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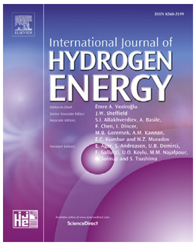

# Impacts of nano-metal oxides on hydrogen production in anaerobic digestion of palm oil mill effluent – A novel approach

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ABSTRACT

In the present study, hydrogen production from palm oil mill effluent (POME) was investigated with the incorporation of nanoparticles (NPs) comprising of nickel (NiO) and cobalt oxides (CoO). The NPs of NiO and CoO were prepared using hydrothermal method and were further applied to analyse, their effect on hydrogen production. The results demonstrated that, a maxima volumetric hydrogen production rate of 21 ml $H_2$/L-POME/h with the hydrogen yield of 0.563 L $H_2$/g-$COD_{removed}$ was obtained with 1.5 mg/L concentration of NiO NPs. On the other hand, the addition of CoO NPs produced maximum volumetric hydrogen production rate of 18 ml $H_2$/L-POME/h with a hydrogen yield of 0.487 L $H_2$/g-$COD_{removed}$ with 1.0 mg/L of CoO NPs. Results showed that addition of optimal concentration of NiO and CoO NPs to the POME enhances the hydrogen yield by 1.51 and 1.67 fold respectively. Besides, this addition of NiO and CoO enhanced the COD removal efficiency by 15 and 10% respectively as compared to an un-additive NPs POME. The toxicity of NPs was also tested using bacterial viability test, which revealed that application of 3.0 mg/L of NiO and CoO NPs to modified Luria-Bertani (LB) medium had 63% and 83% reduction in bacterial cell growth. The results concluded that supplementation of NiO and CoO NPs under an optimal range to the wastewater can improve the hydrogen productivity.

## Introduction

Bioenergy production from renewable biomass mitigates the problems associated with fossil fuel combustion such as fossil fuel depletion and increased greenhouse effect. Hydrogen as a renewable energy source is considered as the one of the carbon free fuel to have the highest energy density by masses (142 MJ/kg), which is about 2.75 times more than other hydrocarbon fuels [1–3]. Statistics reveals that more than 48% of hydrogen is generated from natural resources, while 30%, 18% and 4% are from petroleum, coal, and water electrolysis, respectively [4]. Hydrogen derived from the organic waste has gained significant attention due to advantages such as stabilization of organic waste and energy production from wastes

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[5–7]. Recently, there have been many discussions on the progress of wastewater reuse globally to protect the environment and utilization of sustainable resources to produce valuable by-products like biohydrogen, biomethane etc. [8]. Palm oil mill effluent (POME) is considered as one of the productive renewable biomass for hydrogen production due to its high organic content. POME exhibits a biological oxygen demand (BOD) of 25–50 g/L, chemical oxygen demand (COD) of 50–70 g/L and oil content of 8–12 g/L, which makes it a suitable fermentative medium [9–11].

The anaerobic digestion of complex organic wastewater is one of the promising method to transform waste organics into hydrogen and make the organic waste treatment process highly economic [12]. Micronutrients such as nickel (Ni), cobalt (CoO), iron (Fe), copper (Cu), calcium (Ca), zinc (Zn), molybdenum (Mo) and manganese (Mn) are the basic essential elements for fermentative bacterial growth during anaerobic digestion. Stress response in bacterial cells is induced by excess or absence of the above-mentioned nutrients [13]. However, carbohydrates and lipids accumulation as reserve energy sources ensuing to stress response have been used as strategies for production of biofuels [14]. Hydrogen production through fermentative pathway is mainly catalyzed by hydrogenases and nitrogenases enzymes present inside the hydrogen producers and their active site possess the metal ions as the core elements. Generation of $H_2$ catalyzed by [Ni-Fe] hydrogenases, transports the $e^-$ through intra-molecular $e^-$ transfer chain from redox partner of [Ni-Fe] hydrogenases *e.g.* NADH or NADPH to the active site Simultaneously $H^+$ ions transferred to the active site are subsequently reduced by $e^-$ to evolve hydrogen [15]. In particular, the Ni ions are one of essential constituents of [Ni–Fe] hydrogenases enzymes and presences of Ni ions are very crucial to direct these enzymes within fermentative hydrogen production [16]. Similarly, the role of Ni and Co ion interactions and their fundamental requirement during the fermentative metabolic reactions have already been reported [17]. The bacterium has more than six systems for "Bacterial ion uptake system" of Ni and Co ions, and these systems require high-affinity uptake to improve bacterial metabolic process [18]. The effects of Ni and Co ions on dark fermentative hydrogen production with improved efficiency on applying optimum concentration of Ni and Co have been reported. Wang and Wan studied the Ni ions effects (0–50 mg/L) on fermentative hydrogen production from glucose where the addition of 0.1 mg/L of Ni ions enhanced the hydrogen yield by 65% as compared to the control [19]. Being the Co ions are the core element of corrinoid factor III, which play a key role as a catalyst during bacterial growth; hence optimum concentrations are required for better cell growth [20]. Jarvis et al., stated that an addition of optimal concentration of Co ions to the fermentative medium evidently enhances the biogas production and also helps to maintain the pH of the medium [21].

