



Kinetics of organics removal in swine wastewater treatment using anaerobic moving bed biofilm reactor

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ABSTRACT

In Vietnam, livestock production, especially pigs, plays an important role in the agriculture sector. The number of livestock farms in Vietnam is more than 19,000 with 28 million pigs. However, swine wastewater mainly directed to biogas is finally discharged to ponds and lakes, causing serious environmental problems. This research applied the high-rate anaerobic moving bed biofilm reactor (AnMBBR) to treat swine wastewater. A lab-scale reactor with a working volume of 12 L in which 4 L wheel-shaped polyethylene carrier materials (PE) and 4 L anaerobic inoculum were added. This reactor operated continuously at 35°C ± 2°C in 185 d under the volumetric loading rate with 12.2 kg-COD/m³ d. The average total chemical oxygen demand (COD) removal efficiency was 60% with a methane conversion efficiency of about 54%. A kinetic model referred from Anaerobic Digestion Model No. 1 was used to simulate reasonably the methane production, total COD, total suspended solids as well as the effluent compositions in terms of carbohydrate, protein, lipid, propionate, acetate, and ammonium nitrogen. In regression analysis, linear correlation showed that the simulation results almost corresponded with the experiment results. The model could be employed to design the AnMBBR at a pilot scale for the removal of organic matters in swine wastewater.

Keywords: Anaerobic; Moving bed biofilm reactor; Kinetic model; Swine wastewater

1. Introduction

Nowadays, the livestock sector in Vietnam tends to transfer from a household scale to a centralized scale. The number of livestock farms in Vietnam is more than 19,000 with 28 million pigs [1]. The amount of waste from this activity is approximately 84.5 million ton/y in which 20% of waste is used for biogas, compost, fish food, etc., and the remaining is not treated causing environmental

pollution. Japan International Cooperation Agency (JICA) and Institute of Environmental Technology surveyed 5 farms in the North of Vietnam (Hanoi, Vinh Phuc, Hung Yen, Thai Binh, and Hoa Binh) and showed that each pig consumes 10–40 L/d and produces 25 L/d [2]. Additionally, when the density of livestock increases, the load and the concentration of pollutants raise. To produce 1,000 kg of pork, 84 kg of urine, 39 kg of manure, 11 kg of total solids (TS), 3.1 kg of BOD₅ and 0.24 kg of NH₄⁺-N are daily generated [3].

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As livestock wastewater is a mixture of urine, feces, water to clean livestock cages, this wastewater contains high levels of organic matters, N, P, and microorganisms. However, these characteristics highly vary depending on many factors such as the size of livestock, race, age of animals, diet, temperature, and humidity in the cage, cleaning methods, dilution, storage, and liquid/solids separation. According to Vu et al. [4], the amount of manure discharged daily is 6%–8% of the weight of pigs and with different races, the amount of waste also changed. For medium-sized farms, wastewater was generated in the range of 30–35 m³/d, containing high concentrations of solids, organic matter, nitrogen, and phosphorus, as well as other pollutants [5]. Because of the high concentration of chemical oxygen demand (COD) and nitrogen, swine wastewater is one of the major pollution sources for the environment. Among the wastewater treatment, anaerobic digestion (AD) is a process where microorganisms break down biodegradable materials in the absence of oxygen, producing methane and carbon dioxide as end-products under ideal conditions [6]. This process has been widely applied to decompose swine wastewater. Due to a fast decay rate in anaerobic condition, microorganisms in activated sludge is almost digested completely in a few days. According to Yasui et al. [7] the anaerobic decay rate of heterotrophic organisms (X_{OHO}) in the waste activated sludge (WAS) was estimated to be 0.2/d which was equal to the estimated maximum specific growth rate of methanogens (μ_m) at mesophilic condition [8]. To increase the performance of WAS digestion, it would be necessary to retain biomass within the digester. From the assumption, by adding carrier media into the digester, the combination of the two different processes (biofilm and suspended biomass) was implemented. As a result, the performance of a high-rate anaerobic digester was experimentally evaluated.

High-rate anaerobic digesters have been applied for wastewater treatment in many years because of the high volumetric loading rates (VLRs), low solid waste, low energy consumption, short hydraulic retention times (HRTs), and methane production [9,10]. Most popular high-rate anaerobic digesters include moving bed biofilm reactor (MBBR), fix bed biofilm reactor (FBR), up-flow anaerobic sludge blanket (UASB), and expanded granular sludge beds (EGSB), etc. [10–12]. In which, anaerobic moving bed biofilm reactor (AnMBBR) has been proved to be reliable in treating vinasse, landfill leachate, winery, and dairy [13–16]. However, its application in swine wastewater treatment was rare.

In Vietnam, swine wastewater is mainly directed to biogas and finally discharged to ponds and lakes and the number of studies applied high rate anaerobic treatment is limited. Tran [2] combined anaerobic (internal circulation (IC) and anaerobic baffled reactor (ABR)), aerobic–anoxic (sequencing batch reactor (SBR)) and constructed wetland in treating swine wastewater. The pilot system with a capacity of 30 m³/d reaching COD, total nitrogen (TN), total suspended solids (TSS), and total phosphorous (TP) removal efficiencies were 98%, 96.82%, 99.9%, and 88.85%, respectively. In another research, Nguyen [17] applied UASB and aerobic–anoxic combined membrane filtration to gain high treatment efficiency. With HRT 1.52 d, COD, NH₄⁺, NO₃⁻, TN, and TP removal efficiencies were 98.3%, >99.9%,

88.3%, 97.5%, and 98.3%, respectively. Moreover, to describe and predict the performance of treatment systems, kinetic analysis is a potential technique. Even though Vietnam has some research focusing on this topic, the numbers were not much [18–20].

