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Effect of Polyvinyl Alcohol Gel Coated with Ferrihydrite on Propionic Acid Removal in Anaerobic Wastewater Treatment

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ABSTRACT

Propionic acid is a crucial factor that influences the efficiency of anaerobic wastewater treatment, because its accumulation in the process decreases the pH levels. Therefore, this study focused on an approach that can alleviate this inhibitory effect from propionic acid. Polyvinyl alcohol (PVA) have been used for encapsulating active microorganisms in cell immobilization technology. Using PVA gel coated with Fh (FhPVA) as a biocarrier in the system, propionic acid can be removed to enhance capability of microbes for converting volatile fatty acid (VFA) into methane gas and decrease an inhibitory effect from VFA accumulation in the system. The specific surface areas (SSA) of PVA and FhPVA were estimated employing the methylene blue dye adsorption with spectrophotometric analysis. The adsorption affinity of each type of the media were computed using SSA and the residual propionic acid concentration obtained from the experiment. The SSA were found to be 1.41 $m^2\ g^{-1}$, 0.40 $m^2\ g^{-1}$ for PVA and FhPVA, respectively. From the result, it can be assumed that the impregnation process results in pore blockages, so the surface area of FhPVA is apparently lower than PVA. In addition, the adsorption affinity of FhPVA towards propionic acid is much higher than PVA, which were 19.39 mg $L^{-1}m^{-2}$ and 5.29 mg $L^{-1}m^{-2}$, respectively. Lastly, this study is only the first step that illustrates the probability of using Fh for improving the efficiency of the anaerobic system, but further study is needed for discovering a better approach for coating Fh on the media.

Keywords : propionic acid; ferrihydrite; adsorption affinity; polyvinyl alcohol; methylene blue

INTRODUCTION

An anaerobic process is widely used in industrial wastewater treatment due to several advantages, e.g. cost-effectiveness, when compared to aerobic treatment. Indeed, a thermophilic anaerobic membrane bioreactor (TAnMBR) poses various advantages such as retention of active anaerobic microorganisms by membrane, high biodegradation rate, enhanced biogas generation, inactivation of pathogens, elimination of foaming problem and treatment of as-received hot waste stream from industrial processes. However, single-stage TAnMBR has limitation on different growth rates of acidogenic bacteria and methanogenic archaea. Acidogenesis and fermentative bacteria grow much faster than methanogenic bacteria and have high tolerance level to extreme condition such as temperature and pH [2]. Inversely, methanogens are very sensitive to environmental factor and pH. Therefore, pH is the critical factor that influences the performance of the system. To solve this problem, researchers propose two-stage treatment comprising hydrolytic and methanogenic reactors which can be operated at their optimal conditions. It was reported that use of polyvinyl alcohol hydrogel (PVA) as a biocarrier in the hydrolytic reactor enhanced volatile fatty acid (VFA) production, but a drop in methanogenic reactor performance occurred [3].

Ferrihydrite (Fh) is an amorphous iron oxide particle, which can be found in natural sediments. There are different chemical formulas of Fh, which are influenced by environment such as temperature, humidity, etc. Fundamentally, Fh can be presented as $FeOOH{\cdot}0.4H_2O$ [4]. Michel et al. proposed the ideal structure of Fh (Figure 1) which comprises of FeO_4 and FeO_6 in the ratio of 1 : 4 [5]. Moreover, Fh has high surface area and capability for adsorbing natural organic matter (NOM), metalloids and heavy metals e.g. arsenic [6-7]. The adsorption of NOM on Fh is attributed to the ligand exchange mechanism at acidic condition (Figure 2). Hence, it is anticipated that Fh could adsorb VFAs and gradually release them to water, thus lessoning inhibition of methanogenic archaea by some VFA species. Therefore, this research focused on controlling VFA concentrations in hydrolytic effluent using PVA coated with ferrihydrite for potential application in anaerobic wastewater treatment.

