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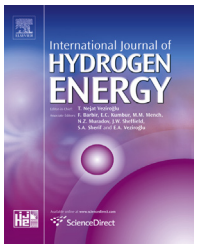

Enhancement effect of hematite and nickel nanoparticles on biohydrogen production from dairy wastewater

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ABSTRACT

The effects of hematite (Fe_2O_3) and nickel oxide (NiO) nanoparticles (NP) on biohydrogen production were investigated using dairy wastewater in batch test. The results showed that, unlike the NiO NP, the maximum hydrogen yield (HY) (16.75 mmol/g COD) and specific hydrogen production rate (SHPR) (42.69 mmol/g VSS.d), representing a 24%, and 43%, enhancement compared to control, respectively, was observed for the sole 50 mg Fe_2O_3/L supplementation. Furthermore, the co-addition of Fe_2O_3 plus NiO NP on biohydrogen production implies that the maximum HY and SHPR of about 17.2 mmol/g COD, and 47.67 mmol/g VSS.d, respectively, can be obtained from dairy wastewater at concentration of 50 mg Fe_2O_3/L, and 10 mg NiO/L, respectively. The highest significant relative enhancement of HY, 27%, and SHPR, 59%, suggests that the co-addition of hematite plus nickel oxide nanoparticles is about 1.2–1.5-fold more effective for enhanced hydrogen recovery from dairy wastewater compared to control, and sole nanoparticles addition. Furthermore, an enhanced biohydrogen production during BHP test can undoubtedly be attributed to an enhanced activity of the *ferredoxin oxidoreductase*, ferredoxin, and *hydrogenase* enzymes by surface and quantum size effects of NPs.

Introduction

An increased concern over environmental impact and economic problems derived from the utilization of fossil-fuel thrust the researchers across the globe to extensively analyze the potentials of biohydrogen produced using dark fermentation (DF) of carbohydrate rich-organic waste and industrial wastewater [1]. Among the various industrial wastewaters, a lactose-rich wastewater generated from cheese and dairy industry has been well-thought-out as a potential substrate for biohydrogen production [2–4]. However, the hydrogen yield (HY) and specific hydrogen production rate (SHPR) during biological hydrogen production from dairy wastewater are low, due to the poor biodegradability, bioactivity and substrate conversion efficiency of hydrogen producing microbes, and therefore, a technology needs further development [1,2]. Although, complexity and poor biodegradability are one of the problems in DF of dairy wastewater, the presence of high content of biodegradable

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organic compound can make dairy wastewater an ideal candidate for biohydrogen production via a microbial process.

Hydrogenase, a key enzyme of the hydrogen production pathways, catalyzes reduction of proton to hydrogen during DF. Based on the metal content present at the active site, the *hydrogenase* enzyme is classified into [Fe–Fe] and [Ni–Fe] *hydrogenase* [5]. The presence of Fe and Ni at the active site of enzyme implies that both the metal's have an important effect on fermentative hydrogen production. To date, a number of studies have reported an enhancement of biohydrogen production by addition of iron and nickel salts using pure carbon source [5]. However, an enhancement of biohydrogen production by addition of iron and nickel using actual industrial wastewater has barely been examined.