Thus, the purpose of this research was to investigate the performance of an AnMBBR and kinetics parameters of the organic degradation process in swine wastewater.

2. Materials and methods

2.1. Continuous experiment reactor

The continuous AnMBBR was carried out at 35°C ± 2°C, pH 7.0–7.5 with a working volume of 12 L (Fig. 1). 4 L anaerobic inoculums were collected from the UASB tank of the Sabeco Beer Manufacturing Plant (Nam Tu Liem district, Hanoi) operated with an MLSS of 20 g/L. The wastewater treatment system of this plant included a UASB-aerobic tank-settling tank with a capacity of 600 m³/d. 4 L of wheel-shaped polyethylene carrier materials (PE) with a specific surface area of 13.3–16.7 m²/kg, size of 15 mm diameter × 10 mm height was added into the AnMBBR.

The swine wastewater for the experiment was obtained from livestock farm with 3,000–5,000 heads in Kim Xa commune, Vinh Tuong district, Vinh Phuc province. The wastewater was collected at pits after washing activities and pre-treated with a 1 mm screen sieve to remove raw waste. After that, it was pumped into the AnMBBR at a flow rate of 1 L/h (HRT of 12 h). The sludge was recirculated for the microbial maintainance, stirring and speeding up the overflow rate at about 0.6–1.0 m/h. The VLR was increased from 4.1 to 12.2 kg COD/m³ d by changing COD concentration in each influent sample.

2.2. Analytical procedure

TSS, COD, TN, ammonium nitrogen, total phosphorus TP, and lipid concentrations were measured according to #2540 D; #5220 D; #4500-N B; #4500-NH₃ F; #4500-P E; and #5520 D in Standard Methods [21], respectively. Carbohydrates (total sugar) and proteins (peptide ponds) concentrations were calorimetrically analyzed using phenol-sulfuric acid and microbiuret methods [22,23] with glucose and egg albumin standard (Kishida Chemical, Japan).

The filtrate of the samples with 0.2 μm microfilter was used to analyze volatile fatty acids concentrations (VFAs) with a high-performance liquid chromatography system equipped with pump LC20AD and detector UV/VIS Shimadzu SPD-20A (Shimadzu, Japan). Symmetry300 C8 column (4.6 mm × 150 mm I.D., Waters Milford, MA, USA) was used for the peak separation where the elute flow rate was set at 0.5 mL/min under 25°C and detector wavelength was 210 nm. Mobile phase included 2 phases: 50% phase A (99.9% acetonitrile and 0.1% formic acid) and 50% phase B (99.9% deionized water and 0.1% formic acid).

Biogas production was measured by the liquid displacement method at normal conditions (25°C, 1 atm) in which saturated sodium chloride was used in the gasometer to minimize the solubility of gases [24]. The volume

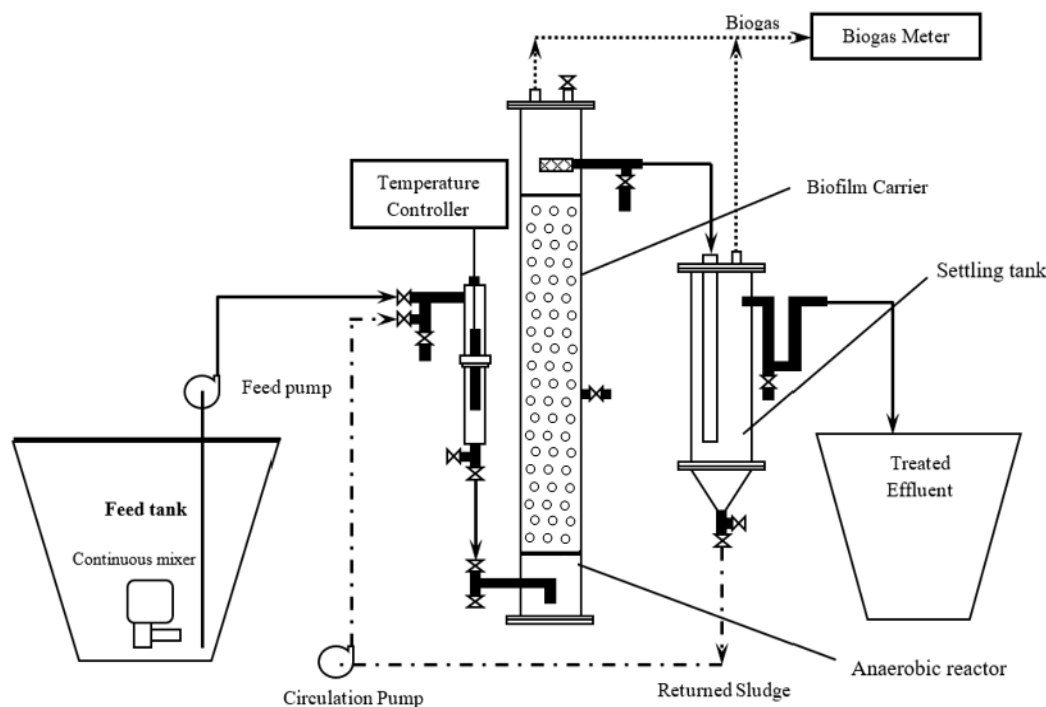


Fig. 1. Anaerobic moving bed biofilm reactor (AnMBBR).

