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The role of coated nanoscale zero-valent iron with magnesium hydroxide in improving methane production during the anaerobic digestion of waste sludge

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Abstract: *This study investigates the role of coated/Fe^0 in improving the anaerobic digestion process for the purpose of increasing methane gas production rate as one of the renewable sources of energy. Up until now, the anaerobic digestion of methane production by utilizing different environmental wastes is facing many challenges including the low conversion of biomass into energy. Therefore, in this work, we used the coated/Fe^0 with magnesium hydroxide as an additive during the anaerobic digestion of waste sludge. Two semi-continuous bioreactors were operated with and without adding the coated/Fe^0 over 70 days. The result showed that the addition of coated/Fe^0 enhanced methane production by 120% compared with the control reactor. The experimental and predicted methane values have proved the great potential of coated/Fe^0 towards the practical applications of AD process.*

Keywords: Anerobic digestion; Methane production; Iron nanoparticles; Coated iron nanoparticles

1. INTRODUCTION

Anaerobic digestion (AD) of environmental wastes for biogas generation has gained substantial research interest over the past decades. This research direction has emerged due to the role of the AD process in reducing environmental pollution and recovering potential energy sources from different types of environmental wastes. Waste sludge is one of the very suitable feedstocks for practicing the AD process because of its abundant organics [1]. Moreover, in most wastewater treatment plants, a total of 38 orders of microbes are existed in the waste sludge, indicating its richness with microorganisms needed for fermentation process [2, 3]. In addition, waste sludge with its huge production amount can be served as a renewable and dependable source of energy.

However, AD has several drawbacks which limit the energy output of the process. The main challenge of the AD is the low conversation rate of the available total organics in the digester into biogas/methane [4]. Therefore, many attempts have been conducted in order to improve the utilization of organics during the AD process. These methods include the pre-treatment of waste sludge (this method might include pH treatment or an ultra-sonication process to break down the large organic fragments into small pieces to accelerate the hydrolysis process which is remarked as the first stage of the AD), adding two feedstocks together which is termed co-digestion, and introducing trace elements in the digesters to enhance the process [5]. The enhancement of biogas/methane production by adding trace elements relies on the working mechanisms of used elements.

Based on our literature survey, zero valent elements were the most used elements for the enhancement of AD process [6-8]. For instance, zero valent iron, copper and silver were investigated to demonstrate their effect on biogas/methane production during the fermentation process. Also, metal oxides have been extensively used for the promotion of biogas/methane generation such as Fe_2O_3, CuO, ZnO, Al_2O_3, etc [9-11]. Most of the used metal oxides have slightly improved biogas/methane, in some cases negatively affect gas production, except iron oxides which largely improved biogas methane production when used in the AD process. Based on many reviews, the utilization of zero valent iron remains the most suitable additive for the enhancement of biogas/methane production during the AD process. The reasons behind the remarkable advantage of using zero valent iron in the digestion process are 1) the addition of zero-valent iron serves as buffering substance in the digesters, maintaining the pH value within the optimum range required for the AD process (6.6 – 7.8). 2) the released iron irons of ferric and ferrous by the corrosion reaction of zero valent iron are utilized directly for the promotion of bacterial growth, leading to enhance digestion process. 3) the produced H_2 by the corrosion reaction of zero valent iron promotes hydrogenotrophic methanogenesis and homoacetogenesis bacteria. 4) the released electrons by the corrosion reaction of zero valent iron contribute for the conversion of CO_2 to CH_2, increasing CH_4 generation ratio within the produced gases [12-14]. This happens when protons in the digester are reduced by the electrons of zero valent iron and then utilized for the conversion of CO_2 into CH_4 as described by equation 1 [15].

$$4Fe^0 + 8H^+ + CO_2 \rightarrow 4Fe^{+2} + CH_4 + 2H_2O \qquad (1)$$

However, the fast corrosion reaction of zero valent iron leads to increase the released amount and rate of electrons, hydrogen, iron ions and reactive oxygen specious. The accumulation of the corrosion products specially in the early stage of AD results in disrupting the digestion process and bacterial growth. Therefore, reducing or controlling the corrosion reaction of zero valent iron is necessary to be suitable additive for the enhancement of AD process. Therefore, the objective of this study was to investigate the role of coating process of nano scale zero valent iron on its performance when used in the anaerobic digesters. Hence, nano scale zero valent iron was coated with magnesium hydroxide through the controlled thermal deposition on the surface.

