

Research Article

VSS Degradation Kinetics in High Temperature Aerobic Digestion and Microbial Community Characteristics

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Piggery wastewater is a kind of high concentration organic wastewater with high concentration of pollutants, large amount of emissions, and serious environmental pollution and is difficult to deal with. Piggery wastewater was treated with autothermal hyperthermia aerobic digestion process (ATAD) and its biodegradation kinetics was studied. The ATAD system was automatically heated up and the reaction temperature rose from ambient temperature of 20°C to a maximum temperature of 64°C. Based on Arrhenius formula, the empirical model is obtained through dimensional analysis. The removal of volatile suspended solids (VSS) was correlated with the initial VSS concentration, water inlet temperature, aeration rate, and agitation rate in the model. In the empirical model, the apparent activation energy was 2.827 kJ·mol⁻¹. The exponentials for the initial VSS concentration, aeration rate, and stirring rate were 1.0587, -0.0976, and -0.1618, respectively. The correlation coefficient of the exponential factor was 0.9971. The VSS removal efficiency predicted by the model was validated with an actual test, showing a maximum relative deviation of 8.82%. Sludge systems show a lower diversity of microbial populations and *Bacillus* occupies a very important position in the reactor. The data obtained will be useful for optimizing piggery wastewater treatment process. The new model provided good theoretical guidance with good practicality.

1. Introduction

With the continuous expansion of pig industry, piggery wastewater production continued to increase [1]. Piggery wastewater contains a lot of nitrogen and organic matters, which has posed serious threats to the environment and human health [2]. There are three main approaches to removing manure from piggery in China, namely, urine-free manure (UFM), combined manure with urine (CMU), and soaked manure with urine (SMU). As a traditional mode, UFM collection has been widely used in China [3, 4]. Numerous studies have been conducted on the treatment of piggery wastewater. For example, Zhang et al. [5] studied anaerobic codigestion of piggery wastewater and food waste and identified the key factors governing codigestion performance. Han et al. [2] investigated the effect of feeding strategy on the treatment of swine wastewater, showing that the feeding ratio had a more significant effect on the removal of phosphorus and nitrogen than on the removal of chemical

oxygen demand (COD) in the sequencing batch reactor (SBR) system.

Pig manure wastewater generally contains high concentrations of COD, N (nitrogen), P (phosphorous), pathogenic bacteria, organic matters, and nutrients [6]. At present, incineration technology is predominant in the treatment of high concentrations of pathogenic microorganisms. However, it exposes many disadvantages, such as high energy consumption and complicated operation [7]. Self-heating high temperature aerobic digestion process uses the thermophilic microbial metabolism (i.e., cell death, hydrolysis, and biosynthesis) so as to achieve the degradation of organic matters and the eradication of pathogens. In this process, the microorganisms use oxygen for their own oxidative decomposition, releasing heat. There are two main roles in the ATAD process: the degradation of organic matters by microorganisms under the presence of active enzymes and the disintegration of extracellular enzymes. The second

TABLE 1: Compositions of the piggery wastewater.

Influent VSS (g/L)	TP (mg/L)	NH ₃ -N (mg/L)	TN (mg/L)	COD _{Cr} (mg/L)	pH
7–55	40–50	1100–1300	1200–1400	5000–6000	8.0–9.0

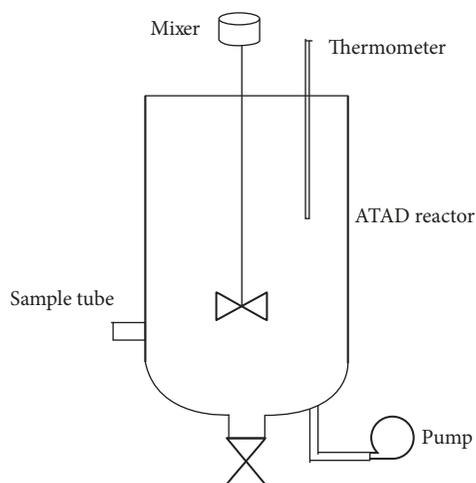


FIGURE 1: The sketch map of the ATAD experimental equipment.

process has a key effect on the inactivation of pathogens and the removal of VSS [8]. ATAD is more stable than other sludge treatments (e.g., anaerobic digestion) and is not susceptible to fluctuations in operating conditions. Therefore, ATAD has gained widespread attention in the field of environmental engineering, and some ATAD processes have been successfully applied in other fields. [9–11].