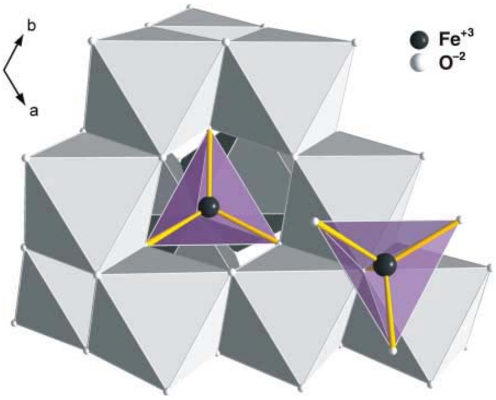

Figure 1 Polyhedral representation of the ideal ferrihydrite structure [7]

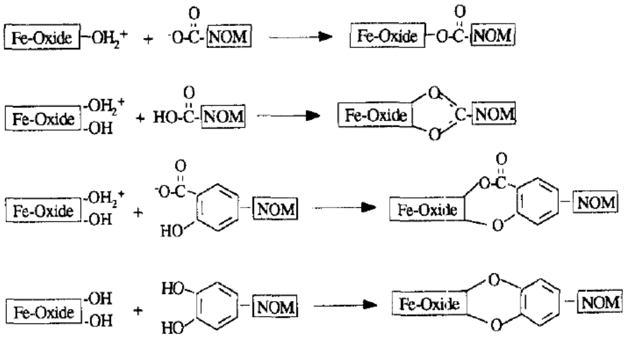

Figure 2 Model for DOM adsorption on iron oxides [3]

METHODOLOGY

1. Preliminary experiment

It is hypothesized that mesoporous Fh could potentially adsorb VFAs. Propionic acid was used in this experiment, because it is the critical inhibitor in an anaerobic process that should be focused on.

1.1 Synthesis of Ferrihydrite impregnated polyvinyl alcohol gel (FhPVA)

Based on the literature review [12-13], PVA (Kuraray Asia Pacific Pte., Ltd.) were pretreated by soaking in HCl (0.1 M) solution for 24 hours. PVA-gel was placed in a PTFE flask, and then 30 mL of 0.1 M of $Fe(NO_3)_3 \cdot 9H_2O$ solution was added. The solution was stirred by magnetic stirrer for 1 hour. After complete agitation, pH was adjusted to 7.0-8.0 by gradually adding 6.0 N of NaOH solution. The reddish precipitation (Fe^{3+}) occurred and coated on PVA. The FhPVA was agitated again by magnetic stirrer for 10 minutes, and washed with Milli-Q water until the EC of supernatant became less than 10 μS/cm.

1.2 The adsorption of propionic acid on FhPVA

The PVA and FhPVA were soaked in 100 mL of propionic acid (1 g/L) for 18 hours. There were two sets of the experiment, which are 1.) with shaking at 200 rpm for 18 hours that refers to as dynamic condition typically encountered in fluidized process and 2.) without shaking that represents static condition of solid-liquid contact. Next, the concentration of propionic acid in the solution was analyzed as the VFA concentration (Method 5560 C in Standard Methods)

1.3 Methylene Blue Dye for specific surface area (SSA) measurement of PVA and FhPVA

The calibration curve consists of five diluted concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 mg L^{-1} of MB solution), which were analyzed using a UV/Vis spectrophotometer at 665 nm. PVA and FhPVA were prepared in Erlenmeyer flasks into five sets that had different volumes (5, 15, 20 and 25 mL). Then, PVA and FhPVA were soaked in 100 mL of MB solution (0.4 mg L^{-1}) with shaking at 200 rpm for 18 hours. The initial MB concentration and the residual MB concentration were used to calculate SSA and to investigate the adsorption affinity.

