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Article

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Enhanced biogas production from modified tapioca starch wastewater

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Abstract

Modified tapioca starch wastewater (MTSW) contains organic and inorganic matters that affected on biological wastewater treatment and biogas production. Especially, the wastewater from chemical modification processes contains high salinity that can inhibit microorganism activities. Zero valent iron is expected to be helpful for creating an enhanced anaerobic environment that might improve the performance of the anaerobic process. The bio-electrochemical system can promote microbial metabolism thereby leading to higher biochemical performance. Result in this study aimed at enhancing performance of upflow anaerobic sludge blanket reactors a treatment for biogas production from MTSW. Three improving methods were compared that included of bio-electrochemical system (BES-UASB), zero-valent iron (ZVI-UASB) and salt tolerance microbial systems (STM-UASB). The experiments were operation by varying hydraulic loading rate (HLR) and organic loading rate (OLR) with values of HLR 0.02, 0.25 m³/m²-h and OLR 7.5, 25 kgCOD/m³-day, respectively. Overall organic removal efficiencies were more than 70% of COD removed for three methods. The highest COD removal was found in BES-UASB that was about 82% of COD removed. The biogas production yields were about 0.33, 0.32 and 0.28 m³/kg-CODremoved for BES-UASB, ZVI-UASB and STM-UASB, respectively. As well as, the highest bio-methane production was found in BES-UASB reactor with more than 60% of biogas compositions.

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Keywords: Modified tapioca starch; High salinity wastewater; Biogas production; Bio-electrochemical system (BES); Zero-valent iron (ZVI); Salt tolerance microorganism

1. Introduction

Modified starch are prepared by physically, enzymatically, or chemically treating native starch to change its properties. Modified starches are used in practically all starch applications, such as in food products as a thickening agent, stabilizer or emulsifier; in pharmaceuticals as a disintegrant; or as binder in coated paper. They are also used in many other applications for industries. The growth of the modified tapioca starch industry in Thailand has resulted severe water pollution as it generates large amount of wastewater. Industrial demand of modified starch

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triggers the rise in number and expanding in scale of tapioca starch factories. The modified starch processes generate wastewater containing organic and inorganic matters that effect on biological wastewater treatment, especially in chemical modification such as oxidized starch processing. A large amount of sodium chloride (NaCl) was produced during the oxidation of modified starch production processes in the wastewater [1]. High salt concentrations cause disintegration of cells because the loss of cellular water (plasmolysis) occurs and eventually causes out ward flow of intracellular water resulting the loss of microbial activity. This phenomenon further affect the treatment with low removal performance of chemical oxygen demands and it also produces deleterious impacts on the inhibition of microbial activity in biogas production [2]. High-concentrations of soluble salts affect microbes via two primary mechanisms: osmotic effect and specific ion effects. Soluble salts increase the osmotic potential (more negative) of water, drawing water out of cells which may kill microbes through plasmolysis. In order to recover optimum renewable energy from waste sources, numerous efforts have been dedicated to the development of various energy efficient anaerobic treatment technologies [3].

ZVI is a reducing agent that is expected to help create an enhanced anaerobic environment that may improve the performance of UASB due to its reductive property. When utilized in an anaerobic environment, ZVI can serve as an electron donor to lower oxidation reduction potential (ORP) and buffer acid produced by acidogens, which are crucial to maintain a stable and favorable condition for methanogens [4]. Bio-electrochemical system (BES) is a newly developed biotechnological device in which the electroactive biofilms enriched at anode surface oxidize acetate into bicarbonate, protons and electrons; the electrons are driven to the cathode and combine with protons to generate H₂ with carbon dioxide to form methane [5]. Electric stimulation can promote microbial metabolism [6], thereby leading to higher biochemical performance. Indeed, there are several previous research of bio-electrochemical methods that have been established and applied in biological electrocatalysis and biofuel cells. In the field of wastewater treatment, it has been reported that hydrogen produced from the cathode can serve as a substrate for denitrification and dechlorination, thereby improving the efficiency of pollutant degradation. Moreover, it is believed that an electric field can enhance the surface reaction by promoting the ion migration rate. Therefore, when an electric field is supplied to the ZVI bed, it is likely to intensify the reaction of ZVI and further improve the anaerobic process [4]. Therefore, this research developed a ZVI-UASB and BES-UASB in our laboratory also comparison with STM-UASB.