During aerobic digestion of sludge, the microorganisms are in the endogenous respiration phase, so the reaction rate and biomass follow the first-order reaction equation [12]. The most commonly used model is Adams proposed model. However, the Radall study found that solid suspended solids decreased during the remaining activated sludge digestion, suggesting that the Adams model is not the same as the actual situation [13]. Gomez et al. [14, 15] did not consider the effect of temperature. They put the ATAD model as ASM1 model.

In order to provide theoretical guidance for wastewater treatment and engineering design, the effects of parameters such as agitation rate, reaction temperature, aeration rate, and influent concentration on VSS removal were studied. The empirical model of laboratory scale was established.

2. Materials and Methods

2.1. Wastewater Sources and Water Quality. The raw manure-free piggery wastewater was collected from a local pig farm in Harbin, China. Influent quality of the wastewater fluctuates along with breeding seasonality. Compositions of the piggery wastewater and the experimental operation parameters are summarized in Table 1.

2.2. ATAD Reaction System. As shown in Figure 1, the device of ATAD consists of a mixing system, an aeration system,

and a thermometer. A water bath was used to maintain the reaction temperature. The main body of the reactor is wrapped with a 2 cm thick insulating material. The effective volume of the reactor is 2.8 L.

In the experiment, a prescribed amount of piggery wastewater was added to the reactor. The stirring speed and aeration rate were adjusted. The temperature of the reaction was measured using a thermometer and adjusted through the water bath. There is a sampling tube in the bottom of the reactor. In order to minimize the heat loss caused by the temperature difference between the environment and the reaction system, the temperature of the water bath is about 5°C lower than the temperature of the reactor (except Section 3.4). In addition, in order to keep the amount of water in the reactor constant, deionized water of the same amount of the same temperature was added to the reactor daily. The reaction temperature was 20–60°C, the stirring rate was 125–215 r·min⁻¹, and the aeration rate was 10–30 L·h⁻¹.

2.3. Analytical Methods. The effects of influent concentration, aeration amount, and stirring speed on the reaction temperature, the removal rate of TSS and VSS, and the reaction time were investigated. TSS, VSS, NH₃-N, phosphorus (P), alkalinity, pH, COD_{Cr}, dissolved oxygen (DO), and temperature were measured once a day, and BOD₅ was measured once every four days. These indicators were used to reflect the operation of the ATAD reactor. At the same time, we also evaluated the number of total flora, roundworm eggs, fecal coliforms, fecal streptococci, and salmonella to assess the contribution of the ATAD process to sludge stabilization. The analytical standard methods were adopted.

Microbial population structure analysis was performed using 454 high-throughput sequencing method; the steps include (1) genomic DNA extraction; (2) PCR amplification; (3) fluorescence quantification; (4) MiSeq sequencing; (5) the OTU division of the sequence.

2.4. Domestication Process. Two liters of activated aerobic sludge, taken from Jilin Sewage Treatment Plant, was placed in a 2.5 L glass reaction vessel combined with aeration and stirring apparatus. The jar was firstly placed in the water bath thermostat and the insulation layer was added around it to prevent heat loss. The temperature of the water bath was compatible with the system temperature (below system 1~2°C). The aeration rate was adjusted to 10~15 L·h⁻¹ and stirring speed to 180~200 r·min⁻¹ [16].

The activated sludge was cultured for 7 days and the temperature and settling ratio (SV) were measured daily. After 7 days of domestication, aerobic sludge volume has been reduced by about 1/3. The temperature can be automatically increased, and the maximum temperature reached 62°C, indicating that the success of domesticated strained.

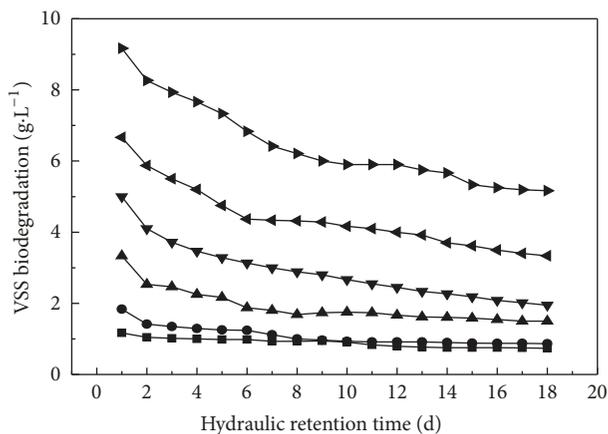


FIGURE 2: Effect of concentration on VSS removal. Concentration/ $\text{g}\cdot\text{L}^{-1}$: ■ 7; ● 11; ▲ 20; ▼ 30; ◀ 40; ▶ 50.

