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Hydrogenation of Carbon Dioxide Using a New Green System of Biogenic ZnO Nanoparticles

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Abstract
Microorganisms create metal nanoparticles (MNPs) after being exposed to toxic metal ions. Nevertheless, the catalytic performance of biosynthesized MNPs has not been investigated in spite of the possibility of utilizing these biological processes in the stable improvement of vital metals (e.g. zinc oxide). This strategy has excellent advantages like high economic efficiency and tolerance of functional groups. DaZnO NPs characteristics were recognized by numerous techniques, including FT-IR, SEM, TEM, XRD, and EDS analyses. In this study, biogenic zinc oxide nanoparticles were produced by the Desulfovibrio alaskensis to reduce carbon dioxide for the preparation of formate salts in an aqueous medium.

Keywords
Desulfovibrio Alaskensis; Green Chemistry; Zinc oxide; Nanocatalyst; Carbon Dioxide

1.INTRODUCTION

Newly, diverse industrial techniques have arisen from non-renewable carbon resources, and carbon dioxide has replaced carbon raw materials. CO_2 is a affordable, profuse, and secure material that stabilizes processes. The transfiguration of CO_2 into advanced commodities is one of the notable concerns in areas where catalysis plays a significant role, like industry and academia [1, 2]. A homogeneous transition metal catalyst helps hydrogenation of CO_2 to formic acid or methanol, cyclic carbonates, or polycarbonates through CO_2/epoxide reaction [3]; fabrication of carboxylic acids with carboxylation of organometallic derivatives [4]; and the generation of amines through reductive methylation. One of the broadest areas of study for the employment of carbon dioxide is the investigation of epoxide reactions [5, 6], where effortlessly-prepared cobalt catalysts are active.

The generation of green synthesis nanoparticles by fungi, bacteria, algae lead, and plants to the large-scale creation of pure metal oxide particles [7]. Various chemical and physical steps are broadly employed to synthesize metal oxide NPs and allow the acquisition of particles with desired properties. Nanoparticle synthesis techniques employing microbes provide stronger dimension control through segmentation in the periplasmic space and vesicles. The rate of intracellular particle generation and thus, the nanoparticle dimension can be partially changed by monitoring factors like temperature, pH, substrate concentration, and exposure time of the substrate [8]. In addition, nanoparticles synthesized by microorganisms are fixed by peptides like phytochelatins, which prevents their accumulation [9]. These peptides are synthesized due to the stress of heavy metals and are a universal mechanism for the separation of metal ions in fungi, plants, and bacteria [10-12].

Zinc oxide nanoparticles have received a lot of attention [13,14]. From an electronic perspective, zinc oxide is a semiconductor with a broad direct slot crystallized in wurtzite [15]. For their attractive characteristics, zinc oxide nanoparticles are applicable in various fields, including the semiconductor-based industry, paint industry [16], water splitting [17], water disinfection [18], and cosmetic industry [19]. To date, various zinc oxide-based nanoparticles have been used in biomedical areas, ranging from cancer treatment to antimicrobial products. The biocompatibility of ZnO is a significant element in bio-related usages [20]. Several studies have shown the dependence of the cytotoxicity of zinc oxide nanoparticles on the morphology and dimension of NPs. Achuth

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Padmanabhan et al. explored the influence of zinc oxide nanoparticles on ovarian cancer through human ovarian cancer cells and discovered that the cellular toxicity of zinc oxide NPs enhances through dimension depletion [21]. Therefore, controlling the form and dimension of zinc oxide NPs cangenerate the most useful product. Doping is another method to improve zinc oxide nanoparticles. So far, different factors like magnesium, indium [22], and aluminum [23] have been doped to ZnO. Production of zinc oxide nanoparticles with excellent characteristics is another way for the amelioration of ZnO nanostructures. To date, diverse zinc oxide nanoparticles have been created and used in bio-related utilizations.