2. Seed sludge enrichment and acclimatization

The two stage TAnMBR consists of 2 reactors: i.e., hydrolytic reactor and methanogenic reactor. To enrich microbes in the reactors, anaerobic seed sludge from UASB reactor, which is operated under mesophilic condition is fed into the reactors. Then, different feeds and environmental conditions are provided for different microbes. Afterwards, the system is acclimatized by gradually increasing temperature step by step which is 2°C, for avoiding thermal shock. Organic loading rate (OLR) of the hydrolytic reactor is increased by 2 kg_{COD} $m^{-3} \cdot d^{-1}$ per time when the reactor performance reaches a stable condition. OLR of the methanogenic reactor is raised by 0.5 kg_{COD} $m^{-3} \cdot d^{-1}$ per time following a former study [3].

3. Two stage TAnMBR optimization

This part is operated at a constant OLR of 6 kg_{COD} $m^{-3} \cdot d^{-1}$ under thermophilic condition (55°C) for the whole experiment. FhPVA may be added as a biocarrier in the hydrolytic reactor to decrease an inhibitory effect from the VFA accumulation in the system and increase capability of methanogens for converting VFA into methane gas, which should increase methane production. FhPVA is utilized in the hydrolytic reactor, which accounts for a volumetric packing ratio of 30%. PVA is kept in a good fluidization by wastewater recirculation.

4. Operation and analytical methods

During sludge acclimatization, COD removal efficiency and gas productivity have been monitored.

5. Specific surface area (SSA) estimation

Information on the adsorption capacity of the FhPVA is very significant for evaluating the adequate amount of FhPVA that is added in the process. Fortunately, Methylene blue (MB) dye adsorption is cheap and simple, and does not require the use of advanced equipment [8]. Therefore, this method has been used as alternative for Brunauer–Emmett–Teller (BET) measurement for determining the total surface area of the samples. The MB molecule has a parallelepiped shape with approximately 17 Å ×7.6 Å ×3.25 Å. So, there are three different ways of the attachment of MB molecule on the materials. This study applied the highest value for calculating SSA. The covered area is about 130 $Å^2$ (1.3 nm^2) per molecule on the condition that the molecule lies on its largest face on the material surface [9-11], which uses to calculate the specific surface area as equation (1):

$$SSA_{MB} = \frac{q_{max} A_{MB} N}{MW_{MB}} \quad (1)$$

where SSA_{MB} is the specific surface area of MB ($m^2\ g^{-1}$), q_{max} is the mass of adsorbed MB in the material ($g_{MB}\ g^{-1}$), A_{MB} is the area occupied by one MB molecule (m^2 molecule^{-1}), N the Avogadro's number (6.02×10^{23} molecule mol^{-1}) and MW_{MB} is the MB molar mass (355.89 g mol^{-1}) [9]. Furthermore, q_{max} can be calculated from equation (2):

$$q_{eq} = \frac{(C_0 - C_{eq}) \text{ x } V}{M} \quad (2)$$

where C_0 is the concentration of the methylene blue solution at starting time (t = 0) (mg L^{-1}), C_e is the concentration of the methylene blue solution at equilibrium time (mg L^{-1}), V is the volume of the solution treated (L) and M is the mass of the adsorbent (g) [8].

RESULTS AND DISCUSSIONS

1. Without shaking for 18 hours

VFA concentrations of the solutions without shaking for 18 hours were presented in Table 1. From the result, Recovery factor (f) was calculated to be 0.36. Percent recovery of the Laboratory Fortified Blank (LFB) was 87.9%. Percent recovery and relative percent difference (%RPD) of the Lab Fortified Matrix (LFM) were 95.2% and 8.02%, respectively. PVA and FhPVA under this condition can adsorb VFA only 4.52-14.4%.