By changing the temperature and sludge volume, the thermophilic bacteria that were domesticated successfully can be used as bacteria into the reactor.

3. Result Analysis

3.1. The Effect of Feed Concentration on VSS Removal Efficiency. Figure 2 shows the degradation results at different feed VSS concentrations in ATAD at an initial temperature of 25°C . The feed VSS concentration varied from 7.00 to 55.00 $\text{g}\cdot\text{L}^{-1}$, and the effluent VSS concentrations ranged from 4.40 to 31.00 $\text{g}\cdot\text{L}^{-1}$ on the 17th day of reaction. Removal efficiency of VSS ranged from 37.14% to 61.00% . When the feed VSS concentration was as high as 40 $\text{g}\cdot\text{L}^{-1}$, the VSS removal efficiency was 52.08% , indicating that the ATAD process was applicable to biodegradation of a wide range of VSS concentrations. However, when the VSS concentration is greater than 30 $\text{g}\cdot\text{L}^{-1}$, the viscosity of material increases so that the mixing is poor and oxygen transfer is inhibited. At low VSS concentrations (below 30 $\text{g}\cdot\text{L}^{-1}$), the self-heating is not enough to maintain a relatively high temperature and degradation rate [17, 18]. The removal efficiency of *Ascaris* eggs in the ATAD system was 100% . When the feed concentration was high (greater than 30 $\text{g}\cdot\text{L}^{-1}$), the removal rates of the total numbers of flora and the number of fecal coliforms and *Streptococcus faecalis* were higher. The removal rate of fecal coliforms reached 99.95% and the fecal coliform removal rate reached 99.99% when the sludge concentration was 40 $\text{g}\cdot\text{L}^{-1}$. When the sludge concentration was 30 $\text{g}\cdot\text{L}^{-1}$, the removal rate of *S. faecalis* was 99.94% . When the feed concentration was high, the organic content was large. Oxidative decomposition of the heat can effectively increase the temperature of the system, which is conducive to the inactivation of pathogens. Thus, the optimum influent VSS concentration is 30.00 $\text{g}\cdot\text{L}^{-1}$.

3.2. The Effect of Stirring Rates on VSS Biodegradation. Better mixing is needed for mass transfer, reaction substrate, DO,

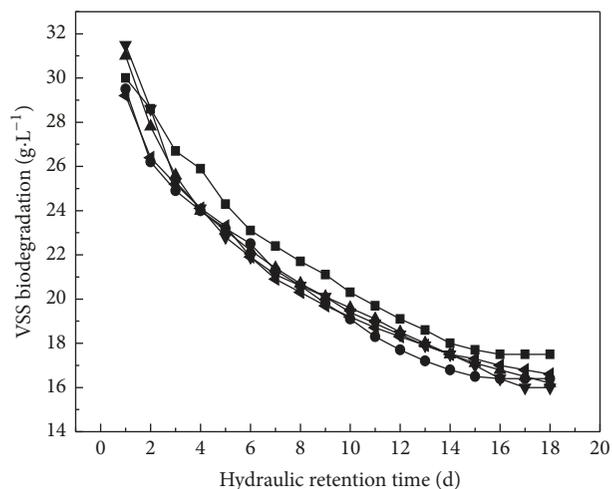


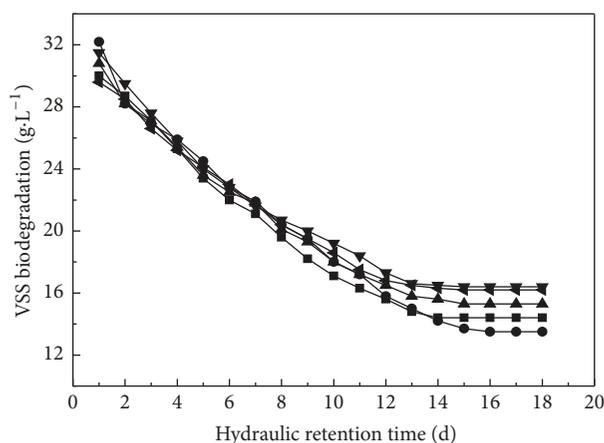
FIGURE 3: The influence of stirring rate on VSS removal. Stirring rate/ $\text{r}\cdot\text{min}^{-1}$: ■ 125; ● 145; ▲ 165; ▼ 185; ◀ 215.

