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Research Paper

Biochemical methane potential enhancement of domestic sludge digestion by adding pristine iron nanoparticles and iron nanoparticles coated zeolite compositions

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A B S T R A C T

Six bioreactors with different additives of nanoscale zero valent iron (nZVI), zeolite, nZVI and zeolite mixture (IMZ), and nZVI coated zeolite (ICZ) particles were tested to evaluate the overall anaerobic digestion performance of domestic sludge under 37 °C. For 14 days' long, the daily biogas production, methane content, pH, soluble chemical oxygen demand (soluble COD), total alkalinity and total ammonia nitrogen variations were measured, and the overall performance of anaerobic digestion was assessed. The results showed that ICZ addition caused a lag period before starting to generate a significant biogas volume then the cumulative production increased more than the other bioreactors, and the higher the iron particles coated zeolite were added the more the biogas generated. Compared to the control bioreactor, the two highest methane contents were depicted with the addition of the only nZVI and the IMZ mixture and the methane content was stimulated up to 88 and 74%, respectively. However, the maximum cumulative methane volume was obtained with supplementing of ICZ particles with a loading of 1000 mg/L of iron nanoparticles.

These results might be attributed to the high reactivity of nanoparticles, which can be assigned to the anaerobic corrosion of nZVI and electrons generation that could be utilized effectively the methanogens utilization and methane production. Considering its high efficiency and good performance, the iron zeolite system can be extended to practical engineering application for biomethane production.

1. Introduction

Studying the waste contamination removal by iron nanoparticles has aroused more and more concerns in the last two decades. The municipal sludge, which contains numerous biodegrade nutrients, was regarded as biomass resource and, conventionally, anaerobic digestion is used to dispose of the biomass, while it can mitigate the pollution and at the same time, generate biogas as a renewable energy source [1,2].

Comprehensive research has been conducted to further increase the anaerobic digestion efficiency and stability or to reduce the water content of sludge which called dewatering process in order to decrease the transportation and disposal costs [3].

The researches were conducted to increase the efficiency of anaerobic digestion process were based on different strategies such as sludge pre-treatment [4], mixing the sludge with several substrates [5] and introducing diverse additives to the digestion system [6,7].

Iron in nanoscale and with zero valence, which is called nanoscale zero valent iron (nZVI), proved a feasible enhancement toward anaerobic digestion performance because it offers a larger specific surface area that increases the surface reactivity [8,9]. The roles of anaerobic digestion enhancement by nZVI supplementations at least are due to the work of nZVI as an electron donor in the redox reaction of anaerobic digestion biological processes or served to eliminate the inhabitation properties of specifically produced gases through the precipitation [6,10].

Yang et al. [5] studied the effect of nZVI on the anaerobic of sludge from Columbia waste water treatment plant for 14 days under 37 °C, and the nZVI dissolution showed a slow release of hydrogen, which enabled hydrogentrophic methanogenesis and increased methane production. However, the methanogenesis inhabitation through the anaerobic digestion process is atributted to the disruption of cell integrity that anZVI particles caused.

nZVI easily agglomerates into a larger iron groups because of its high surface energy and intrinsic magnetic interaction. The magnetic attractive forces between the nanoparticles affect its dispersion stability, therefore ferromagnetic dispersions form a chain-like aggregates

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[11]. These will reflect on decreasing in performance and efficiency of nZVI addition [9,12].

Generally, anaerobic digestion has four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis [13]. Nonetheless, low methane yield due to low hydrolysis rate shortens the performance of whole digestion process [14]. Therefore, a new effective approach for increasing the methane yield from the anaerobic digestion of municipal activated sludge must be developed.

Recently published researchers focus on increasing the reactivity and the performance of nZVI by supporting the nanoparticles onto carrier additives to overcome the inhibitory effects of nanoparticles agglomeration and to strength the contacts between microorganisms and nZVI particles. Khalil et al. concluded that the ratio 2:1 of nZVI to activated carbon as a support was the optimum ratio that caused the highest nitrate and phosphate removal from aqueous solutions [9] whereas Fateminia et al. studied the effect of freshly nZVI-copper bimetallic supporting on zeolite, and the results proved a great advantage of nitrate anions removal from groundwater under un-buffered conditions [15].

Zeolite is a non-cytotoxic mineral composed of silica, aluminum, and oxygen [16] and it is distinguished by its systematic structure that consists of plenty of channel and pore cavities. Owing to these properties, the zeolite can trap nanoparticles inside its pores and immobilize the nZVI particles on its surface [17]. It's also considered that zeolite in presence of nanoparticles can work an inorganic cation exchanger which means can offer high ion exchange capacity, compatibility, and selectivity with the natural environment [18].

This suggests that the activated sludge digestion exposed to nZVI coated zeolite (ICZ) will be promoted while zeolite will serve as an adsorbent carrier for nZVI particles due to its high uptake ability. Planting the nZVI particles on zeolite may be a suitable pathway to enforce the contact between microorganisms and the nZVI species, and as a result, cell membrane disruptions that nZVI caused will be prevented [6]. Hence, coating the nZVI particles on a carrier may be feasible strategy to increase the overall performance of anaerobic digestion process.