2. Material and method

2.1. Biodegradation

The combined MTSW were sampling from a tapioca starch factory in Thailand. The MTSW samples were analyzed according to the methods given in the Standard Methods for the Examination of Water and Wastewater. Biodegradation was calculated from the measured and Total COD (TCOD) and BOD 20 days with inhibited nitrification.

2.2. Feed wastewater

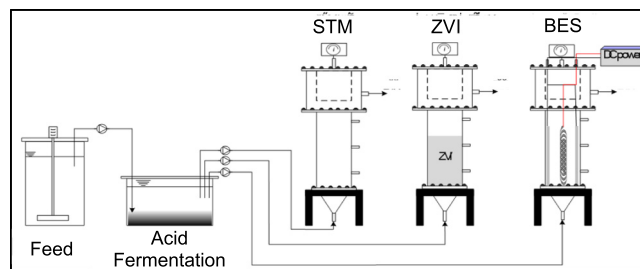
An artificial wastewater was used in this study. Specifically, Starch powder 11 g/L, NH₄HCO₃ 1.13 g/L, NaCl 22 g/L and KH₂PO₄ 1.76 g/L. The trace elements were added according to the following composition: Na-Acetate 1 g/L, MgSO₄ 3.76 g/L and CaCO₃ 2 g/L

2.3. Enrichment of seed sludge

The initial seed sludge was isolated from the sediments at the bottom of an equalization tank in the tapioca starch factory. This tank received MTSW with a high starch content and salinity. The enrichment process was carried out to cultivate mixed culture naturally in the seed sludge. Initial mixed liquor suspended solids (MLSS) of the wastewater and sludge mixture was 1500 mg/L. The enrichment process continued for 3 months until the MLSS level above 3000 mg/L and 60% COD removal were achieved.

Table 1. Operating conditions.

Condition	RUN I	RUN II
Flow rate (L/d)	15	
pH	7	
TDS (mg/l)	20,000	
Inflows (L/d)	15	15
Recirculation flows (L/d)	0	173
OLR (kg/m ³ -day)	7.5	25
HLR (m ³ /m ² -h)	0.02	0.25

**Fig. 1.** Schematic diagram of the experiments.

2.4. Experimental setup

The experimental setup consisted of a polyethylene tank of 100 L capacity for storing MTSW, an acid fermentation tank that operated by HRT 36 hr and three UASB unit as shown in Fig. 1. The three UASB systems were made of acrylic columns, with internal diameter of 20 cm. The total height of the UASB reactors was 110 cm with the operating conditions in Table 1. A ZVI-UASB reactor contained a packed with scrap iron at the bottom of reactor by weight about 795 g or by ratio about 25g/L reactor [7]. A BES-UASB reactor, anode was a pair of iron plate (width 10 cm × Length 60 cm), which was fixed in parallel onto the inside wall of the reactor. The iron spring cathode (10 cm wire diameter and 60 cm length) was installed in the center of the reactor to be situated in the sludge bed. This reactor was supplemented with a low external power at 0.4 V [5]. Prior to use, scrap iron and the electrode materials were washed with diluted HCl and then deionized water to clean their surfaces.

3. Results and discussion

3.1. Biodegradation

The ratio of BOD/COD is often used as an index to evaluate biodegradability of wastewater. BOD/COD > 0.45 indicates that biodegradability is very good; BOD/COD = 0.45, biodegradability is good; BOD/COD = 0.2–0.3, biodegradability is poor; BOD/COD < 0.2, biological treatment is unsuitable [8]. Biodegradability of the wastewater could be continuously characterized by BOD/COD ratios during the period of 20 days as shown in Fig. 2. The BOD/COD ratios were found to be 0.19 and 0.15 for TBOD₂₀/TCOD and SBOD₂₀/TCOD, respectively. The results indicated that the MTSW contained high amount of biologically resistant organics. These suggested that the residual COD of MTSW may be comprised of high salinity and its can be inhibited metabolic of microorganism.