and thermophilic bacteria. Mixing rate is an important factoring affecting mass transfer, reaction substrate, concentrations of DO, and thermophilic bacteria [1]. The feed VSS concentration was 29.20 – 31.50 $\text{g}\cdot\text{L}^{-1}$, and the reaction temperature finally reached 62°C from room temperature. The effects of stirring rate on the VSS degradation are shown in Figure 3. At the same feed VSS concentration and aeration rate, low mixing intensity (below 185 rpm) was not enough for fully mixing, adequate endogenous respiration, complete heat release, quick increase of self-heating rate in the system, and high VSS removal rate. However, when the stirring rate was increased to 215 rpm, the self-heating rate in the system declines and was $4.0^{\circ}\text{C}\cdot\text{d}^{-1}$ in the first 12 days, with a maximum VSS removal efficiency of 43.15% . When the stirring rate was 185 rpm, the biodegradation rate of VSS increased by 6.05% compared to that at 215 rpm. *Ascaris* egg removal rates had reached 100% . When the stirring rate was 185 rpm, the removal rate of the total bacterial population was the highest, reaching 99.95% . Higher mixing intensity may dissipate more reaction heat and decrease the temperature in the system. Thus, 185 rpm was considered as the optimal stirring rate.

3.3. The Effect of Aeration Rate on VSS Biodegradation. At the VSS concentration of 30 $\text{g}\cdot\text{L}^{-1}$, five different aeration rates (10 , 15 , 20 , 25 , and 30 $\text{L}\cdot\text{h}^{-1}$) were used at stirring rate of 185 rpm with running for 18 days. When the aeration rate was 10 $\text{L}\cdot\text{h}^{-1}$, the average temperature rising rate in the reactor is $2.07^{\circ}\text{C}\cdot\text{day}^{-1}$, the system temperature reaches 61°C with the removal rate of VSS reaching 52% . When the aeration rate was 20 $\text{L}\cdot\text{h}^{-1}$, the VSS removal rate was the most efficient, reaching 50.32% , while the sludge stabilization standard was achieved, and the final temperature of the system reached 63°C . When the aeration rate was 30 $\text{L}\cdot\text{h}^{-1}$, the removal rate of VSS was 45.27% , which was 12.8% lower than that of 15 $\text{L}\cdot\text{h}^{-1}$. When the oxygen supply was less than 15 $\text{L}\cdot\text{h}^{-1}$, the oxygen needed for aerobic digestion of microorganisms cannot be

TABLE 2: The rate constants in the empirical model.

Temperature (°C)	K (mg/L·d)	Correlation coefficient
20	1.1391	0.9963
30	1.1845	0.9847
40	1.22	0.9831
50	1.2718	0.9927
60	1.3073	0.9914

FIGURE 4: The influence of aeration rate on VSS removal. aeration rate/L·h⁻¹: ■ 10; ● 15; ▲ 20; ▼ 25; ◀ 30.

satisfied, resulting in poor microbial activity and slow VSS degradation. When the aeration rate is more than 20 L·h⁻¹, the aeration will make the system heat dissipation, which will lead to the system temperature decrease, thereby affecting the removal of VSS. Under different aeration rates, the removal rates of *Ascaris* eggs were all 100%. When the aeration rate was 15 L·h⁻¹, the removal rate of total number of bacteria was the highest, reaching 99.99%. As shown in Figure 4, the removal rates of VSS were the highest at the aeration rate of 15 L·h⁻¹, which is considered as the best rate under the experimental conditions.

3.4. The Effect of Temperature on VSS Biodegradation. In general, the effect of temperature on reaction rate may be described by Arrhenius-type formula. The action rate increases with temperature considerably due to the exponential function of temperature [19]. Therefore, high temperatures were generally chosen. The influent VSS was about 30 g·L⁻¹, the aeration rate was 15 L·h⁻¹, and the stirring rate was 185 rpm. The temperature changed in the range of 20–60°C. Figure 5 shows that the VSS biodegradation rate increased with temperature significantly. At 60°C, the VSS removal rate was 61.19%, increasing by 22.48% compared with that at 20°C, and it was increased by 4.94% at 50°C. For the cost-effective and efficient removal of VSS, it was advantageous to maintain higher temperature. The maximum temperature obtained from self-heating was 64°C in the process.