Recently, an application of nanoparticles (NP) to enhance bioactivity and metabolite recovery during dark fermentation has gained enormous attention due to unique surface and quantum size effects of NP's. In dark fermentation, the NADPH or ferredoxin based hydrogen production process uses NADPH as an electron donor. In this pathway, hydrogen is directly generated from NADPH by NADPH dependent *[FeFe]hydrogenase/or[NiFe]hydrogenase* or indirectly by ferredoxin dependent *hydrogenase* via the intermediate electron carrier ferredoxin. In principle, the nanoparticles have been reported to enhance *ferredoxin oxidoreductase* activity by increasing electron transfer rate owing to an enhanced surface and quantum size effects [6–8]. Therefore, an enhancement of *ferredoxin oxidoreductase* activity in response to NPs addition has been considered to be important to increase the hydrogen production yield during dark fermentation [8]. To date, an application of iron and nickel NP's to enhance biohydrogen production from pure carbon source viz. glucose, sucrose, etc., have sporadically been reported [6–11]. Zhao et al. [6] studied the impact of Fe_3O_4 NP on biohydrogen production from glucose and observed the HY of 7.97 mmol/g COD at concentration of 400 mg/L. Han et al. [7] studied the effect of hematite NP's (in the range of 0–1600 mg/L) on biohydrogen production from sucrose and found that hematite dose of 200 mg/L is optimum to recover 9.34 mmol H_2/g COD. Furthermore, Mohanraj et al. [8] studied the effect of phytosynthesized iron oxide NP's on biohydrogen production from glucose, and sucrose, and observed the maximum HY of 10.78, and14.00 mmol/g COD, at concentration of 125, and 200 mg/L, respectively. Another report by Beckers et al. [9] studied the effects of Fe NP encapsulated in porous silica on biohydrogen production, and observed the HY of 11.46 mmol/g COD at concentration of 135 mg/L using glucose as a source. On the other hand, Mullai et al. [10] studied an effect of nickel oxide NP on biohydrogen production from glucose, and observed HY of 13.53 mmol/g COD at concentration of 5.67 mg/L. Another report by Malik et al. [11] evaluated an effect of iron oxide NP on biohydrogen production from distillery wastewater and observed the HY of 1.97 mmol/g COD at concentration of 50 mg/L.

As apparent from the aforementioned literature, all the previous studies evaluated the effect of iron and nickel NP's on biohydrogen production using pure carbon source. Furthermore, there is only a single study reported [11] for an application of NP for an enhancement of biohydrogen production from actual industrial wastewater. However, to date, there is no previous study addressing the effect's iron and nickel NP on biohydrogen production from dairy wastewater despite their potential to enhance *hydrogenase* activity, HY, and SHPR, which are conducive for hydrogen production. Therefore, in the present study, a novel attempt has been made to evaluate the potentials of hematite (Fe_2O_3) and nickel oxide (NiO) NP for enhancement of biohydrogen production from dairy wastewater. Furthermore, the novelty of present work lays primarily an application of co-addition of hematite plus nickel oxide NP for enhancement of biohydrogen recovery, owing to physic-chemical advantages [6] that are discussed here. Therefore, there are three-fold objectives of the present study to enhance understanding of biohydrogen production from dairy wastewater as follows: (1) application of Fe_2O_3 NP for an enhancement of biohydrogen production from dairy wastewater. (2) Application of NiO NP for an enhancement of biohydrogen production from dairy wastewater. (3) Application of co-addition of Fe_2O_3 plus NiO NP for an enhancement of biohydrogen production from dairy wastewater.

Material and methods

Dairy wastewater and seed sludge

Dairy wastewater (COD, 25,000 mg/L; BOD, 10,200 mg/L; TS, 2300 mg/L; SS, 500 mg/L; TDS, 1800 mg/L; pH 7.2) collected from the Government Dairy Society, Nagpur, India was used as a substrate. A fresh dairy wastewater was stored at temperature 4 °C to avoid degradation and prior to use, the dairy wastewater was filtered through the 1-mm sieve to remove any larger particles.

An anaerobic sludge (17–20 g VSS/L), collected from the anaerobic digester tank of Purti Power and Sugar Ltd, Nagpur, was boiled at 90 °C for 20 min to inhibit methanogenic microbes and to form a seed sludge enriched with hydrogen-producing bacteria (HPB) [1,12].

Synthesis of nanoparticles

The Fe_2O_3 NP's were synthesized by chemical precipitation followed by thermal decomposition method as described by Darezereshki et al., 2012 [13].

The NiO NP's were synthesized by chemical precipitation method. Nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), sodium hydroxide (NaOH), oleic acid, de-ionized water, and ethanol (CH_3CH_2OH, 99.93%) were used in the experiments. All the chemicals were of analytical grade. The synthesis procedure was as follows: $Ni(NO_3)_2{\cdot}6H_2O$ was dissolved in de-ionized water to form a solution of the concentration of 0.5 M. The NaOH solution (0.5 M), added with 1 g of oleic acid, was dropped to this solution with the vigorous stirring at room temperature. The light-green precipitate was then collected by filtration and rinsed three times with de-ionized water and ethanol. The washed precipitate was dried at 50 °C overnight followed by calcinations at 550 °C for 2 h.

Experimental procedure

Batch experiments were carried out in 125 mL serum bottles with working volume of 100 mL, comprised of dairy