2. MATERIALS AND METHODS

2.1 Sample collection

The waste sludge sample was collected from the pre-stage of the AD at wastewater treatment plant in Fukuoka city, Japan. The sludge sample was characterized for its pH, Oxidation Reduction Potential (ORP), Chemical Oxygen Demand (COD), Total Solid (TS), and Total Volatile Solid (TVS). The used sample contains 2975 mg of COD, 2.5 g/L of TS, and 2 g/L of TVS. The ORP and pH values were -24 mV and 6.9, respectively.

2.2 Synthesis of bare and coated iron particles

The bare zero valent iron and its coated form with magnesium hydroxide were carried out to be used as additives in the anaerobic digesters. The preparation of nano scale zero valent iron was performed according to the following chemical reduction reaction [16-18]:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2 \quad (2)$$

For 1.0 g preparation of nano scale zero valent iron, 0.58 M of sodium borohydride (BH_4^-) were prepared in 100 mL and drop wisely added to 0.093 M of ferric chloride (Fe^{3+}) which was dissolved in 200 mL. The above solutions were prepared using deionized water which was deoxygenated by purging it with N_2 gas for 10 min. The synthesis of nano scale zero valent iron was performed in a free oxygen flask through the continuous purging of N_2 gas in the reaction flask. After the complete addition of sodium borohydride solution, 5 min of aging time were given to ensure the full nucleation of the synthesized nano scale zero valent iron particles. During the synthesis process, a continues mixing was provided with a mixing speed of 400 rpm to avoid forming any aggregates of iron particles. Finally, the formed particles were collected using vacuum filtration apparatus and then washed with deionized water and dried before being used in the experiment or in coating process with magnesium hydroxide. To prepare the coated nano scale zero valent iron, 1 g of nano scale zero valent iron was added in 1 L ethanol and then ultrasonicated for 30 min to ensure the full dispersion of iron particles. Next, Mg^{2+} and OH^- solutions which were dissolved in ethanol were injected sequentially into nano scale zero valent iron solution at a flow rate of 3 rpm. The ions concentrations were governed to coat nano scale zero valent iron particles with a coating ration of 0.5 (Mg/Fe^0: 0.5). The coating process were performed at 50 ± 1.0 ºC to ensure the thermal deposition of $Mg(OH)_2$ on the surface of nano scale zero valent iron. Also, N_2 gas was provided during the deposition of $Mg(OH)_2$ on the surface nano scale zero valent iron to ensure the free oxygen medium. After the complete addition of Mg^{2+} and OH^-solution into zero valent iron solution, an aging time of one hour was given to ensure the full precipitation of $Mg(OH)_2$ on the surface of zero valent iron particles. Finally, the coated iron particles were collected using vacuum filtration apparatus, washed, and dried before being used in the experiment. The morphological structure of the nano scale zero valent iron before and after the coating with $Mg(OH)_2$ was investigated using transmission electron microscopy (TEM).

2.3 Biogas/methane production experiment

The production of biogas/methane was conducted using a semi-continuous system which was operated for 70 days. The main reason of using the semi-continuous was to investigate the long-term production of biogas/methane under the addition of the coated iron particles to ensure the stability and reproducibility of biogas/methane under the new conditions. In detail, we operated two reactors as described in Fig. 1. The first reactor was operated as a control reactor to investigate natural generation of biogas/methane from waste sludge. Whereas the second reactor was operated by adding the coated iron particles by dosing 25 mg of coated iron particles per gram volatile solid. This dosage was determined based on the optimized dosage obtained from our previous report [19]. The reactors were operated with a size of 1 L of sludge. The waste sludge was acclimated under anaerobic conditions for 24 days. The acclimation time was conducted at150 rpm of mixing and 38 °C. Thereafter, the semi-continuous was running at the same operation conditions on day 24, the addition was adding and withdrawing 70 mL of sludge every day (Organic loading ratio (OLR) = 0.1425 gTVS/L/d). The produced biogas was regularly measured using the water displacement method, and analyzed by gas chromatography, GL Sciences Inc., Japan), in order to determine the ratio of CH_4 in produced gas.