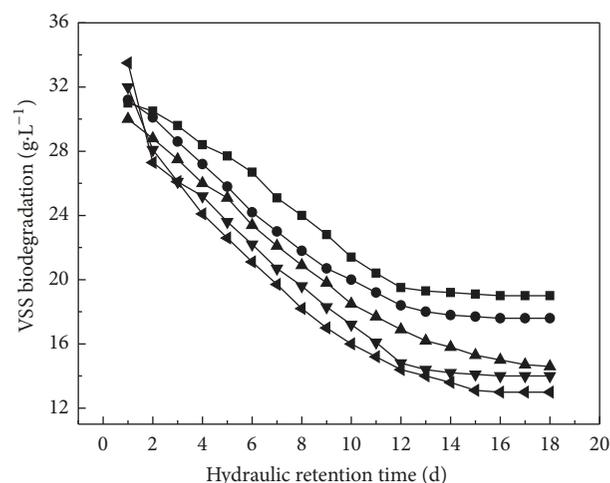


FIGURE 5: Effect of temperature on VSS degradation. Temperature/°C: ■ 20; ● 30; ▲ 40; ▼ 50; ◀ 60.

4. Empirical Kinetic Model for VSS Biodegradation

4.1. Arrhenius-Type Empirical Kinetic Model. The empirical kinetic model is an Arrhenius-type equation [19–21]. By dimensional analysis [22–24], the equation can be written as follows:

$$\frac{d(\text{VSS})}{dt} = -k^0 \exp\left(\frac{-Ea}{RT}\right) \cdot \text{VSS}^m \cdot O^n V^q, \quad (1)$$

$$\frac{d(\text{VSS})/dt}{dT} = -k^0 \exp\left(\frac{-Ea}{RT}\right) \cdot \text{VSS}^m \cdot O^n V^q \cdot \frac{Ea}{RT^2}, \quad (2)$$

where k^0 , Ea , m , n , and q could be determined by experiments.

4.2. Regression Results and Model Validation. At different temperatures, the reaction rates were shown in Figure 5. The rate constant $k[\exp(-Ea/RT)]$ in the model was obtained by the least square regression method. The regression was achieved from the second day to the twelfth day. The k value was calculated from the regression equation. The results obtained are shown in Table 2.

By the logarithm of the Arrhenius formula, the relationship between $\ln k$ and $1/T$ was obtained, which resulted in a straight line. From the slope, the apparent activation energy could be calculated, and from the intercept the factors can be obtained (as shown in Figure 6), which are 2.827 kJ·mol⁻¹ and

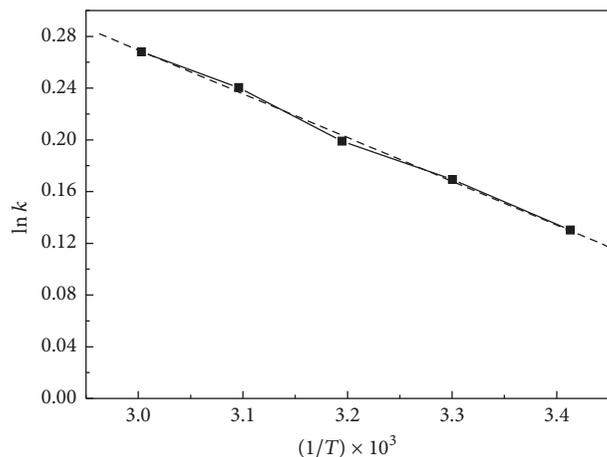


FIGURE 6: The relationship between $\ln k$ and $1/T$. —■— regression coefficient of 0.9971; ----- $\ln k = 1.2846 - 0.3384/T$.