3.2. Sludge enrichments

The acclimatization was done step-wise until a COD removal approximately 60% could be achieved. The changes in the biomass concentration along with the F/M ratio and COD removal efficiencies were noticed. Acclimatization of salt tolerance microbial took about 15 days. The change in the COD removal efficiency is given in Fig. 3. It was found that after 15 days, the COD removal efficiency with bottom sludge of modified starch wastewater equalization

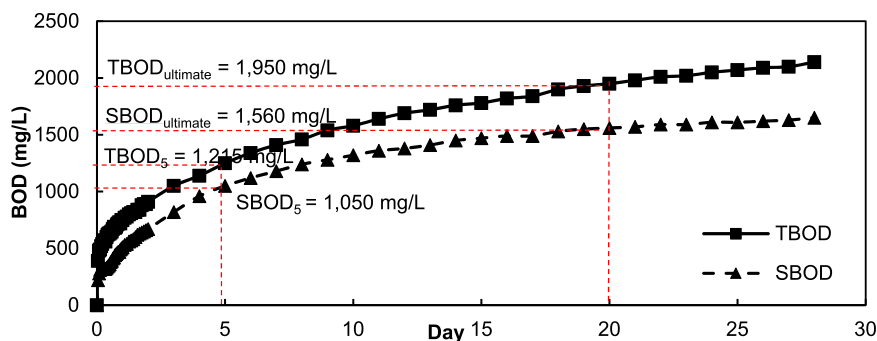


Fig. 2. The relationship between TBOD and SBOD values with duration.

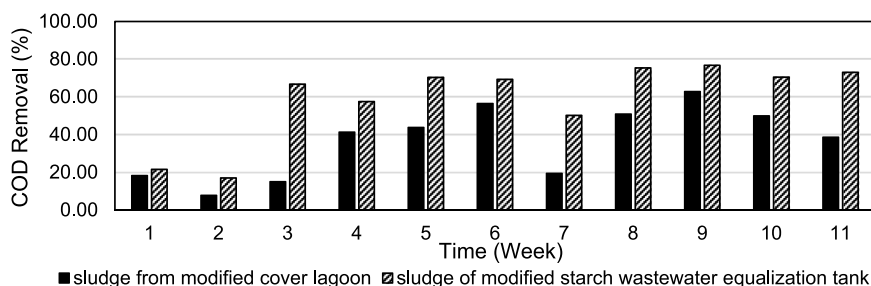


Fig. 3. The COD removal efficiency of acclimatization.

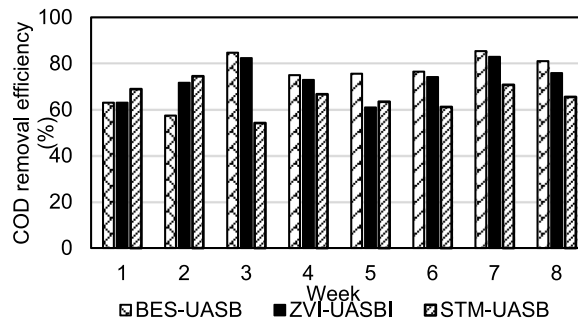
tank was higher than that of sludge from modified cover lagoon, The COD removal efficiency reached 63.11% in bottom sludge of modified starch wastewater equalization tank compared to 13.93% in the sludge from modified cover lagoon. This indicates that, bottom sludge of modified starch wastewater equalization tank could probably be more effective in MTSW than the sludge from modified cover lagoon.