Table 1 VFA concentration of the solution without shaking for 18 hours

Sample	Volume of NaOH (mL)	[VFA] (mg/L)	[VFA]/f (mg/L)
[NaOH] = 0.0340 N			
Method blank (MB)	0.05	1.02	2.82
Laboratory Fortified Blank (LFB)	15.6	317.22	878.53
Propionic acid (1g/L)	8.9	361.08	1000.00
PVA	15.25	310.08	858.76
PVA (LFM; Lab Fortified Matrix)	32.1	653.82	1810.73
FhPVA	15.2	309.06	855.93
FhPVA (Duplicate)	16.95	344.76	954.80

2. With shaking at 200 rpm for 18 hours

VFA concentrations of the solutions with shaking at 200 rpm for 18 hours were shown in Table 2. From the result, Recovery factor (f) was calculated to be 0.34. Percent recovery of the Laboratory Fortified Blank (LFB) was 117%. Percent recovery and relative percent difference (%RPD) of the Lab Fortified Matrix (LFM) was 93.2% and 3.33%, respectively. PVA and FhPVA under this condition can adsorb VFA 19.2-26.7%.

Table 2 VFA concentration of the solution with shaking at 200 rpm for 18 hours

Sample	Volume of NaOH (mL)	[VFA] (mg/L)	[VFA]/f (mg/L)	Average (mg/L)
[NaOH] = 0.0355 N				
Method blank (MB)	0.00	0.00	0.00	0.00
Laboratory Fortified Blank (LFB)	18.75	399.71	1165.34	1165.34
Propionic acid (1g/L) 1	16.35	348.55	1000.00	343.22
Propionic acid (1g/L) (Duplicate) 2	15.85	337.89	1000.00	
PVA 1	11.8	251.55	733.39	770.68
PVA 2 (Duplicate)	12.4	264.34	770.68	
PVA 3 (Triplicate)	13.0	277.13	807.87	
PVA (LFM; Lab Fortified Matrix) 1	27.65	589.44	1718.49	1702.96
PVA LFM (Duplicate) 2	27.15	578.78	1687.42	
FhPVA 1	12.35	263.28	767.57	761.36
FhPVA 2 (Duplicate)	11.8	251.55	733.39	
FhPVA 3 (Triplicate)	12.6	268.61	783.11	

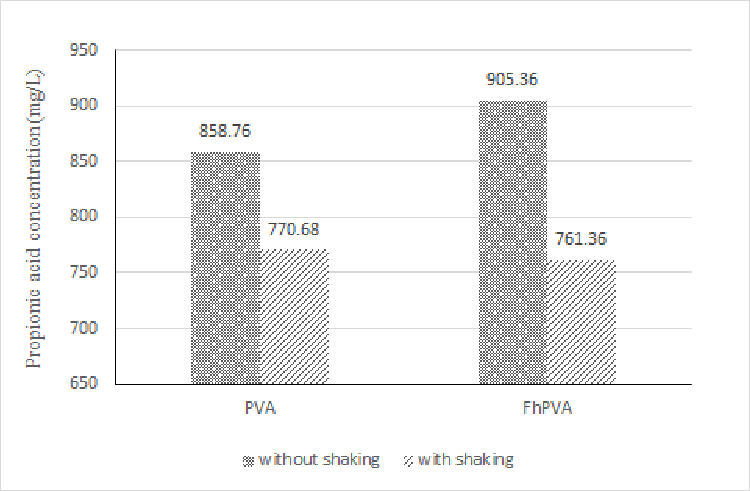

Figure 3 Comparison of residual propionic acids between two conditions; 1.) without shaking 2.) with shaking at 200 rpm for 18 hours

Figure 3 compares residual propionic acids between two experiments, namely without shaking (representing static condition of solid-liquid contact) and with shaking after 18-hour contact time. The usage of 18 hours is for the purpose of simulating HRT in the hydrolytic reactor, which is considered sufficient for adsorption equilibrium. The results confirm the adsorption of VFA on FhPVA, and shows that FhPVA can adsorb VFA slightly better than PVA. In addition, shaking solution at 200 rpm enhanced the diffusion of the propionic acid into media pores, which leads to higher adsorption as it can be seen in Figure 3.