2.4 Kinetic investigation

In this study five models were tested to investigate their fitting with the experimental accumulative biogas/methane profiles. The models help in predicting methane yield, determining methane production potential, showing the daily maximum methane production, and presenting the required lag phase to initiate the generation of methane gas. Non-linear excel solver used to solve all models by considering minimizing sum of squared errors (SSE). The models were applied and used as follows:

Richards model: y = A. (1 + d.exp (1 + d). exp [µmA (1 + d) (1 + 1d) (1 + 1d) (λ-t)]) (1d)
Gompertz model: Y = Aexp-exp[(µmeA) (λ-t) +1]
Logistic model: y = A/(1 + exp[4µmA(λ-t)+2])
Firstorder model: y = A. (1-exp[-kt])
Conemodel : y = A[1 + (kt)-n

3. RESULTS

The effect of bare and coated/Fe^0 on methane production was investigated first in batch experiments. The addition of bare/Fe^0 was slightly improved methane production by 4.6%. On the other hand, the addition of the coated/Fe^0 was highly improved methane production by 46.6% over 55 days of fermentation.

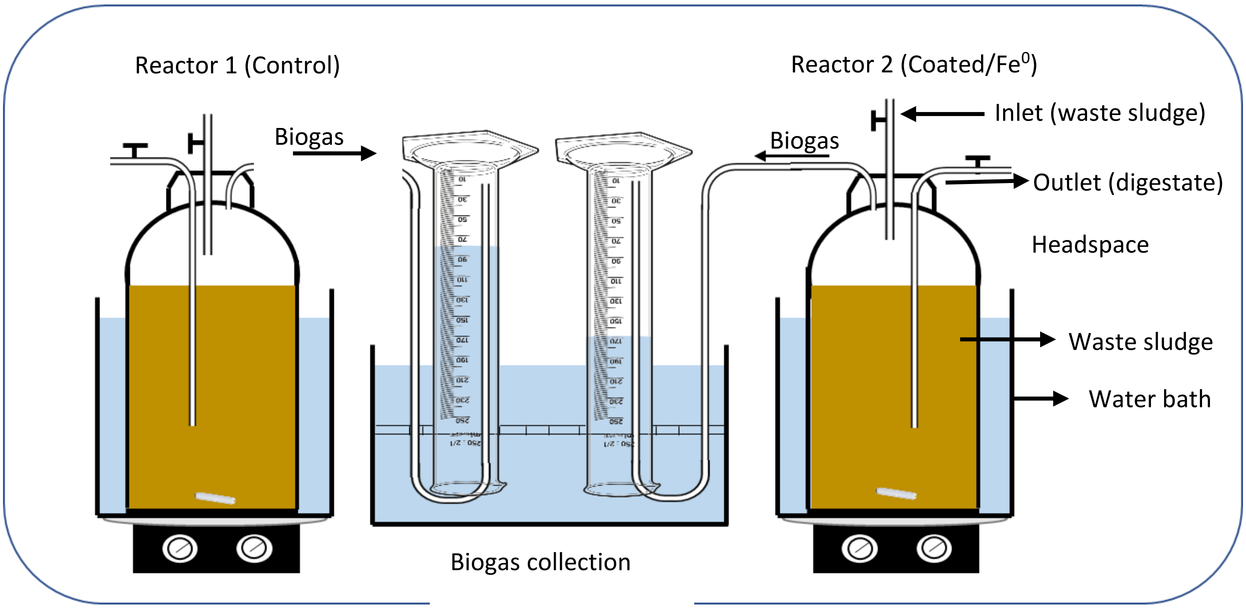


Fig. 1. Schematic diagram of anaerobic digestion semi-continuous system Where y: cumulative methane yield ($mLCH_4gVS^{-1}$), A: methane production potential ($mLCH_4gVS^{-1}$), d: the shape coefficient of the curve, μ_m: daily maximum methane production ($mLCH_4gVS^{-1}d^{-1}$), λ: lag phase (day), t: time (day), e: exp (1) = 2,7182, and k: first order rate constant.