3.3. Treatment efficiencies

Two OLR were evaluation for three UASB systems the treatment for MTSW including of $7.5 \text{ kgCOD/m}^3\text{-d}$ for RUN I and increasing to $25 \text{ kgCOD/m}^3\text{-d}$ by a recirculation flow for RUN II. The overall influent and effluent concentrations are showed in Table 2. In RUN I, three UASB systems operated in parallel for 106 days. A BES-UASB reactor is achieved the highest organic removal was about 76.52% and 86.47% of TCOD and TBOD removal, respectively. However, the organic contents was removed gradually in all two of ZVI-UASB and STM-UASB reactors were about 74.4% and 65.2% of TCOD removal, respectively. This can be explained by ZVI is added into an anaerobic reactor, it not only serves as an electron donor, but is also expected to help create an enhanced anaerobic environment that may improve the performance of reactors used for wastewater treatment [9]. Moreover, this reaction may have intensified in response to the application of electricity to the ZVI. Also, iron was documented as a component of the essential enzymes that drive numerous anaerobic reactions. Oleszkiewicz and Sharma [10] reported limited conversion of COD at deficient concentrations of iron. Thus, ZVI could be responsible for the significant COD removal. In this process, the ZVI reaction was the major reason for the improved performance, but the reaction might be weak [4]. The electric field could intensify the ZVI reaction so as to enhance the roles of ZVI in anaerobic process. This results can be confirms electric field is supplied to the ZVI bed, it is likely to intensify the reaction of ZVI and improve the anaerobic process. In RUN II, the inflow rate in UASB reactors remained the same as in RUN I but the HLR was increased from 0.02 to $0.25 \text{ m}^3/\text{m}^2\text{-h}$ by recirculation of 173 L/d . The organic removal improved as indicated by the efficiencies for TBOD reaching up to 92.6%, 92.1 and 91% in BES-UASB, ZVI-UASB and STM-UASB, respectively. This was probably due to the recirculation of UASB effluents.

Table 2. Organic removal efficiency of the treatment system.

Parameters	Influents (mg/L)	Effluents (mg/L)						
		Acid	RUN I			RUN II		
			BES-UASB	ZVI-UASB	STM-UASB	BES-UASB	ZVI-UASB	STM-UASB
TCOD	16,700 ± 3503	16,000	4466	3366	5100	1818	1963	2109
SCOD	10,533 ± 3826	8200	2566	2633	1833	1054	1345	1127
TBOD	5083 ± 2617	4760	687	536	551	395	423	480
SBOD	668 ± 287	630	451	295	289	226	367	452
TKN	152.7	147.9	130.9	145.3	123.7	98.7	92.1	102.2
TP	48.3	36.6	25.4	26.5	25.6	14.1	15.3	15.5

**Fig. 4.** COD removal efficiency of RUN I.**Table 3.** Biogas production and compositions.

	RUN I			RUN II		
	BES-UASB	ZVI-UASB	STM-UASB	BES-UASB	ZVI-UASB	STM-UASB
Yield gas (m ³ /kgCOD _{removed} -d)	0.34	0.26	0.23	0.33	0.32	0.28
(L _{gas} /L _{ww})	3.89	2.63	2.38	3.34	3.56	2.57
L _{CH4} /L _{ww}	2.5	1.6	1.3	2.3	2.1	1.4
CH ₄ (%)	63.1	60.4	54.5	67.43	59.62	54.36
CO ₂ (%)	24.1	23.8	22.1	21.3	24.4	26
H ₂ S (ppm)	963	986	1012	1039	1107	2126

3.4. Biogas production and gas compositions

Overall average gas production and composition could be observed as data in Table 3. During RUN I that operate at 7.5 kgCOD/m³-d for RUN I. Biogas in two reactors of ZVI-UASB and BES-UASB are higher than STM-UASB. The organic removal improved as indicated by the efficiencies for TBOD reaching up to 89.4% and 86.7% in ZVI-UASB and BES-UASB, respectively. The highest biogas production was found in BES-UASB that about 3.89 Lgas/L_{ww} (0.34 m³/kgCOD_{removed}-d) as well as for the methane composition that reaching up to 63% in biogas. These evidenced that coupled the electromethanogenesis into an UASB reactor to improve anaerobic methanogenesis for high organic load rate acetate wastewater treatment, and they noted the beneficial role of anodic oxidization in degrading acetate, which reduced the risk of acetoclastic methanogens inhibition and maintained a stable performance. In RUN II, the highest biogas production was also found in BES-UASB that about 3.34 Lgas/L_{ww} (0.33³/kgCOD_{removed}-d) that seem to be not difference capable in RUN I. However, TCOD removal efficiency was reaching up to 82.17%. This indicated that BES-UASB be maintained a stable performance. In case of ZVI-UASB and STM-UASB, the biogas production were increase due to the recirculation of UASB effluents. These may cause of organic and iron contents in recirculation flow (see Figs. 4 and 5).