The current study reports that biogenic ZnO nanoparticles created by Desulfovibrio alaskensis are active catalysts for catalytic depletion of CO_2 for the synthesis of formate salt under environmental situations. The reaction has a wide range, can accelerate dramatically in membrane related to TPGS micelles, and act better than other heterogeneous NP catalysts created microbially or by chemical synthesis. Overall, this represents a unique character of the metal depletion path in Desulfovibrio spp. That is particularly suitable for the production of highly active MNP catalysts (for utilization in organic synthesis).

2.EXPERIMENTAL

2.1. Synthesis of DaZnO NPs through microwave technique

Freshly made $Zn(CH_3COO)_2{\cdot}2H_2O$ stock solution (0.04 M in H_2O) was released in the cell suspension to D. alaskensis cells of 0.002 M. The centrifuge tubes were incubated in an anaerobic chamber at 45 ˚C for 20 hours. The biogenic nanoparticles (DaZnO NPs) were centrifuged for 15 min and cleansed with 40% acetone in H_2O.

2.2. Catalytic hydrogenation of CO_2

1M KOH solution (15 mL) and DaZnO NPs (5 mg) were added to a 100 mL high-pressure stainless steel reactor vessel. Next, the reactor vessel was pressurized with CO_2 and H_2 gases (10:10, CO_2/H_2). The reactor vessel was warmed up to 60 °C and stirred at 400 rpm for eight hours. Upon the completion of the reaction, the reactor was cooled at environment temperature. Finally, the reactor was depressurized, the reaction mass was collected in a sample vial, and centrifuged to eliminate DaZnO NPs.

3.RESULTS AND DISCUSSION

In this study, we explored whether bacteriogenic ZnO NPs from Desulfovibrio alaskensis G20 (DaZnO NPs) can catalyze the hydrogenation of CO_2 to formate. Following Wallace et al. [24], the depletion of carbon dioxide was explored. For this purpose, DaZnO NPs were prepared from anaerobic cultures of Desulfovibrio alaskensis G20 in the attendance of $Zn(CH3COO)_2{\cdot}2H_2O$.

To explore the surface functional group of products, FTIR analysis was used (Figure 1) and the FT-IR spectrum of DaZnO had a climax at 543.9 cm-1. [25] EDX analysis was done to evaluate the purity of the products. The presence of Zn, and O confirmed that the DaZnO sample could be properly fabricated (Figure 2). Figure 3 shows the XRD patterns for DaZnO catalysts at high and low angles. The analysis of XRD, which can be beneficial to identify mean crystallite size and crystalline anatomy was employed to check DaZnO nanostructures. As can be seen, they were properly matched with pure fluorite DaZnO. Furthermore, there were no impurities. The mentioned patterns were in accordance with the Hexagonal Phase of DaZnO (JCPDS card No. 01-089-0510).

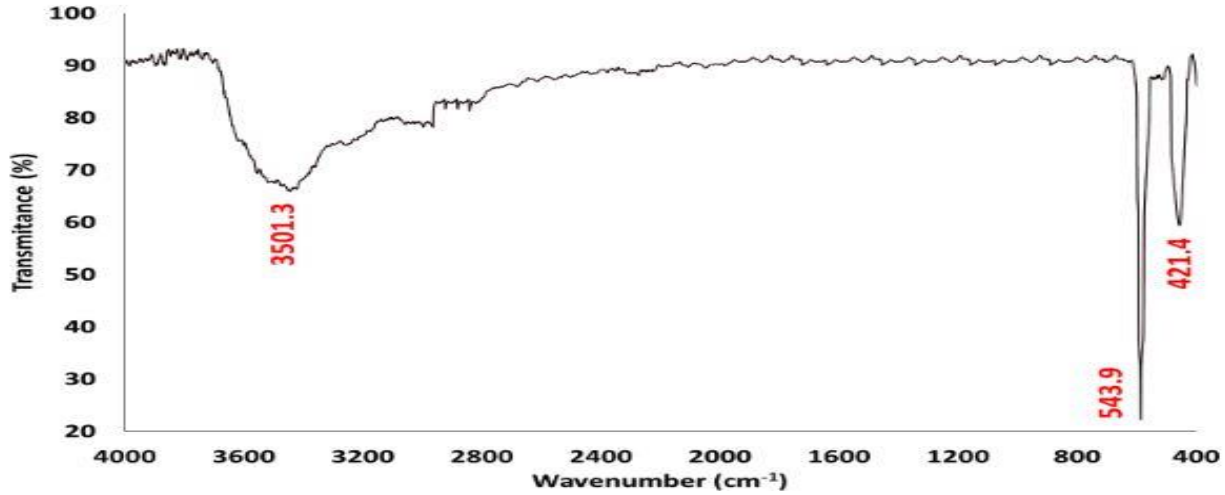

Fig 1. FT-IR spectrum of as-prepared DaZnO NPs.