These results were clearly showed the slight improvement in methane production by the addition of bare/Fe^0. This slight improvement could be attributed to the rapid corrosion reaction of bare /Fe^0. The rapid corrosion of bare/Fe^0 leads to the accumulation of corrosion reaction products in the anaerobic digesters, especially in the early stage of AD process. The accumulation of the corrosion reaction products, including electrons, Fe^{2+}, Fe^{3+}, H_2, and ROS, disrupts the promotion of bacterial growth. On the other hand, the slow/moderate release of the corrosion reaction products in the anaerobic digesters enhances the growth of bacteria which enhances the AD process and gas production. Therefore, in order to control the corrosion reaction of bare/Fe^0, we coated the bare/Fe^0 with a layer of magnesium hydroxide. Magnesium hydroxide was chosen for the coating of bare/Fe^0 due to the following reasons: 1) Magnesium is well known as one of the trace elements that could be unitized by microorganisms, implying that the coated layer on the surface of Fe0 will not possess any destructive effect on microorganisms in the anaerobic digesters. 2) Magnesium hydroxide has several features such as its low preparation cost, high surface area, non-magnetization, and low solubility constant [20, 21]. These special characteristics make it as a perfect coating substance for the bare/Fe^0 compared with the other coating substances. Coating of bare/Fe^0 with magnesium hydroxide results in slowing
releasing rate of the corrosion reaction production. This was proved by mentoring the released iron ions (Fe^{2+}, Fe^{3+}) in the digesters as they are representative or indicators for the corrosion rate of bare/Fe^0. Results showed that (not shown) the coated/Fe^0 had lower release of iron ions compared with the bare/Fe^0. The results were very interesting where the addition of the coated/Fe^0 highly contributed to improve the performance of anerobic digesters. A remarkable increase in biogas/methane production was observed in the batch experiments when the coated/Fe^0 was added. This improvement is mainly attributed to role of the coating layer of magnesium hydroxide in reducing the corrosion rate of the bare/Fe^0 which resulted in improving methane production by 46.6 % as shown in Fig.2. Therefore, in order to investigate the stability of the enhanced methane production as well as its reproducibility, a semi-continuous operation of two bioreactors was conducted as described in Fig. 1. The accumulative methane gas production was improved by 120% over 70 days of operation compared with the control reactor as shown in Fig. 3. We applied different models, including Gompertz, Logistic, First order, and Cone models, in order to evaluate the kinetic of methane production potential in the semi-continuous system. The models were applied in order to investigate their suitability in describing the production of methane gas from the degradation of waste sludge. The models were applied to describe methane production generated in the

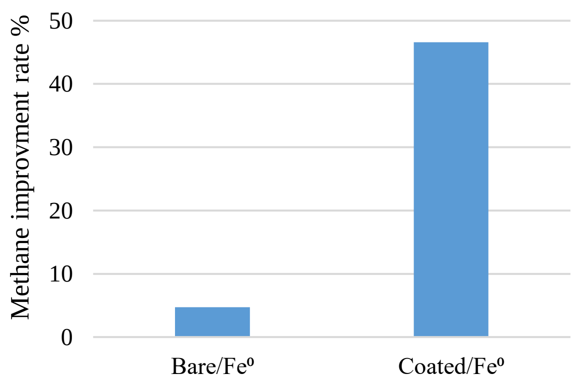


Fig. 2. Effect of bare and coated/Fe^0 on methane production during the anaerobic digestion of waste sludge using batch experiments setup.