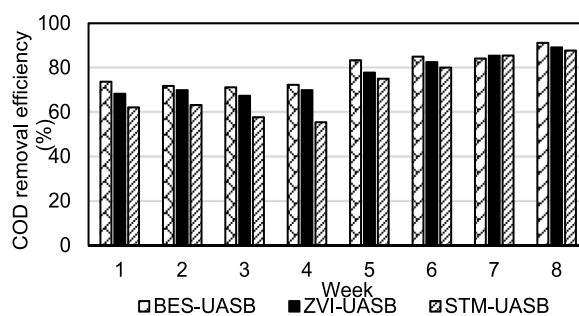


Fig. 5. COD removal efficiency of RUN II.

Table 4. Volatile organic acids and acetate in the system.

Parameter	System			
	RUN I		RUN II	
	VFA (mg/l)	Acetate (mg/l)	VFA (mg/l)	Acetate (mg/l)
Feed	–	335.4	–	893.9
Acid	1667	1454.8	2775.4	1555.2
BES-UASB	155.8	73.2	230.2	10.5
ZVI-UASB	233.8	77.6	201.2	11.5
STM-UASB	249.4	112.2	267	16.8

3.5. Accumulated volatile fatty acids and acetate-degrading

High VFA concentrations cause pH values to decrease, and result in toxic conditions in the reactor. In anaerobic digesters with low buffering capacity, pH, partial alkalinity and VFAs are reliable indicators for process imbalance, however, in highly buffered systems, pH changes can be small, even when the process is extremely stressed, and only VFAs can be considered reliable for process monitoring [11]. Overall accumulated VFAs seems to be not toxic on methanogenic bacteria during two runs as results shown in Table 4. The dominant metabolic pathway for methane formation was confirmed to be via the syntrophic acetate oxidation coupled with hydrogenotrophic methanogenesis, responsible for 90%–99% of the CH₄ formation.

3.6. Sludge characteristics

Extracellular polymeric substances (EPS) secreted by bacteria can mediate cohesion as well as adhesion of cells, which is crucial to maintenance of the structural integrity of anaerobic granules. Therefore, the EPS content of the sludge is an important factor in anaerobic granulation. Proteins and polysaccharides are the two dominant compositions in extracted EPS, which are believed to represent the entire EPS of the sludge. After each run of operation, these two compositions extracted from the sludge of each reactor and from the inoculum were analyzed. As shown in Table 5, the level of proteins and polysaccharides extracted from reactor BES-UASB was the highest during two operation runs but seem nearly the content of ZVI-UASB, and them were higher than the levels in STM-UASB. The different EPS contents in the three reactors may be related to Fe²⁺ leaching. EPS preferred to bind with divalent metals to form a stable three dimensional structure to maintain the structural integrity of the granule, which was important for the response of the granule to stressful changes. Thus, as the Fe²⁺ content of the sludge increased, more EPS was bound and immobilized in the sludge [4].

4. Conclusion

Coupling ZVI and BES system showed the great potentials to stimulate the overall performance of UASB reactor for MTSW. The combined systems maintained the comparatively higher methane yield and COD removal efficiency over the single UASB process through the entire process. Specifically, hydraulic circulation may intensify the ZVI

Table 5. Composition of extracellular polymeric substances (EPS) extracted from reactor sludge.

Sludge	RUN I		RUN II	
	Proteins (mg /g VSS)	Polysaccharides (mg/g VSS)	Proteins (mg/g VSS)	Polysaccharides (mg/g VSS)
BES-UASB	6.95 ± 0.8	1.1 ± 0.9	9.41 ± 1.8	0.7 ± 0.1
ZVI-UASB	6.4 ± 2	1.35 ± 0.7	9.27 ± 2.2	0.66 ± 0.1
STM-UASB	5.7 ± 2.6	1.63 ± 1.2	7.8 ± 1.3	0.7 ± 0.3

reaction, thereby enabling the reactor to operate well at decreased operational temperature and reduced HRT, which would minimize the cost of construction and operation for wastewater treatment.

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