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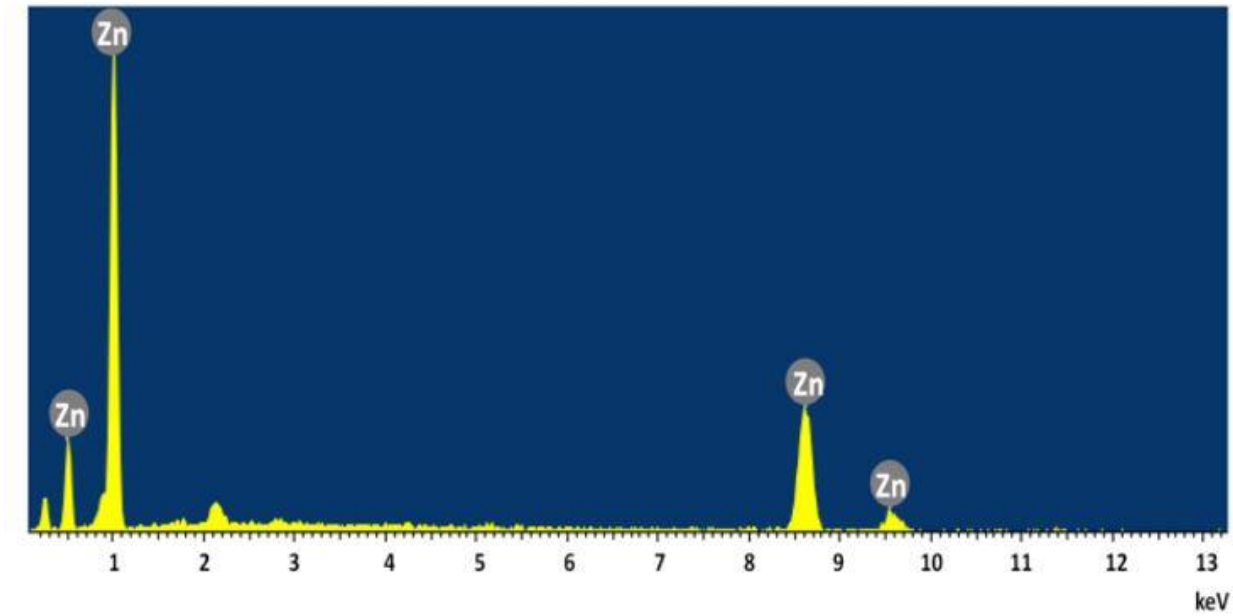

Fig 2. EDX analysis of prepared DaZnO nanocomposites.

