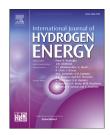
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Nanoparticles augmentation on biogas yield from microalgal biomass anaerobic digestion

Asad A. Zaidi ^a, Feng RuiZhe ^a, Yue Shi ^{a,*}, Sohaib Z. Khan ^{b,c}, Kashif Mushtaq ^d

^a College of Power and Energy Engineering, Harbin Engineering University, Harbin 150001, PR China

^b Department of Mechanical Engineering, Faculty of Engineering, Islamic University of Madinah, Madinah, P. O. Box 170, Saudi Arabia

^c Department of Engineering Sciences, PN Engineering College, National University of Sciences and Technology, Karachi 75350, Pakistan

^d Massachusetts Institute of Technology Portugal Program, Faculty of Engineering, University of Porto (FEUP), Portugal

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ABSTRACT

This study evaluates the influence of metal and metal-oxide nanoparticles (NPs) on biogas production from green microalgae *Enteromorpha*. The concentration of metallic NPs (Ni, Co) was 1 mg/L and oxides NPs (Fe₃O₄, MgO) was 10 mg/L. An anaerobic digestion was carried out batch-wise with working volume, operating temperature, mixing rate and hydraulic retention time as 500 ml, 37 °C, 150 rpm and 170 h, respectively. The measurements of chemical oxygen demand (COD), volatile fatty acids (VFAs), reducing sugar and biogas production were observed to monitor effectivity of nanoparticles. The results showed that NPs has moderate positive influence in biogas production until 60 h of retention time but significantly improve afterward. The maximum total biogas yield of 624 ml was achieved by Fe₃O₄ NPs whereas highest biohydrogen, 51.42% (v/v) was achieved by Ni NPs. The cumulative increase in biogas production for Fe₃O₄, Ni, Co and MgO NPs was 28%, 26%, 9% and 8%, respectively. A modified Gompertz and Logistic function model were used to determine kinetic constants of the reaction. The logistic model has the better predicting ability for microalgae anaerobic digestion.

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Introduction

Anaerobic digestion is the biochemical and microbiological degradation process of organic substrates which takes place in the absence of oxygen [1]. Liquid and solid waste such as high organic content waste water, sewage sludge and organic fraction of municipal solid waste (MSW) can be treated by anaerobic digestion [2]. It can also be used to treat animal manure, energy crops, food waste, microalgae and agricultural residues [3].

The anaerobic digestion process consists of four main conversion phases of organic matter into biogas namely; hydrolysis, acidogenesis, acetogenesis and methanogenesis [4]. In the first phase large and complex organic matter such as

* Corresponding author. College of Power and Energy Engineering, Harbin Engineering University, Harbin 150001, PR China. E-mail address: shiyue@hrbeu.edu.cn (Y. Shi).

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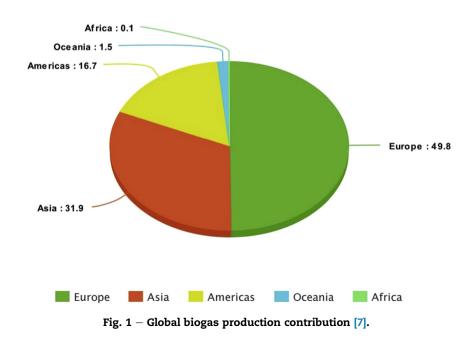
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carbohydrates, fats and proteins react with water to form monomers by the assistance of hydrolytic bacteria. During the second phase conversion of monomers into volatile fatty acids (VFAs) is carried out by the aid of fermentative bacteria. The third phase involves the transformation of VFA into acetic acid, carbon dioxide (CO_2) and hydrogen under the action of acetogenic bacteria. During the final phase, methanogenic bacteria convert acetic acid and hydrogen into methane (CH_4) and CO_2 [5]. Biogas is produced by anaerobic digestion and typically has a calorific value of 21–24 MJ/m³ [6]. The production of biogas has increased rapidly since 2000 [7]. Continent wise global biogas production contribution from Global Bioenergy Statistics 2017 by World Bioenergy Association (WBA) is shown in Fig. 1.

The concerns about expansion in bioenergy sector during past decade have driven a number of scientists and researchers to pursue innovative solutions for its production. Nanotechnology is one of the emerging branches of science. From a materials point of view, it deals with materials having one of the dimensions less than 100 nm. Nanotechnology can be applied in bioenergy field for the purpose of feedstock modification and catalysis that is more efficient. Nanomaterials include nanoparticles (NPs), nanofibers, nanotubes; nanosheets and others have been employed for bioenergy production [8].

NPs have a high surface to volume ratio, which increases the chemical reaction sites. It is generally hypothesized that trace metals improve the digestion process by exciting the bacterial action causing an increase in biogas production during anaerobic digestion [6]. Trace metals worked as an electron donor in an anaerobic digestion process. They increase the total consumption of hydrogen methanogens and activity. They release ions and contribute to the production of key enzymes [9]. They can also optimize the microbial population, change the hydrolysis fermentation types and stimulate the acetic acid content [10]. It has been reported that iron, cobalt and nickel were successfully exciting the production of methanogens in digester sludge [11]. In another study, Qiang et al. [9] stated that the development of anaerobic bacteria during enzyme synthesis is reliant on the presence of iron, nickel, and cobalt. Comparison of the effects of micronutrients of NiCl₂, Fe₂O₃, CoCl₂, (NH₄)6Mo₇O₂₄ along with their NPs with cattle manure slurry on biogas production is carried out by Juntupally et al. [12]. They concluded that all NPs have an increasing effect on biogas as compared to their micronutrients. NiCl₂ micronutrient and Ni NPs produced the highest biogas production. In another study conducted by Abdelsalam et al. [13], comparison of Ni, Co and Fe₃O₄ NPs on biogas production was obtained with anaerobic digestion of livestock manure. This study also showed an increase in biogas production by NPs of these trace metals during anaerobic digestion. Ambuchi et al. [14] studied the response of Fe2O3 NPs on anaerobic granular sludge during beet sugar industrial wastewater treatment. He reported that due to the utilization Fe₂O₃ NPs as conduits for electron transfer toward methanogens improves biogas production.

An intriguing raw biomass, other than conventional organic wastes used for the production of bioenergy, is Aquatic Algal [15]. It can be sourced from natural algal bloom or mass cultivation, is considered a promising substrate for hydrogen fermentation [16]. Hydrogen has high energy content on a mass basis as compared to hydrocarbon fuels [17]. The main benefit of hydrogen as a fuel is the absence of CO_2 , CO and hydrocarbon emissions. Photo-fermentation is commonly applied process to treat microalgae for biohydrogen production. However, hydrogen production through this process remained less effective as the oxygen production during photo-fermentation impede the activity of hydrogenase enzymes and eventually stop the hydrogen production [18]. In recent years, dark fermentation of microalgae biomass for biohydrogen production has received increasing consideration [19]. Low biohydrogen potential were obtained through the dark fermentation method, therefore, a



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