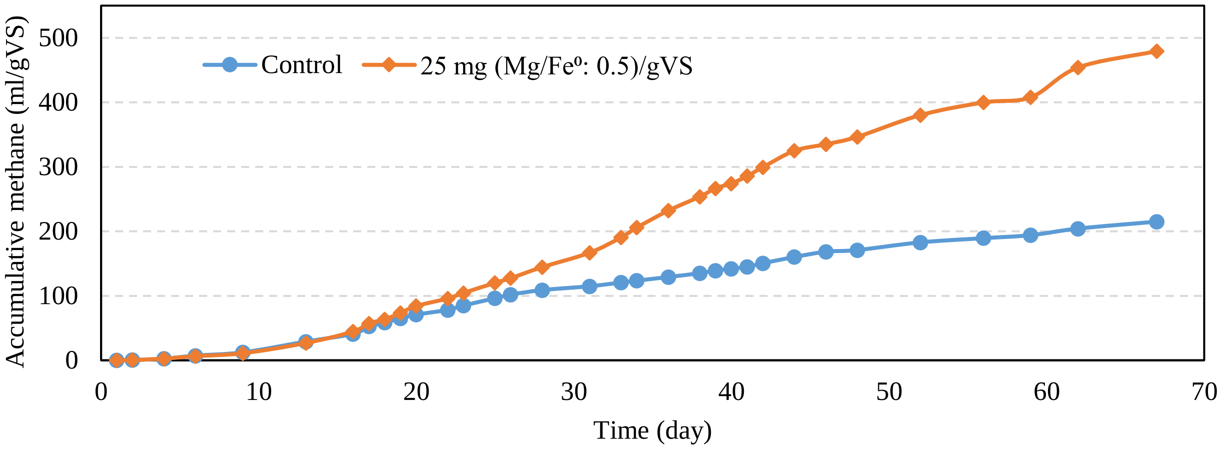
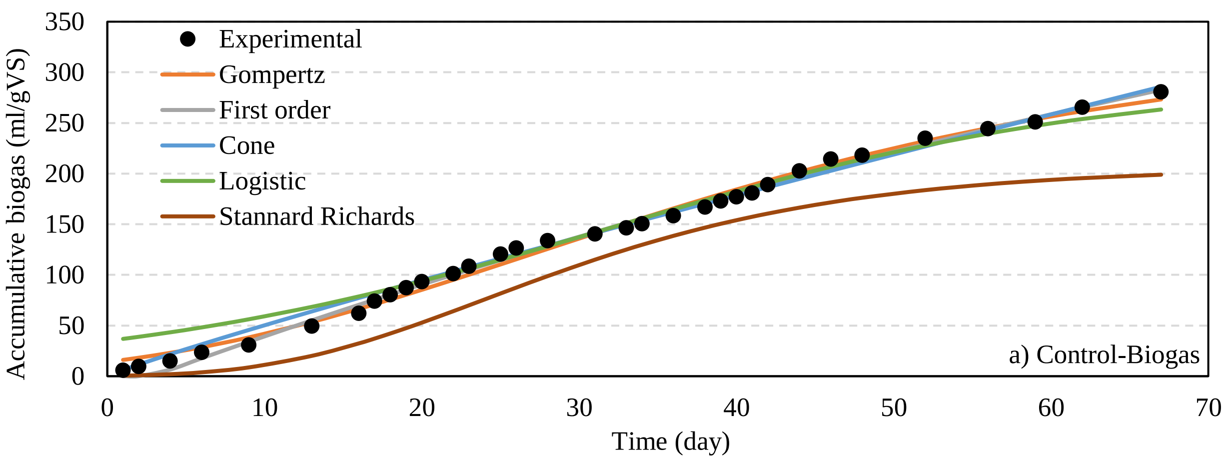


Fig. 3. Effect of coated/Fe^0 on methane production over 70 days of digestion in the semi-continuous system.

semi-continuous bioreactors in the presence and absence of coated/Fe^0. The modeled results of biogas and methane production are shown in Fig.4. Results showed that the Gompertz model was the fittest model with the experimental accumulative biogas and methane production curves, whether in the presence or absence of the coated/Fe^0. All Gompertz model parameters including the daily maximum methane production, methane production potential, and lag phase were obtained. The results suggested that the AD of waste sludge with the addition of coated/Fe^0 at the optimum conditions (dosage: 25 mg/gTVS; coating ratio: Mg/Fe^0:0.5) experienced higher biogas and methane production. Based on the model values, the production potential of methane gas was 693.8 mL/g TVS in the presence of coated/Fe^0, whereas it was only 328.4 mL/gTVS in the control reactor. In addition, the daily maximum methane production in presence of coated/Fe^0 was 11.2 mL/gTVS/d and was only 5.1 mL/gTVS/d in the control reactor.