of biogas at standard conditions was calculated by replaced biogas volume with the difference of pressure between the inside and outside of the gasometer as shown in the following equation. This equation was modified from [25]. Also, biogas was collected in gas sampling bags to measure the concentration of methane gas using Portable Biogas Analyser (Geotech Biogas 5000, UK).

$$V_0 = \frac{T_0}{T \cdot P_0} \left[\left((P - P_w - \rho \cdot g \cdot b_1) \cdot A \cdot a_1 \right) - \left((P - P_w - \rho \cdot g \cdot b_2) \cdot A \cdot a_2 \right) \right] \quad (1)$$

Here V_0 is the volume of biogas (m^3); T_0 is the temperature at normal condition (K); P_0 is the pressure at normal condition (Pa); P is the atmospheric pressure (Pa); P_w is the vapor pressure (Pa); ρ is the density of the liquid (kg/m^3); g is the acceleration due to gravity (m/s^2); a_1 is the height of gas before measurement (initial level) (m); a_2 is the height of gas after measurement (measurement level) (m); b_1 is the height of liquid before measurement (initial level) (m); b_2 is the height of liquid after measurement (measurement level) (m); A is the cross sectional area (m^2).

2.3. Dynamic simulation

Dynamic simulation of the AnMBBR was performed focusing on responses of methane production, total COD, TSS as well as the effluent constituents in terms of carbohydrates, proteins, lipids, propionate, acetate, butyrate, and ammonium nitrogen. For the simulation of the reactor performances and biological degradability of the wastewater organics mathematically, a kinetic model was referred from

Anaerobic Digestion Model No. 1 (ADM1) [26]. However, due to concentrations of valerate and lactate in the swine wastewater, and the digestate were very low throughout the experimental period, they were not included in the model. A process simulator (GPS-X ver.7.0, Hydromantis Environmental Software Solutions, Inc., Canada) was used to program the model and numerically solved the set of differential equations. The simulation layout for the reactor is shown in Fig. 2. To express the concentrated biomass in the AnMBBR, a solid-liquid separator was customized to entrap the relevant state variables in the system. Therefore, the diffusion resistance of soluble substrates in the biofilm was considered in the model. As listed in Table 1, the set of active biomass concentrations in the inoculum was used for the simulation. The active biomass concentrations were calculated from the biomass yield coefficients in the literature [26]. Firstly, a set of first-guess kinetics was applied to conduct the simulation. When the calculated concentrations of the substrate in the effluent did not match those measured, these parameters were calibrated and the simulation was again conducted.

3. Results and discussion

3.1. Composition of swine wastewater

The swine wastewater was used for the influent of the AnMBBR in 185 operation days and the constituents of the swine wastewater are listed in Table 2. In this, 4 samples corresponding to 4 VLRs from 4.1 to 12.2 $\text{kg-COD}/\text{m}^3 \text{d}$.

This wastewater had neutral pH (7.12–7.53) and contained high organics (TCOD fluctuated from 2,015–6,373 mg/L),

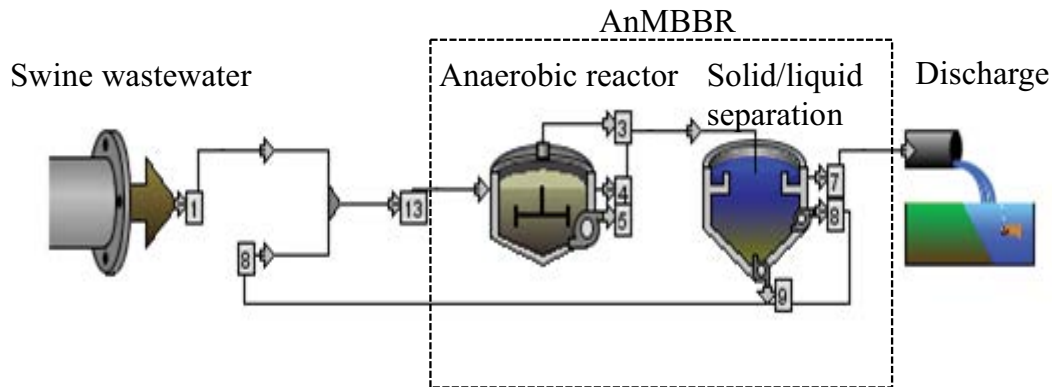


Fig. 2. Simulation layout of AnMBBR.

