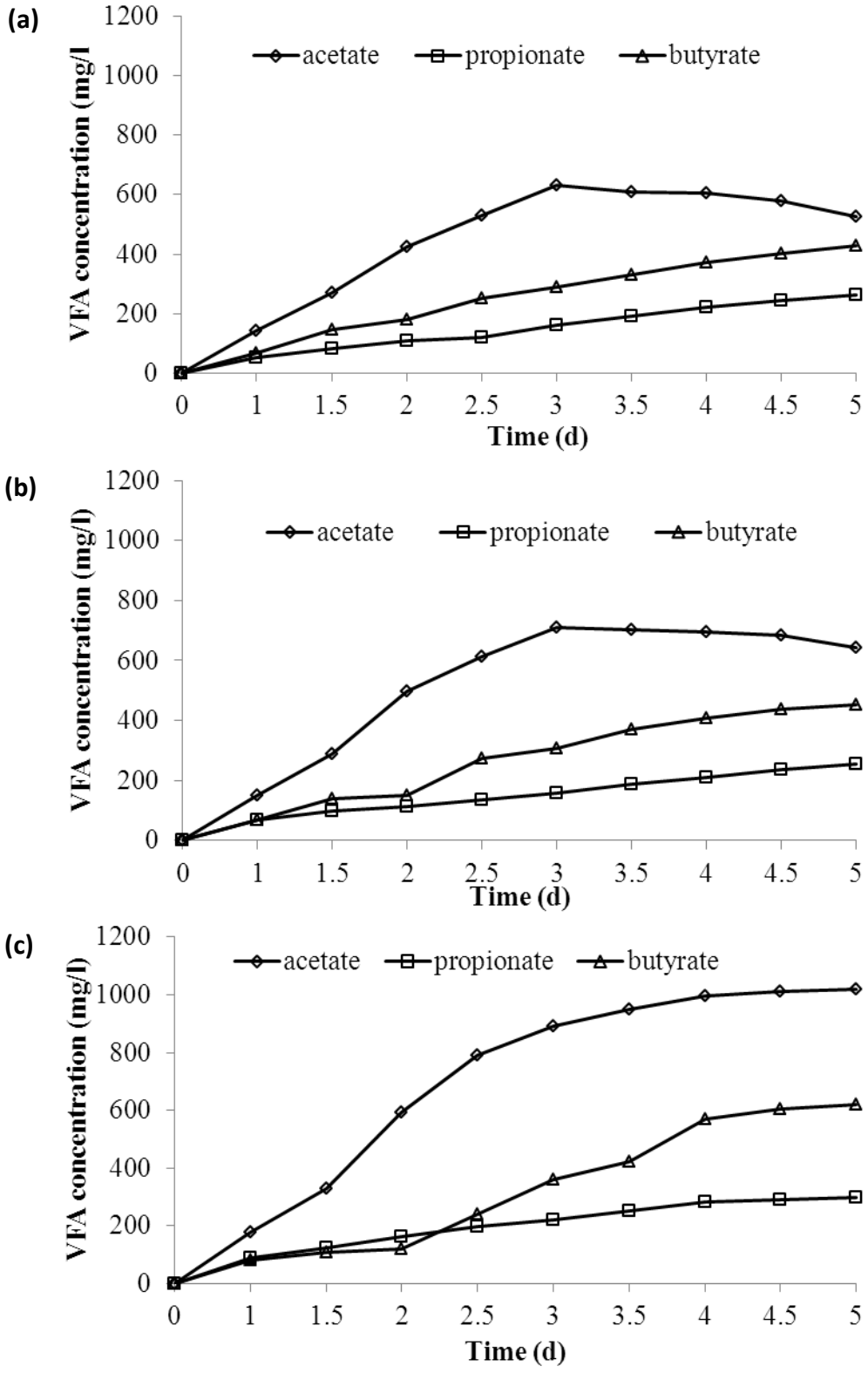

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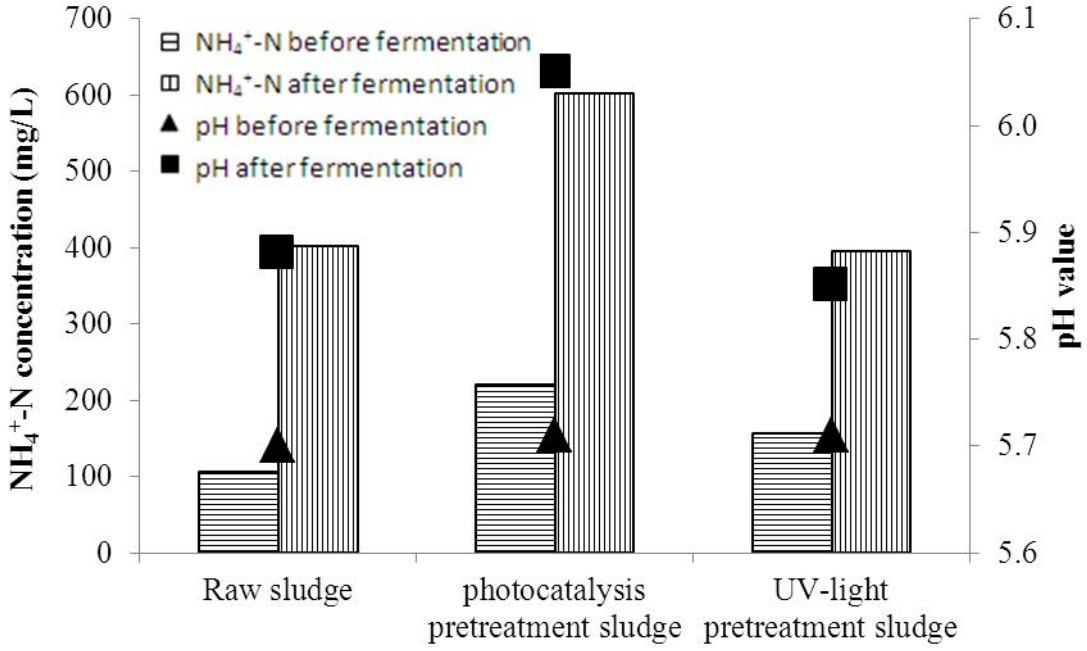

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