4. CONCLUSIONS

This study provided cheap, fast, and straightforward solution to confront the main challenge of the AD technology which is representative by the low conversion efficiency of the total biomass into biogas. This study added a significant enhancement in biogas and methane generation rate by adding a novel coated nanomaterial into the anaerobic digesters, serving as an accelerator for the generation process. In detail, the bare/Fe0 particles were coated using magnesium hydroxide and used to increase the production rate of biogas/methane. In the preliminary batch experiments, the bare and coated/Fe^0 improved methane gas production by 4.6 % and 46.6%, respectively. This improvement was observed at the optimum coating ratio of 0.5 (Mg/Fe0: 0.5) and at the optimum dosage of 25 mg/gTVS. The improved methane production by the addition of the coated/Fe0 is attributed to slow corrosion reaction of Fe^0 after being coated with magnesium hydroxide. This was further proved by monitoring the corrosion reaction products of Fe^0 before and after the coating process where the results showed the slow release of iron ions (Fe^{2+} and Fe^{3+}) of Fe^0 after being coated with magnesium hydroxide. Also, both of bare/Fe^0 and magnesium hydroxide were added separately in the digesters, and both did not contribute highly in enhancing methane production, indicating that the enhanced methane production by the addition of coated/Fe^0 was due to the synergetic effect of combining the two materials. In the semi-continuous system, the optimum ratio (Mg/Fe^0:0.5) and the optimum dosage (25 mg/gTVS) were applied in semi-continuous system and output of biogas and methane were improved by 95 and