3. Methylene Blue Dye for specific surface area (SSA) measurement of PVA and FhPVA

The calibration curve consists of five diluted concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 mg L^{-1} of MB solution), which were analyzed using a UV/Vis spectrophotometer at 665 nm. The standard curve (figure 4) shows a good linear regression; $y = 2.0785x - 0.0442$, with R-square value of 0.9971. The residual MB concentration was calculated by substituting the value of the absorbance into “y” in the equation mentioned above. As can be seen in Table 3 and Figure 5. The declining trends occur in both PVA and FhPVA when increasing the volume of the media. Remarkably, the virgin PVA can adsorb MB more than FhPVA, indicating that PVA has a higher surface area than FhPVA. The residual MB of PVA (25 ml) is 0.2486 mg L^{-1}, while FhPVA one (25 ml) is 0.3511 mg L^{-1}. The SSA were found to be 1.41 m^{2} g^{-1}, 0.40 m^{2} g^{-1} for PVA and FhPVA, respectively (Table 4). From the result, it indicates that the impregnation process leads to pore blockages, so the surface area of FhPVA is obviously lower than PVA (approximately 70%).

The adsorption amounts (from Figure 3) were normalized by SSA, attained by the MB adsorption, to assess preferential adsorption of propionate. Surprisingly, the adsorption affinity of FhPVA towards propionic acid is much higher than PVA, which were 19.39 mg L^{-1}m^{-2} and 5.29 mg L^{-1}m^{-2}, respectively (Table 4). Evidently, the advantage of having high adsorption affinity and the disadvantage of pore blockages make the removal efficiency of propionic acid by FhPVA only slightly differ from that by original PVA. To enhance FhPVA application, further studies may focus on three main issues which will be described in the following section.

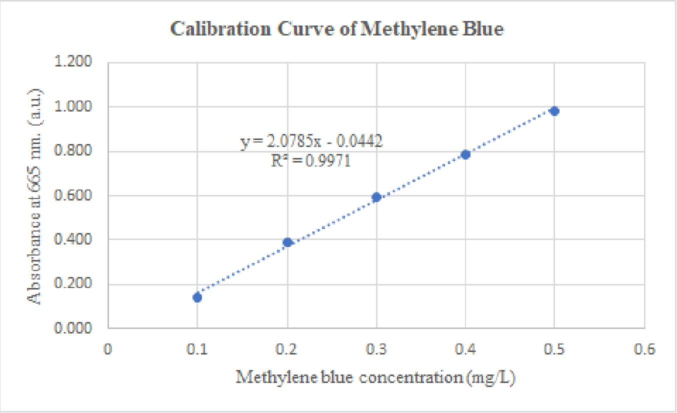

Figure 4 Calibration curve of methylene blue (0.1, 0.2, 0.3, 0.4 and 0.5 mg L^{-1}) based on the UV/Vis absorbance at 665 nm.

Table 3 Residual Methylene blue concentration

Sample	Volume of media (mL)	Absorbance 1 (a.u.)	Absorbance 2 (a.u.)	Average (a.u.)	Residual [MB] or C_{eq} (mg/L)
Method blank	0	0.778	0.783	0.781	0.3968
PVA 5 mL	5	0.709	0.704	0.707	0.3612
PVA 10 mL	10	0.584	0.584	0.584	0.3022
PVA 15 mL	15	0.564	0.563	0.564	0.2924
PVA 20 mL	20	0.519	0.519	0.519	0.2710
PVA 25 mL	25	0.473	0.472	0.473	0.2486
FhPVA 5 mL	5	0.760	0.763	0.762	0.3876
FhPVA 10 mL	10	0.731	0.732	0.732	0.3732
FhPVA 15 mL	15	0.723	0.723	0.723	0.3691
FhPVA 20 mL	20	0.700	0.698	0.699	0.3576
FhPVA 25 mL	25	0.686	0.685	0.686	0.3511

