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Nickel-graphene nanocomposite as a novel supplement for enhancement of biohydrogen production from industrial wastewater containing mono-ethylene glycol

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ABSTRACT

The impact of Ni nanoparticles (NPs) and Ni-graphene nanocomposite (Ni-Gr NC) on hydrogen production from industrial wastewater containing mono-ethylene glycol (MEG) via anaerobic digestion was investigated. Batch reactors were supplemented with different dosages of Ni NPs and Ni-Gr NC ranging from 0 to 100 mg/L. Maximum hydrogen yields (HYs) of 24.73 ± 1.12 and 41.28 ± 1.69 mL/gCOD$_{initial}$ were achieved at a dosage of 60 mg/L for Ni NPs and Ni-Gr NC, respectively. Substantial improvements of 23% and 105% in hydrogen production were registered at an optimum dosage of 60 mg/L for Ni NPs and Ni-Gr NC, respectively, compared with the control without nanomaterials addition. However, increasing the dosage of Ni NPs and Ni-Gr NC to 100 mg/L resulted in a significant decrease in HY to 20.80 ± 1.12 and 24.24 ± 1.13 mL/gCOD$_{initial}$, respectively. A non-linear regression model revealed that the higher maximum hydrogen production (129% improvement) could be achieved at a dosage of 50 mg/L Ni-Gr NC and an initial pH of 5.0. Economic and environmental revenues due to bioenergy recovery from MEG-containing wastewater were also estimated.

1. Introduction

The progress in innovative technologies related to renewable energy has received extensive attention globally due to the limitations of fossil fuels. Utilization of fossil fuels also greatly influences climate change as a consequence of greenhouse gas emissions (CO_x, NO_x, etc.) [1]. Hydrogen is an alternative energy source that provides substantial benefits such as being renewable, efficient, and environmentally-friendly, with only water as the end-product of the combustion. The net heat generated from hydrogen combustion (120 MJ/kg) is greater than that of most other available fuels (methane, ethane, diesel, etc.) [2]. Therefore, emphasizing on the technological development of hydrogen production from non-conventional sources such as wastewater is a promising approach for the countries suffering from limited energy resources.

Fortunately, most of industries, including petrochemical, produce huge amounts of end-of-pipe effluent, often characterized by a high organic content. Mono-ethylene glycol (MEG) is widely used in petrochemical products, such as ethylene glycol/oxide, engine coolants, aircraft runway deicers, and, particularly, polyethylene terephthalate [3]. Wastewater containing MEG is discharged into the environment causing severe health problems, especially in developing countries. The elimination of this pollutant from wastewater is essential for environmental conservation. Several treatment processes, including biological treatment (anaerobic and aerobic), phytoremediation, catalytic oxidation, and membrane filtration have been investigated for MEG removal from wastewater [4–11]. Among these techniques, anaerobic digestion (AD) is preferable for valorization of industrial wastewater because it can treat high organic content waste, has low bio-

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mass production, has low operation and maintenance costs, and produces biofuels (i.e., hydrogen, methane and bioethanol) [12–15]. Particularly, optimization of fermentative biohydrogen production as green energy source from industrial wastewater (that represents the first-stage of AD process) still needs much more emphasis.

A promising solution to increase hydrogen production from AD is supplementation with nanoparticles (NPs) [16–18]. Appropriate doses of metal NPs can supply biologically available metal nutrients for bacteria via their dissolution in the culture media, though excess metal NPs may inhibit microbial activity [17]. This phenomenon has been proved by the results obtained by Han et al., [17], which showed a gradual release of iron out of hematite NPs. Previous studies have consistently demonstrated the potential benefits of using Fe-based NPs for bio-hydrogen production from AD of glucose compared with supplementation with iron sulfate [17,19,20].

Nickel is the core of [Ni—Fe] hydrogenase enzyme structure, and therefore, it is essential for the catalytic production of hydrogen and the associated microbial performance [21]. Moreover, [Ni—Fe] hydrogenases are common among fermentative bacteria, whereas the [Fe—Fe] hydrogenases are restricted to a few species of bacteria [22]. Thus, [Ni—Fe] hydrogenases enzymes are particularly important when mixed cultures of bacteria, including sludge from domestic wastewater plants, are used for biohydrogen production. In addition, supplementing cultures with Ni ions enhances the dehydrogenase enzyme activity, the associated ethanol production, and the growth of relevant bacterial species [23]. The supplementation of NiO NPs improved hydrogen production from AD of glucose, dairy wastewater and distillery wastewater by 22.70%, 16.04%, and 23.49%, respectively [21,22,24].

The immobilization of metal and metal oxide NPs on support materials, such as graphene sheets, is one of the innovations implemented to enhance the effects of NPs [25]. Indeed, successful applications of metal NPs immobilized on graphene have been reported in various research areas, including catalysts, optical and electronic applications, hydrogen storage, and biosensors [26]. In addition, Mcpherson and Vincent [27] noted that the relevant electron transfer rates of different types of enzymes, including [Ni—Fe] hydrogenase and dehydrogenase enzymes, are enhanced by adsorption on graphite NPs. A substantial promotion in coenzyme F_{420} was resulted upon addition of up to 120 mg/L nano-graphene [28]. Moreover, supplementation of magnetite/graphene oxide (MGO) nanocomposite improved the bio-hydrogen production by 42% from gelatinaceous wastewater, whereas no results were reported for solely using magnetite NPs in order to show the net increase associated with the MGO nanocomposite [16].