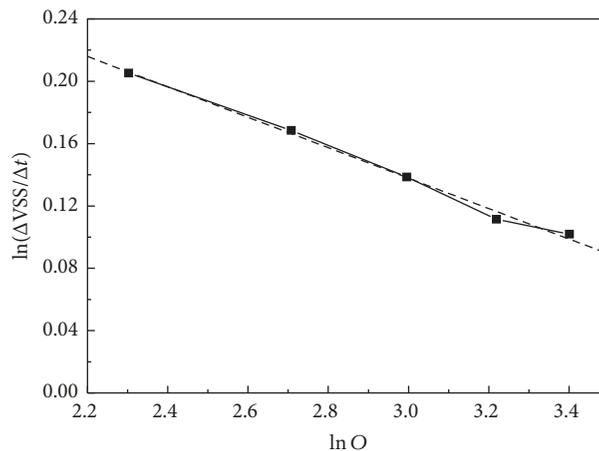


FIGURE 8: The relationship between VSS biodegradation rate and aeration rate. —■— regression coefficient of 0.9943 for n ; ----- $\ln(\Delta VSS/\Delta t) = 0.4308 - 0.0976 \ln O$.

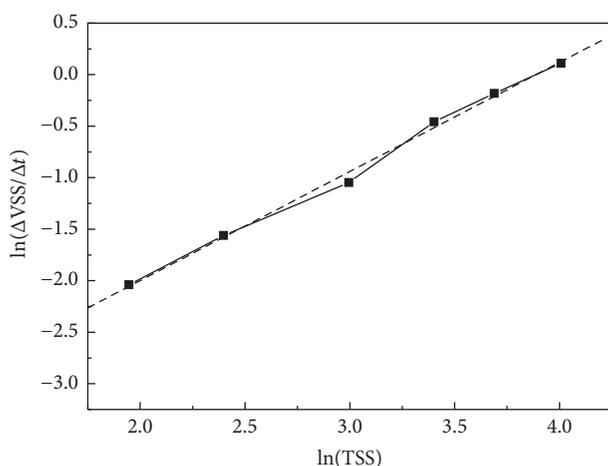


FIGURE 7: The relationship between VSS biodegradation rate and its concentrations. —■— regression coefficient of 0.9955 for m ; ----- $\ln(\Delta VSS/\Delta t) = 1.05871 \ln(VSS) - 4.1165$.

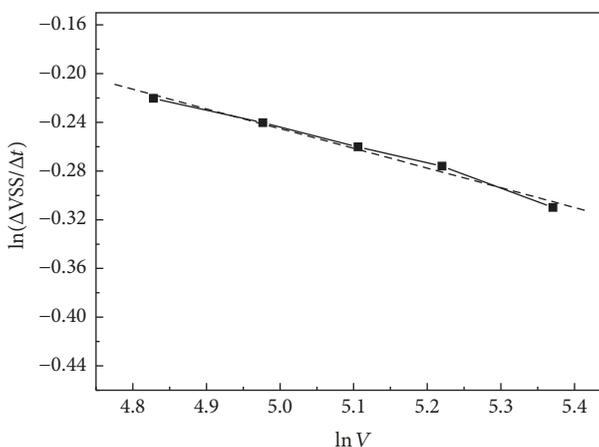


FIGURE 9: The relationship between VSS degradation rate and stirring rate. —■— regression coefficient of 0.9872 for q ; ----- $\ln(\Delta VSS/\Delta t) = 0.5637 - 0.1618 \ln V$.

$3.59 \text{ (g}\cdot\text{L}^{-1}\text{)}^{-1.0587} \cdot \text{(ml}\cdot\text{s}^{-1}\text{)}^{0.0976} \cdot \text{(r}\cdot\text{min}^{-1}\text{)}^{0.1618}$, respectively. The correlation coefficient for k^0 is 0.9971. By substituting both sides of formula (1), the exponents m , n , and q in the equation were obtained from the data in Figures 2, 3, and 4, respectively. The values of m , n , and q are shown in Figures 7–9, which are 1.0587, -0.0976 , and -0.1618 , respectively. The reaction order for VSS concentration is 1.0587 in this study, which is different from the first-order reaction kinetics obtained by Liu et al. [25, 26] for the aerobic sludge digestion or biological system [21].

The VSS concentration at time t , VSS_t , was obtained according to (2) as follows:

$$VSS_t = VSS_0 - 3.59 \times \left[\exp\left(-\frac{2826.76}{RT}\right) - \exp\left(-\frac{2826.76}{RT_0}\right) \right] \times t \quad (3)$$

$$\times VSS_0^{1.0587} \times O^{-0.0976} \times V^{-0.1618}.$$

The data calculated by (3) is compared with the average of the experimental data, which is shown in Table 3. Table 3 shows that the maximum deviation is 8.82%, so the VSS removal efficiency can be predicted by (3).