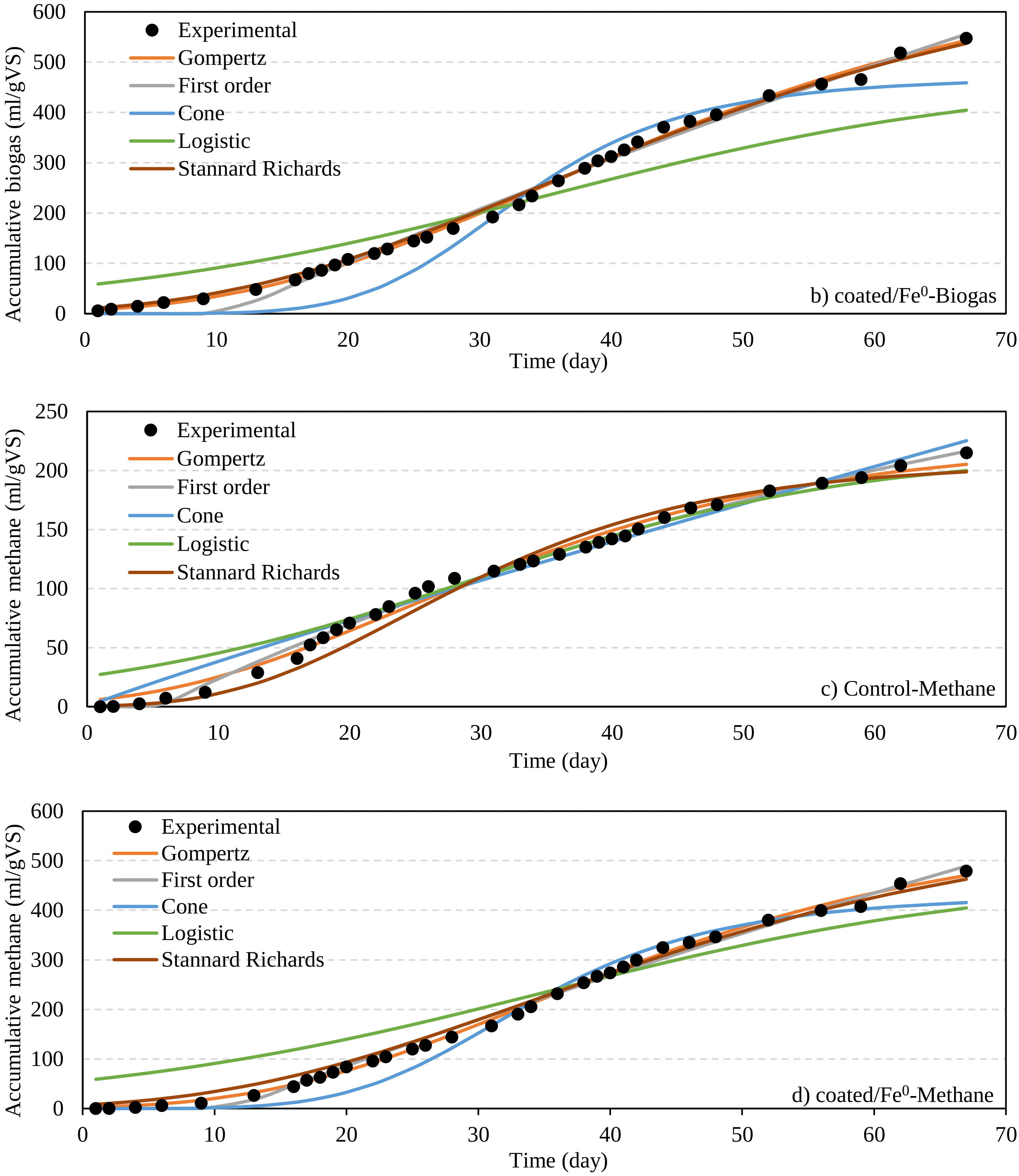


Fig. 4. Experimental accumulative biogas and methane production profiles during the operation of semi-continuous system and their fitting with models; a) biogas production in the control reactor, b) biogas production in the reactor operated with the addition of coated/Fe^0, c) methane production in the control reactor, and d) methane production in the reactor operated with the addition of the coated/Fe^0.

120%, respectively compared to the control reactor. In general, the experimental and predicted methane values have proved the great potential of coated/Fe^0 towards the practical applications of AD process.

Acknowledgments

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5. REFERENCES

[1] H.-Y. Jin, Z.-W. He, Y.-X. Ren, C.-C. Tang, A.-J. Zhou, F. Chen, et al., Role and significance of co-additive of biochar and nano-magnetite on methane production from waste activated sludge: Non-synergistic rather than synergistic effects, Chemical Engineering Journal. 439 (2022) 135746.

[2] R. Eljamal, I. Kahraman, O. Eljamal, I. P. Thompson, I. Maamoun, G. Yilmaz, Impact of nZVI on the formation of aerobic granules, bacterial growth and nutrient removal using aerobic sequencing batch