A Ni-graphene nanocomposite (Ni-Gr NC) synthesized by a simplified method is proposed in this study as a supplement for enhancement of biohydrogen generation by AD of industrial wastewater containing MEG. This is in order to combine the unique properties of graphene as support material with Ni-based NPs as Ni ions supplier. To our knowledge, supplementation of Ni-Gr NC for biohydrogen production has not been yet investigated so far, with particular emphasis on the potential improvement compared with Ni NPs alone. Accordingly, the main objectives of this study are to (1) assess the effect of using Ni NPs at different dosages on the biohydrogen production from industrial wastewater containing MEG, (2) study the potential increase in biohydrogen production at different doses of Ni-Gr NC, and (3) investigate the effect of initial pH values on the hydrogenation process at a fixed Ni-Gr NC dose. Furthermore, a non-linear regression model was applied for prediction of the optimum conditions (i.e., Ni-Gr NC dose and initial pH) for maximum biohydrogen production. Finally, the economic and environmental profits resulting from energy recovery were estimated.

2. Materials and methods

2.1. Culture and MEG-containing synthetic wastewater

Mixed culture bacteria were harvested from the thickener of a domestic wastewater treatment plant. Large particles were removed from the sludge by an aluminum sieve with a pore size of 2 mm. The seed sludge characteristics are presented in Table 1. Prior to the batch-wise experiments, the acclimatized seed sludge was subjected to a heat shock pretreatment at 105 °C for 30 min to inhibit methanogenic activity [29]. The characteristics of the MEG-based synthetic wastewater are shown in Table 1. Mono-ethylene glycol (MEG) was purchased from Sigma-Aldrich Company. The nutrients NH_4Cl and KH_2PO_4 were supplemented to the wastewater at a mass concentration ratio of COD/N/P = 400/7/1 [30]. A bicarbonate pH buffer and trace nutrients essential for microbial growth (e.g., Co, Fe, Cu, Mn, Zn) were also added according to Krishna et al. [31] (Table 1). All of the chemicals were analytical grade and used without further purification to prepare the synthetic wastewater.

2.2. Synthesis of supplemented nanomaterials

2.2.1. Ni nanoparticles

The Ni NPs were synthesized according to the method reported by Kahani and Molaei [32]. Briefly, $NiCl_2$ (0.1 g) was dissolved in ethylene glycol (6 mL), forming a green solution. The solution was kept at 120 °C under constant stirring condition. Then, hydrazine (1 mL) was added and a blue nickel hydrazine complex precipitated. NaOH solution (3 mL) was added to the mixture and the mixture turned black, indicating the formation of Ni NPs. Finally, the mixture was centrifuged, washed with ethanol and dried at 50 °C to obtain the Ni NPs.

2.2.2. Ni-graphene nanocomposite (Ni-Gr NC)

Ni-Gr NC was synthesized via chemical reduction of $NiCl_2$ and graphene oxide (GO) using hydrazine as a reducing agent. First, GO was synthesized from graphite powder, according to Hummer's method [33]. Graphite powder (3.0 g) was added to concentrated H_2SO_4 (70 mL) in an ice bath and the solution was mixed at constant stirring rate. $KMnO_4$ (9.0 g) was slowly added, and the reaction was kept at a temperature below 20 °C. The reaction vessel was transferred to a 40 °C water bath and stirred vigorously for 30 min. Deionized water (150 mL) was added, and the solution was stirred for 15 min at 95 °C. Additional deionized water (500 mL) was added, and then 30% H_2O_2 solution was slowly added. As a result, the solution changed from dark brown to

Table 1
Characteristics of seed sludge and MEG-containing wastewater.

Seed sludge		Synthetic wastewater	
Parameters	Value[a]	Constituents	Value (mg/L)
TS (g/L)	48.74 ± 1.73	$C_2H_6O_2$ (MEG)	4700
VS (g/L)	28.14 ± 1.52	COD[b]	6000
TSS (g/L)	43.26 ± 0.23	NH_4Cl	401.18
VSS (g/L)	27.46 ± 1.78	KH_2PO_4	65.91
VSS/TSS (%)	63.48	$NaHCO_3$	326
COD_{total} (g/L)	68.28 ± 0.12	$CoC1_2{\cdot}6H_2O$	1.20
$COD_{soluble}$ (mg/L)	2090 ± 24	$FeC1_3$	5
$COD_{particulate}$ (g/L)	66.19 ± 0.10	$CuSO_4{\cdot}5H_2O$	5
NH_4—N (mg/L)	138.30 ± 9.40	$MgSO_4{\cdot}7H_2O$	39
pH	6.72 ± 0.06	$MnSO_4{\cdot}4H_2O$	13.90
		$CaCl_2{\cdot}2H_2O$	36.80
		$ZnC1_2$	5

[a] Values represent mean ± standard deviation.
[b] COD equivalent to MEG.