Table 4 Special surface area and adsorption affinity of PVA and FhPVA

Sample	Volume of media (mL)	Mass of media (g.)	q_{eq} (mg/g$_{\cdot media}$)	X_m (mol$_{MB}$/g$_{\cdot media}$)	SSA average (nm^2/g$_{\cdot media}$)	Adsorption of propionic acid per media (mg/L/g$_{\cdot media}$)	Adsorption of propionic acid per area (mg/L/m^2)
PVA 5 mL	5	5.1250	0.6947	1.95×10^{-6}	1.410 m^2/g$_{\cdot media}$	7.4598 mg/L/g$_{\cdot PVA}$	5.2898 mg/L/m^2
PVA 15 mL	15	15.3750	0.6790	1.91×10^{-6}			
PVA 20 mL	20	20.5000	0.6137	1.72×10^{-6}			
PVA 25 mL	25	25.6250	0.5783	1.62×10^{-6}			
FhPVA 5 mL	5	5.1250	0.1784	0.50×10^{-6}	0.400 m^2/g$_{\cdot media}$	7.7607 mg/L/g$_{\cdot FhPVA}$	19.3945 mg/L/m^2
FhPVA 15 mL	15	15.3750	0.1799	0.51×10^{-6}			
FhPVA 20 mL	20	20.5000	0.1913	0.54×10^{-6}			
FhPVA 25 mL	25	25.6250	0.1784	0.50×10^{-6}			

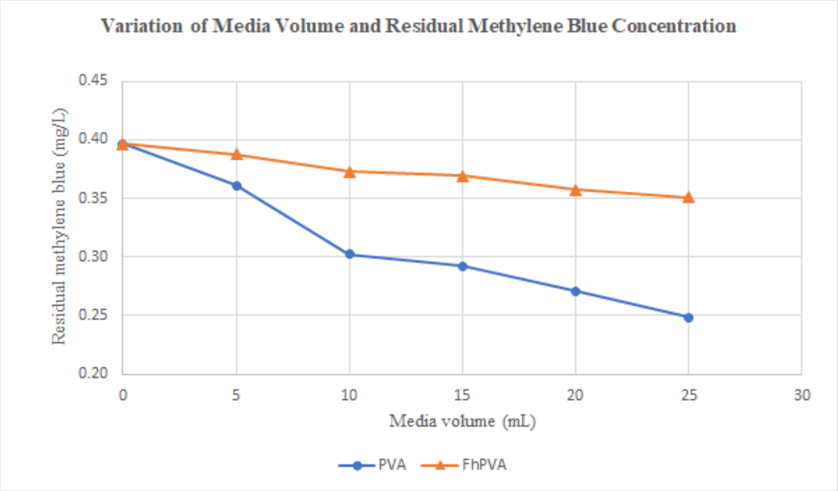

Figure 5 Variation of media volume and residual methylene blue concentrations

IMPLICATION OF THIS STUDY

Because the overall result shows that the removal efficiency of propionic acid by FhPVA has not been remarkably enhanced, when compared to the virgin PVA. Nonetheless, FhPVA has much higher adsorption affinity than PVA despite substantial decline in the specific surface area. This suggests that the impregnation of Fh on PVA is not preferable, probably because there was insufficient amount Fh coated on PVA and blockages of PVA pores by Fh particles, or PVA surface is unsuitable for coating with Fh. Research would like to suggest further studies as following information;

1.) Discover better approach of impregnation Fh on PVA at a higher amount Fh on the PVA surface.
2.) Focus on alternative technique that can alleviate pore blockages in FhPVA.
3.) Different materials can be used as a substitute for PVA, which provide appropriate surface for Fh impregnation.

CONCLUSION

The specific surface area of FhPVA was lower than PVA by about 70%, but FhPVA exhibited a remarkably higher adsorption affinity than PVA (approximately 3.5 times). This study does not only indicate the advantage of FhPVA in anaerobic wastewater treatment, but also reveals some of the imperfection of the impregnation, which can be improved in the further studies. The ongoing experiments are done for investigating the effects of FhPVA on performance improvement of Two-stage TAnMBR.

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