Table 1
List of initial biomass concentrations for simulation

| Microorganisms | Concentration (mg-COD/L) |
|--------------------------------|--------------------------|
| Sugar degrader | 100 |
| Amino acid degrader | 100 |
| Long chain fatty acid degrader | 100 |
| Butyrate degrader | 100 |
| Propionate degrader | 100 |
| Acetate utilizer | 100 |
| Hydrogen utilizer | 100 |

carbohydrates (117–770 mg/L), and proteins (970–1,897 mg/L). Besides, there was a significant amount of TSS in the wastewater (1,381–2,507 mg/L) while lipid concentrations were measured to be low (0.7–15.4 mg/L). In addition, concentrations of VFAs (acetate: 16–409 mg/L, propionate: 8.4–184.7 mg/L, and butyrate: 0.0–96.0 mg/L), total nitrogen (255–663 mg-N/L) and total phosphorus (38–117 mg-P/L) were detected in the composition of the swine wastewater.

Comparing to Tran Van Tua's research, in piggery wastewater, organic matter accounts for 70%–80% of the composition including leftovers, cellulose, protein, amino

acid, fat, carbohydrate compounds, and their derivatives. Most organic substances are biodegradable; however, some substances are difficult to decompose such as aromatic, polycyclic, chlorinated organic compounds. Inorganic substances account for 20%–30%, including sand, soil, salt, urea, ammonium, chloride, sulfate, etc. High contents of TN and TP were also found, in which 80%–90% of TN is ammonium [2].

3.2. Anaerobic digestion process

Methane production rate, VLR, total COD, and TSS are plotted as shown in Fig. 3. The initial VLR was 4.1 kg-COD/m³ d and continued to increase to achieve the VLR of 12.2 kg-COD/m³ d after 185 d of operation. MPR was corresponding with the increase and decrease of VLR. It suggests that the substrates in the reactor were biodegraded and converted into methane gas. However, the average methane conversion efficiency obtained 54% during the operation of the AnMBBR. The kinetic of the methanogens on the growth was estimated from the increase/decrease of MPR. Meanwhile, TCOD concentration kept in the range of 615–3,060 mg/L and TSS fluctuated from 436 to 1,140 mg/L. High TSS concentration proved that a significant amount of un-biodegradable particulates still

Table 2
Compositions of swine wastewater

| Parameters | Unit | Sample 1 (day 0–14) | Sample 2 (day 15–51) | Sample 3 (day 52–153) | Sample 4 (day 154–185) |
|---------------|----------|---------------------|----------------------|-----------------------|------------------------|
| pH | – | 7.3–7.4 | 7.28–7.4 | 7.12–7.53 | 7.28–7.51 |
| TCOD | mg-COD/L | 2,015–2,553 | 2,459–3,635 | 4,725–5,806 | 6,065–6,373 |
| TSS | mg/L | 1,813–1,955 | 1,695–1,979 | 1,381–2,507 | 1,822–2,118 |
| Carbohydrates | mg/L | 117–263 | 209–617 | 287–680 | 389–770 |
| Proteins | mg/L | 1,012–1,869 | 1,059–1,792 | 970–1,897 | 1,176–1,582 |
| Lipid | mg/L | 0.77–2.27 | 0.73–1.70 | 1.00–15.40 | 5.00–7.60 |
| Acetate | mg/L | 16.0–149 | 106–353 | 16.0–409 | 264–353 |
| Propionate | mg/L | 8.4–106.3 | 17.2–103 | 18.9–184.7 | 78.7–129.7 |
| Butyrate | mg/L | 10.6–96 | 0.0–92.1 | 2.0–94.0 | 9.3–15.3 |
| TN | mg-N/L | 255–476 | 433–591 | 391–599 | 467–663 |
| TP | mg-P/L | 38–82 | 52–100 | 63–117 | 67–86 |