reactor. Environmental Technology & Innovation. 19 (2020) 100911.
[3] K. Bensaida, R. Eljamal, K. Eljamal, Y. Sughihara, O. Eljamal, The impact of iron bimetallic nanoparticles on bulk microbial growth in wastewater, Journal of Water Process Engineering. 40 (2021) 101825.
[4] K. Lueangwattanapong, F. Ammam, P. M. Mason, C. Whitehead, S. J. McQueen-Mason, L. D. Gomez, et al., Anaerobic digestion of Crassulacean Acid Metabolism plants: Exploring alternative feedstocks for semi-arid lands. Bioresour Technol. 297 (2020) 122262.
[5] B. Guo, J. Hu, J. Zhang, Z. Wu, Z. Li, Enhanced methane production from waste activated sludge by potassium ferrate combined with ultrasound pretreatment. Bioresource Technology. 341 (2021) 125841.
[6] L. Otero-González, J. A. Field, R. Sierra-Alvarez, Inhibition of anaerobic wastewater treatment after long-term exposure to low levels of CuO nanoparticles, Water Research. 58 (2014) 160-168.
[7] S. Karri, R. Sierra-Alvarez, J. A. Field, Zero valent iron as an electron-donor for methanogenesis and sulfate reduction in anaerobic sludge, Biotechnology and bioengineering. 92 (2005) 810-819.
[8] M. A. Ganzoury, N. K. Allam, Impact of nanotechnology on biogas production: A mini-review, Renewable and Sustainable Energy Reviews. 50 (2015) 1392-1404.
[9] H. Mu, Y. Chen, N. Xiao, Effects of metal oxide nanoparticles (TiO2, Al2O3, SiO2 and ZnO) on waste activated sludge anaerobic digestion, Bioresource Technology. 102 (2011) 10305-10311.
[10] H. Mu, Y. Chen, Long-term effect of ZnO nanoparticles on waste activated sludge anaerobic digestion, Water Research. 45 (2011) 5612-5620.
[11] E. Casals, R. Barrena, A. García, E. González, L. Delgado, M. Busquets-Fité, et al., Programmed iron oxide nanoparticles disintegration in anaerobic digesters boosts biogas production, Small (Weinheim an der Bergstrasse, Germany). 10 (2014) 2801-2808.
[12] K. Bensaida, I. Maamoun, R. Eljamal, O. Falyouna, Y. Sugihara, O. Eljamal, New insight for electricity amplification in microbial fuel cells (MFCs) applying magnesium hydroxide coated iron nanoparticles, Energy Conversion and Management. 249 (2021) 114877.
[13] O. Eljamal, K. Jinno, T. Hosokawa, Modeling of Solute Transport with Bioremediation Processes using Sawdust as a Matrix, Water, Air, and Soil Pollution. 195 (2008) 115-27.
[14] O. Eljamal, K. Jinno, T. Hosokawa, Modeling of biologically mediated redox processes using sawdust as a matrix, Proceedings of Hydraulic Engineering. 51 (2007) 19-24.
[15] M. Zhang, J. Li, Y. Wang, Impact of biochar-supported zerovalent iron nanocomposite on the anaerobic digestion of sewage sludge, Environmental Science and Pollution Research. 26 (2019) 10292-10305.
[16] O. Eljamal, R. Eljamal, I. Maamoun, A. M. E. Khalil, T. Shubair, O. Falyouna, et al. Efficient treatment of ammonia-nitrogen contaminated waters by nano zero-valent iron/zeolite composite, Chemosphere. 287 (2022) 131990.
[17] R. Eljamal, O. Eljamal, I. Maamoun, G. Yilmaz, Y. Sugihara, Enhancing the characteristics and reactivity of nZVI: Polymers effect and mechanisms, Journal of Molecular Liquids. 315 (2020) 113714.
[18] R. Eljamal, O. Eljamal, A. M. E. Khalil, B. B. Saha, N. Matsunaga, Improvement of the chemical synthesis efficiency of nano-scale zero-valent iron particles, Journal of Environmental Chemical Engineering. 6 (2018) 4727-4735.
[19] R. Eljamal, I. Maamoun, K. Bensaida, G. Yilmaz, Y. Sugihara, O. Eljamal, A novel method to improve methane generation from waste sludge using iron nanoparticles coated with magnesium hydroxide, Renewable and Sustainable Energy Reviews. 158 (2022) 112192.
[20] I. Maamoun, K. Bensaida, R. Eljamal, O. Falyouna, K. Tanaka, T. Tosco, et al., Rapid and efficient chromium (VI) removal from aqueous solutions using nickel hydroxide nanoplates (nNiHs), Journal of Molecular Liquids. 358 (2022) 119216.
[21] I. Maamoun, O. Falyouna, R. Eljamal, K. Bensaida, K. Tanaka, T. Tosco, et al., Multi-functional magnesium hydroxide coating for iron nanoparticles towards prolonged reactivity in Cr(VI) removal from aqueous solutions, Journal of Environmental Chemical Engineering. 10 (2022) 107431.