In this present study, a new different composites materials were freshly prepared for the anaerobic digestion enhancement of domestic activated sludge. Supporting the nZVI by zeolite to obtain ICZ might promise to increase the biogas cogeneration, methane yielded and degrade the organic matter because ICZ composite compounds facilitate the adsorption capacity. Thus, the ICZ composite will benefit from the advantages of both iron nanoparticles and zeolite material while coated zeolite by nZVI will disperse the iron nanoparticles and therefore increase the number of active sites for the microbial activities of anaerobic digestion processes.

The effect of two different nZVI particles loadings have been examined and the performance on biogas production of this novel composite ICZ was tested based on modified biochemical methane potential test, and compared with that of the bioreactors exposed to only nZVI particles or zeolite material. For comparison, the batch experiments were also carried out with no additive and with the mixture of both nZVI and zeolite labelled (IMZ).

Daily biogas cogeneration, methane content, pH, total ammonia nitrogen, total alkalinity, and soluble chemical oxygen demand (soluble COD) concentrations were checked to examine the detailed anaerobic digestion performance in order to provide the evidence for enhancement of anaerobic digestion by the addition of nZVI and zeolite composites.

2. Materials and methods

2.1. Chemicals

Commercial raw zeolite powders which has a particle size in micrometer scale was purchased from Sigma company, Germany. The Ferric chloride hexahydrate salt ($FeCl_3{\cdot}6H_2O$) that used for preparing the iron nanoparticles and ICZ composites was purchased from Junsei Chemical, Japan. The reductant agent of sodium borohydride ($NaBH_4$) was purchased from Sigma-Aldrich, USA. All the chemicals used in this work were employed as delivered without further purification and all the aqueous solutions have been nitrogenized for 20 min prior to usage.

2.2. Sludge waste

The sludge used in the digestion experiment was sampled from Mikasagawa wastewater purification center, one of the main sewage treatment plant in Fukuoka city, the southern part of Japan. The samples were taken exactly from the carrier pipeline that transfers the thickened sludge from the gravity thickener to anaerobic digester. The average characteristics of the activated sludge samples used in these experiments were: pH, 6.2; total solid fraction, 1.64%; volatile solids (%), 74.9; organic loading rate (kg VS/m^3 × d), 0.374; total alkalinity (mg $CaCO_3$/L), 494; soluble COD (mg/L), 3873 and total ammonia nitrogen concentration (mg/L), 150.

2.3. Preparation of the pristine nZVI and iron coated zeolite

For preparing ICZ with two different nZVI particles loadings (500 and 1000 mg/L) to obtain ICZ 500 and ICZ 1000 composite, two ferric salt of masses (2.5 and 5 g) were separately mixed with 2 g of zeolite in 120 mL of deionized water. Hydrochloric acid was added to adjust the initial solution pH to meet the range between 3 and 4 to overcome any supposed associated interference in the liquid phase of iron concentration measurements caused by iron precipitation. The ferric salt and zeolite aqueous mixture was vigorously stirred for 30 min at ambient temperature. The prepared aqueous mixture was then placed in a four-neck flask. 120 mL of $NaBH_4$ aqueous solution was introduced drowsily to the four-neck flask at a rate of one litter per hour. The formed ICZ composites were then washed three times with deionized water. The whole preparation steps were carried out under a nitrogen atmosphere.

For the comparison purpose, only zeolite was used and only pristine nZVI was also prepared under the same experimental condition but without mixing the ferric salt solution with zeolite material. A mixture of prepared nZVI and zeolite (IMZ) was also used in this study.

2.4. Methods of characterization

Transmission electron microscopy (TEM, JEM-ARM 200F, JEOL Co., Japan) was used to observe the surface characteristics and morphology of the nZVI, zeolite and prepared ICZ compositions. The particle size diameters were defined by laser scattering particle size analyzer (SALD-2300, Shimadzu Co., Japan). In addition, the surface area micromeritics (3Flex Surface characterization, USA) was used to measure the additives surface area based on nitrogen adsorption technique at −196 °C. Identification of chemical compounds and crystal structure of the particles was examined using X-ray diffractometer (XRD, TTR, Rigaku, Japan) with graphite monochromatic Cu Kd radiation, scanning speed was set at 2° min^{-1} and goniometer scanning was from 3° to 90°.

2.5. Sorption kinetics study

For examining the adsorption kinetics of zeolite, one gram of zeolite and 100 mL of 50 mg/L deoxygenated ferric solution was introduced into a plugged conical flask under 150 rpm stirring. At predetermined time intervals, samples were withdrawn from the solution and the concentrations of dissolved iron were immediately analyzed.

The purposes to investigate the zeolite adsorption kinetics and capacity for the ferric ions are mainly first to determine the needed time for zeolite to reach the equilibrium time of adsorption and to determine the adsorption capacity on the equilibrium time. These purposes will be