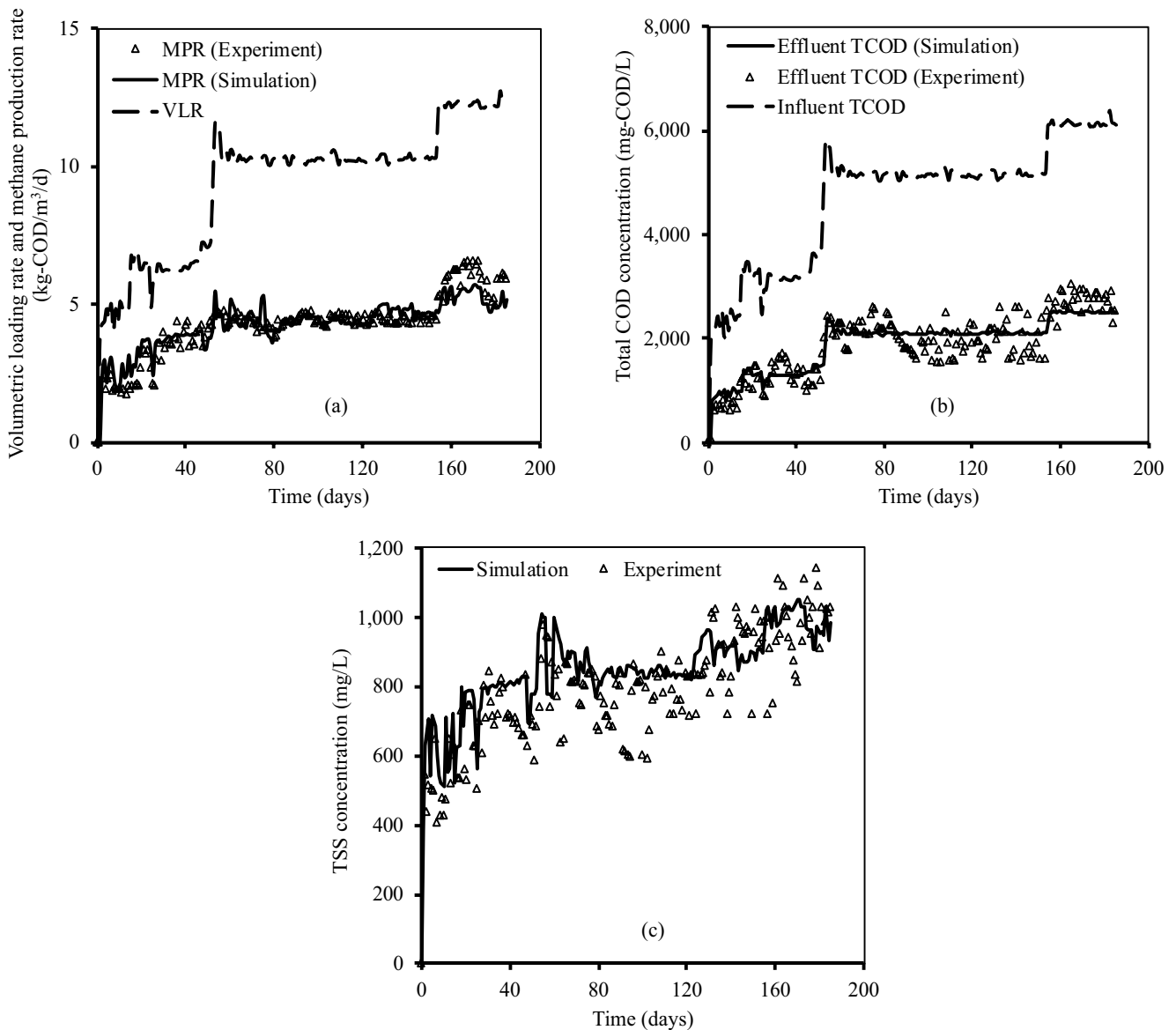


Fig. 3. (a) Volumetric loading rate and methane production rate, (b) TCOD, and (c) TSS concentration in the AnMBBR.

maintained in the reactor and detached biofilm. TCOD removal efficiency corresponded with the change of VLR and obtained an average value of 60%. The response of TCOD and TSS concentrations were reasonably simulated except for some data plots of TSS due to the analytical failure.

The effluent constituents in terms of carbohydrate, protein, lipid, and ammonium nitrogen are shown in Fig. 4 together with the simulation results. Comparing the total carbohydrate concentration in the influent (Table 2), removal efficiency reached 71% on average. It is indicated that almost carbohydrates were degraded, while approximately 46% of proteins (635 mg/L) still retained in the reactor. Besides, due to the concentration of lipids accounted for 0.1% in swine wastewater, its decomposition was insignificant (about 2.6 mg/L in effluent). The ammonia nitrogen in swine wastewater was not almost degraded in anaerobic condition and produced from the

protein decomposition [27,28] therefore the concentration was kept in the high concentration (325 mg-N/L).

During 185 d of operation, the VFAs appeared in the reactor with low concentrations (acetate: 15.3 mg/L, propionate: 11.2 mg/L, and butyrate: 4.6 mg/L on average). Even though the VLR increased to 12.2 kg-COD/m³ d, the reactor still worked well as shown in Fig. 5. It is reasonable to assume that this is a suitable environment (pH from 7.0 to 7.5, low VFAs concentrations) for the microorganism in anaerobic digestion. As a result, part of biodegradable particulate hydrolyzed completely and converted into methane at high VLRs as shown in the study of Liu et al. [28] and Van Anh et al. [29]. However, because antibiotics and growth promoters use behaviors in livestock husbandry in Vietnam, it results in the accumulation of these toxic in manure and wastewater. Siegrist et al. [8] defined that at least 45 antibiotics were