5. Microbial Community Structure Characteristics

The sludge aerobic digestion system is affected by the digestion temperature and the source of sludge, and the population of thermophilic microorganisms is more complex. Studies have shown that there are clostridium species other than aerobic thermophiles in high temperature aerobic reactors. Based on OTU cluster analysis results, Table 4 shows the analysis of various types of bacteria and their share of the results.

As can be seen from Table 4, the sludge system showed a lower level of microbial population diversity; a total of seven species were detected. More than 89% of the thermophilic

TABLE 3: Relative deviation between experimental and calculated VSS concentrations.

Reaction time (d)	Measured value (mg/L)	Calculated value (mg/L)	Relative deviation/%
40°C			
3	27.5	26.88	2.25
6	23.4	23.76	-1.54
9	19.8	20.64	-4.24
50°C			
3	26.1	27.38	-4.90
6	22.2	22.76	-2.52
9	18.3	18.14	0.87
60°C			
3	26.1	27.5	-5.36
6	21.1	21.5	-1.90
9	17.0	15.5	8.82

TABLE 4: ATAD reactor strain analysis.

Serial number	Species name	Proportion/%
1	<i>Bacillus stearothermophilus</i>	32%
2	<i>Bacillus thermocloacae</i>	22%
3	<i>Bacillus licheniformis</i>	15%
4	<i>Brevibacillus</i>	11%
5	<i>Sphaerobacter thermophilus</i>	9%
6	<i>Schineria larvae</i>	7%
7	<i>Clostridium</i>	4%

microorganisms in the device belong to the genus *Bacillus*, with a large number of *Bacillus stearothermophilus* being the most abundant species in *Bacillus* (32% of isolates), followed by *Bacillus stearothermophilus* (22% of isolates). In addition to the species of aerobic thermophilic bacteria in the system, there are other thermophilic microorganisms such as *Schineria larvae* and Clostridia. Ugwuanyi study found that only when the sludge digestion temperature is higher than 55°C, the *Bacillus stearothermophilus* becomes the dominant population. When the digestion temperature was 50°C, *Bacillus licheniformis* and *Bacillus coagulans* became the dominant species. The types of thermophilic bacteria are affected by sludge source and other factors. There may be great differences in the types of thermophilic bacteria in ATAD reactors of different wastewater treatment plants, but *Bacillus* plays a very important role in the reactor.

6. Conclusions

An empirical biodegradation kinetic model of Arrhenius-type was obtained in the ATAD test for the treatment of pig-gery wastewater. The indices of VSS concentration, aeration rate, and agitation rate are m , n , and q , respectively. Each index is solved by logarithmic differential method. The values of m , n , and q are 1.0587, -0.0976, and -0.1618, respectively. In the experimental temperature range, the apparent activation energy E_a is 2.827 kJ·mol⁻¹, the preexponential factor k^0 is 3.59 (g·L⁻¹)^{-1.0587}·(ml·s⁻¹)^{0.0976}·(r·min⁻¹)^{0.1618}, and the correlation coefficient for k^0 is 0.9971. The relative deviation between the data obtained from the empirical formula and

the experimental data is less than 8.82%. Sludge systems show a lower diversity of microbial populations. More than 89% of the thermophilic microorganisms in the device belong to the genus *Bacillus*. The model provides theoretical guidance for wastewater treatment and engineering design.

Nomenclature

E_a :	Activation energy, J·mol ⁻¹
K :	Rate constant
k^0 :	Preexponential factor
M :	Reaction order of total suspended solids
N :	Exponent of aeration rate
O :	Aeration rate, ml·s ⁻¹
q :	Exponent of stirring rate
R :	Gas constant (=8.3145 J·mol ⁻¹ ·K ⁻¹)
T :	Reaction temperature, K
T_0 :	Room temperature, K
VSS:	Concentration of volatility suspended solids, g·L ⁻¹
VSS ₀ :	Influent concentration of VSS, g·L ⁻¹
VSS _{t} :	Concentration of VSS at time t , g·L ⁻¹
t :	Reaction time, min
V :	Stirring rate, r·min ⁻¹ .

Conflicts of Interest

The authors declare that they do not have any commercial or associative interest that represents conflicts of interest in connection with the work submitted.

Acknowledgments

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