Nano-scale particles have unique and exciting features compared to the bulk form properties, due to extremely large surface area with high catalytic activity [22]. Over the years, few attempts have been made to explore the benefits or role of nanoparticles (NPs) on fermentative hydrogen production. Researchers suggested that the optimum concentration of metallic ions released from NPs could increases the microbial activities during anaerobic digestion. Li et al. indicated that metal ions released from nanoparticles could combine with $S^{2-}$ during the anaerobic digestion process to relieve the inhibitory effect of $S^{2-}$ on bacterial growth [23]. Wang et al. reported that low amount of NPs have the ability to prompted the fermentative bacterium and activities of key enzymes (protease, AK and Coenzyme $F_{420}$)during anaerobic digestion [24]. The impact of NPs on bacterial metabolic process in anaerobic digestion system have yet to be investigated. However, few studies have been reported on the impact on NPs on hydrogen production in anaerobic digestion. For instance, Mullai et al., reported the effects of Ni NPs on fermentative hydrogen production from glucose showing an increase in the hydrogen yield by 22.7% with reference to the control [25]. Gadhe et al., investigated the effects of hematite and Ni oxide NPs on fermentative hydrogen production using dairy wastewater as substrate [26]. They concluded that an addition of 50 mg/L of hematite and 10 mg/L of Ni NPs enhanced the hydrogen yield by 23.8% and 16% respectively as compared to the control [26].

The catalytic activity of nickel nanoparticles on anaerobic digestion has been studied and proven the enhanced bioactivity of microorganism for hydrogen production, these work focused on hydrogen production from synthetic medium [25] and wastewater [26]. The impact of Co oxides nano particles on anaerobic digestion also has been performed using raw manure and suggested the positive impact on anaerobic digestion of waste [27]. In contrast to Ni ions, so far no studies have been reported on effect of Co NPs on the fermentative hydrogen production from POME in recent literature.

To the best of our knowledge no study has been conducted to assess the effect of on Ni and Co oxide NPs on hydrogen production from industrial wastewater specially palm oil mill effluent. However, it is worth understanding the impact of Ni and Co oxide NPs on biohydrogen production from anaerobic digestion of POME. In this framework, the aim of the present study was to investigate the impact of Ni and Co NPs on hydrogen production from POME. In order to achieve this goal, firstly the NPs of Ni and Co oxides were prepared and characterized. Then we used the prepared NPs as the additive to POME to investigate its effect on biological hydrogen production. Lastly, a bacterial viability test was performed using prepared NPs to analyse the toxicity effect.

## Material and methodology

### Substrate and inoculum

Raw POME was collected from the final discharge point of Felda palm oil industry, Lepar Hill Gambang, Pahang, Malaysia. The collected sample was initially filtered by passing through a standard laboratory sieve (R20 cm 100 mesh/aperture 0.15 mm) in order to remove solid and coarse aggregates from POME. It was preserved and refrigerated at 4 °C prior to use in the study, in order to decrease the biological degradation and acidification. Prior to fermentation POME was sterilized by autoclaving at 121 °C for 20 min to ensure the removal of indigenous microorganism. The physiochemical characteristics of filtered POME are provided in Table 1.

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