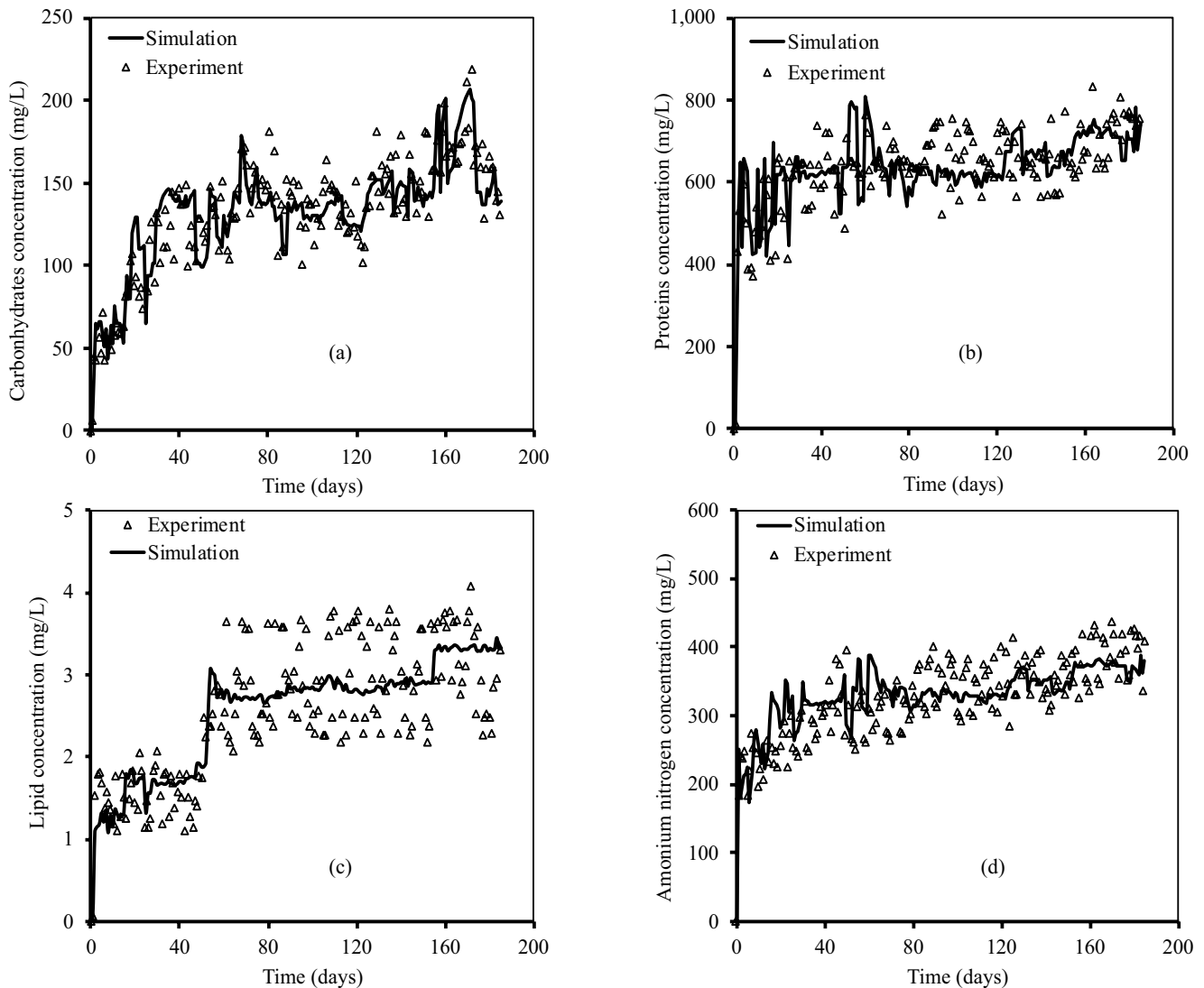


Fig. 4. (a) Carbohydrates, (b) proteins, (c) lipids, and (d) ammonium nitrogen concentration in the AnMBBR.

used in pig and poultry production from July 2019 to March 2010 on 270 entities, in 3 localities of the Red River Delta (RRD). Coyne et al. [30] explored antimicrobial in 36 pig farms in the Nam Dinh Province (North) and the Dong Nai Province (South) of Vietnam. According to Galí et al. [31] antibiotics have problematic effects on microorganisms and the performance of anaerobic processes. Therefore, the presence of antibiotics and other micropollutants in swine wastewater has been suggested to be the actual toxic agents that inhibited biogas production (methane conversion efficiency of about 54%) even with low VFAs concentrations.

3.3. Kinetic parameters

The initial biomass concentrations (Table 1) were used to simulate the performances of the AnMBBR. The entrapped proportions of acidogens (sugar, amino acid, long-chain fatty acid, butyrate, and propionate degrader) and methanogens (acetate and hydrogen utilizer) were calculated to

be 80% and 60% [29]. This proved the important role of bio-film in the anaerobic digestion process in keeping the relevant active biomass to improve the degrading of organic matters. Comparing to the default values in the references [8,26,31–41] these kinetics were in the reasonable range except for some parameters (maximum specific rate of amino acid, butyrate, propionate, acetate, and hydrogen) as shown in Table 3. Kinetic parameters were carried out by a trial-and-error approach to match the experiment and simulation curves. For example, the disintegration rate (r_1) was estimated from TCOD concentration, while kinetics for carbohydrate hydrolysis (r_2) and sugars (r_5) were estimated from the concentrations of carbohydrates and organic acids. The kinetics for protein hydrolysis (r_3) and amino acids (r_6) came from a variety of proteins and ammonium nitrogen concentrations. The kinetics for lipid hydrolysis (r_4) and long-chain fatty acids (r_7) were obtained from the increment and decrement of lipid concentrations. For uptake of butyrate (r_8) and propionate (r_9), the kinetics attended

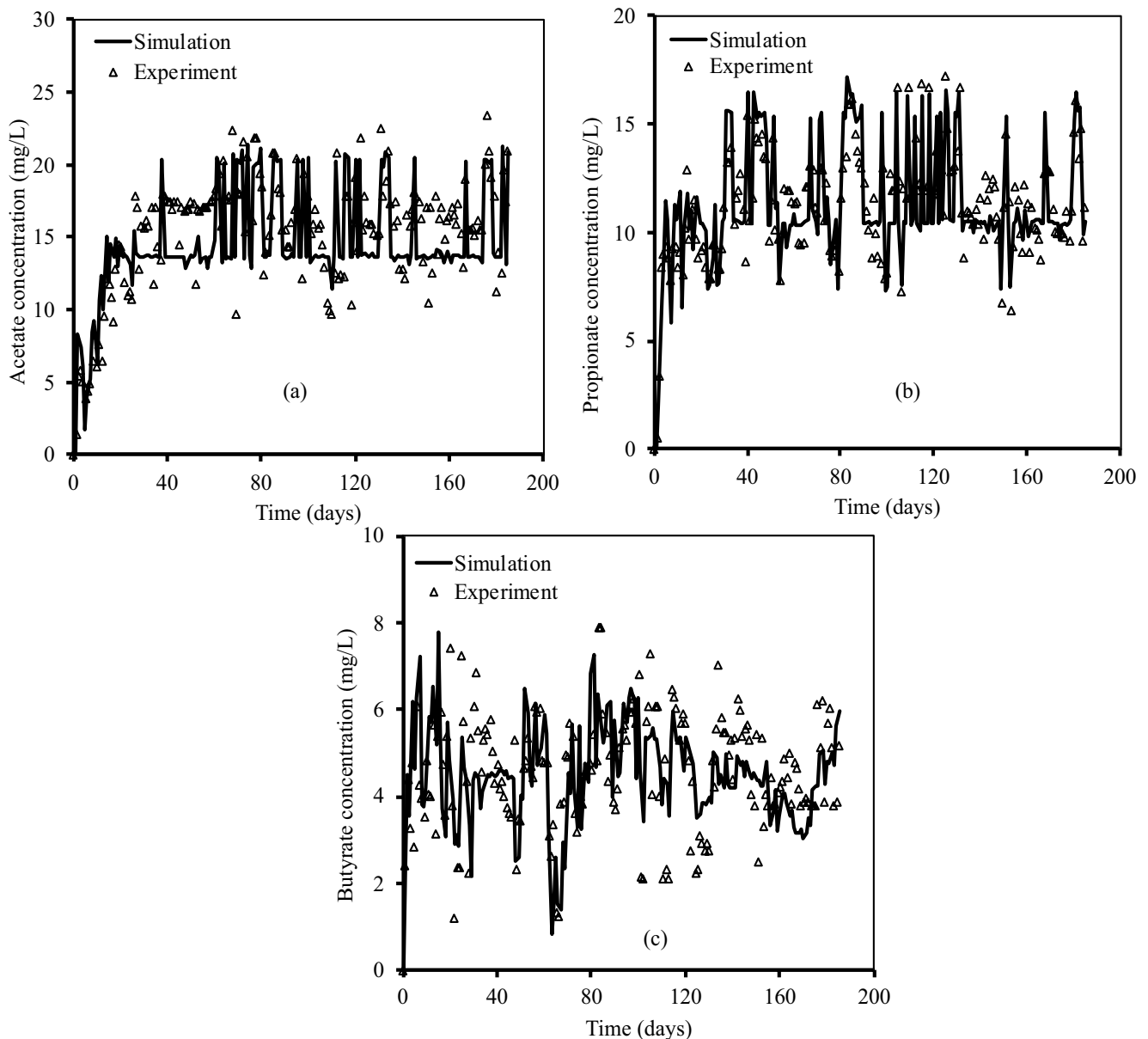


Fig. 5. Volatile fatty acids (VFAs) concentrations (a) acetate, (b) propionate, and (c) butyrate in the AnMBBR.

by focusing on the concentrations of organic acids. Acetate concentrations were used to calibrate the kinetics of acetoclastic methanogen (r_{10}), whilst kinetics of the acetoclastic and hydrogenotrophic methanogen (r_{10} and r_{11}) were estimated by MPR. The specific decay rates (r_{12} – r_{18}) on the dynamic simulation were obtained from some literature.

3.4. Model fitting

As shown in Figs. 3–5 the observed and model expected data (calculated) almost fitted. In addition, in regression analysis, linear correlation with equation $y = ax$ was shown between the model calculated results and the observed ones (Fig. 6). The correlation is significant at a value ≈ 1 or >1 and R^2 value $\rightarrow 1$. It can be seen that, simulation results in MPR, TCOD, carbohydrate, protein, lipid,

acetate, and butyrate with good value (0.99–1.00) and high R^2 value (0.5–0.81) except low R^2 value of butyrate (0.25). Although other parameters had lower a and R^2 value, these numbers still were in the acceptable range.

4. Conclusions

This research proved that the high-rate AnMBBR could be applied to treat the swine wastewater in Vietnam, where biogas reactors are currently mainly used to solve the problem. Most of the organics in the wastewater were biodegradable and converted to methane gas. The average TCOD removal efficiencies were 60% with a methane conversion efficiency of about 54% during 185 d of operation with VLR increased from 4.1 to 12.2 kg-COD/m d. A kinetic model referred from ADM1 simulated reasonably

Table 3
List of kinetics for anaerobic degradation of the swine wastewater

| Process | Maximum specific rate (d ⁻¹) | | Half-saturation coefficient (mg-COD/L) | |
|---------------------------------------------|------------------------------------------|--------------------------|----------------------------------------|---------------------|
| | This study | References | This study | References |
| r1 Disintegration rate | 2.88 | 0.5–3 [21,32,33] | Nil | |
| r2 Hydrolysis of carbohydrate | 8.98 | 0.5–10 [21,28,33] | Nil | |
| r3 Hydrolysis of protein | 4.92 | 1–10 [21,26,33] | Nil | |
| r4 Hydrolysis of lipid | 5 | 5–10 [21,26,33] | Nil | |
| r5 Uptake of sugars | 100 | 27–125 [21,25,29] | 50 | 3–90 [21,25] |
| r6 Uptake of amino acid | 150 | 27–53 [8,21,25] | 30 | 7.5–70 [21] |
| r7 Uptake of long chain fatty acid | 30 | 0.6–363 [21,25,26,35] | 40 | 24–1,000 [21,25,26] |
| r8 Uptake of butyrate | 0.1 | 5.3–41 [21,29,31] | 10 | 12–298 [21,29] |
| r9 Uptake of propionate | 130 | 0.16–23 [21,25,26,34,36] | 10 | 20–100 [21,25,26] |
| r10 Uptake of acetate | 84 | 0.37–19 [21,25,26,34] | 15 | 0.2–150 [21,25,26] |
| r11 Uptake of hydrogen | 105 | 2–64 [21,25,26,29] | 0.007 | 0.007–1 [21,25,26] |
| r12 Decay of sugar degrader | 0.21 | 0.02–0.8 [21,25,31] | Nil | |
| r13 Decay of amino acid degrader | 0.001 | 0.02–0.8 [8,21,25] | Nil | |
| r14 Decay of long chain fatty acid degrader | 0.001 | 0.01–0.06 [21,25,27] | Nil | |
| r15 Decay of butyrate degrader | 0.001 | 0.027–0.03 [8,21,29,31] | Nil | |
| r16 Decay of propionate degrader | 0.041 | 0.01–0.2 [21,25] | Nil | |
| r17 Decay of acetate utilizer | 0.001 | 0.004–0.05 [21,25,29] | Nil | |
| r18 Decay of hydrogen utilizer | 0.04 | 0.009–0.3 [21,25] | Nil | |

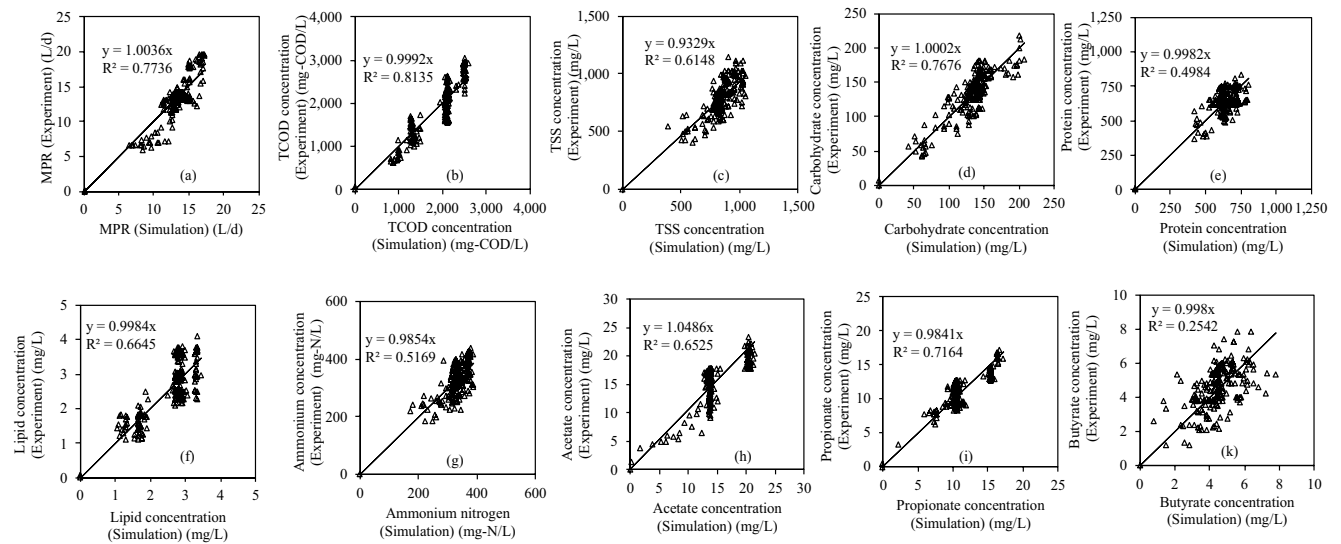


Fig. 6. Model fitting for (a) MPR, (b) TCOD, (c) TSS, (d) carbohydrate, (e) protein, (f) lipid, (g) ammonium nitrogen, (h) acetate, (i) propionate, and (k) butyrate.

the methane production, TCOD, total suspended solid as well as the effluent compositions in terms of carbohydrate, protein, lipid, propionate, acetate, butyrate, and ammonium nitrogen. In regression analysis, linear correlation showed that the simulation results almost fitted with the experiment results. This research is also one of the studies applying modeling in wastewater treatment in Vietnam. The model could be employed to design the AnMBBR at

a pilot scale for the removal of organic matters in swine wastewater.

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