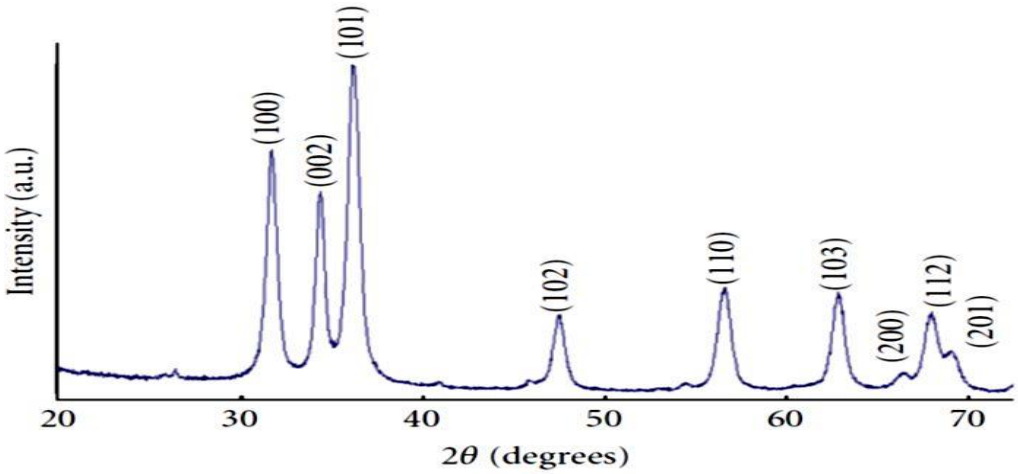

Fig 3. XRD pattern of as-prepared DaZnO NPs.

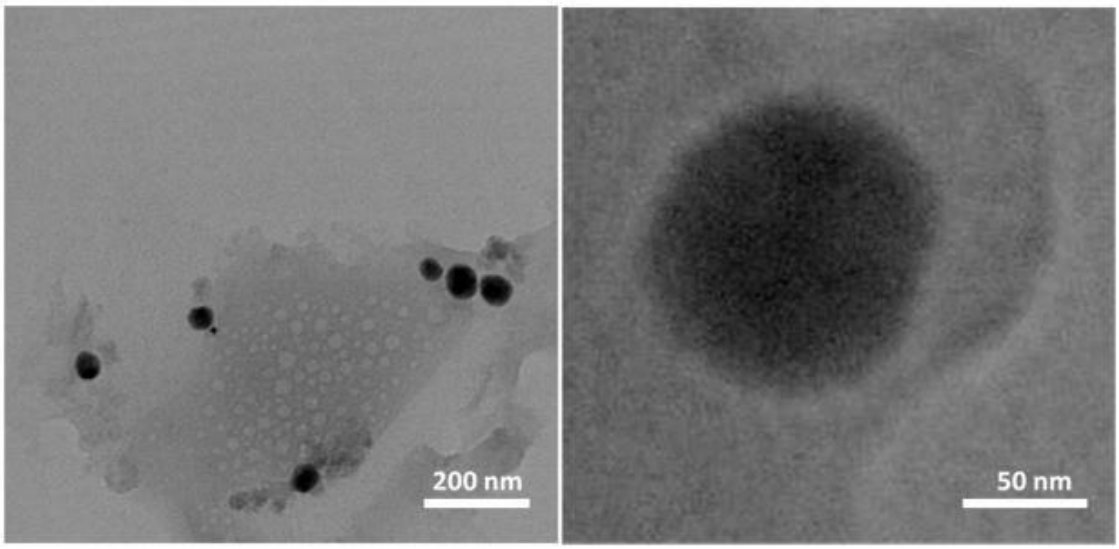

Fig 4. TEM images of DaZnO NPs.

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To investigate the reasons, Transmission Electron Microscopy (TEM) was employed. Results revealed that the addition of TPGS-1000 prepared very regular micelles at the cell outer level. Figure 4 shows the DaZnO NPs had a dimension of about 150 nm. The prepared catalyst and several larger structures were well dispersed, showing the coalescence/aggregation of each NPs.

Figure 7a exhibits the impression of heat on the yield and selectivity of the ultimate good. Taking into account the sensitivity of the catalytic activity to the heat of the reaction, the potency of the ultimate product escalated with risinghe at from 50 oC to 60 oC. Nevertheless, temperatures above 80 oC didn't changed performance. The sensitivity of the potency to the reactiontime at 60 oC is depicted in Figure 7b. As can be seen, increasing the reaction time enhanced the potency, and 98 % CO_2 was converted within 8 h. Therefore, DaZnO NPs were considered suitable nanocatalysts for the hydrogenation of carbon dioxide to formate. Figure 7c depicts the impression of volumes of water on the potency of the ultimate product in the partnership of DaZnO NPs. The potency of the ultimate product enhanced to 98% in 10 mL of water. In addition, the impression of the mass of DaZnO NPs as a catalyst on the reaction was probed under several situations. The potency escalated to 69% upon the addition of 4.0 mg DaZnO NPs (Figure 7d). When the mass of DaZnO NPs elevated to 5.0 mg, the potency of the product enhanced to 98%.

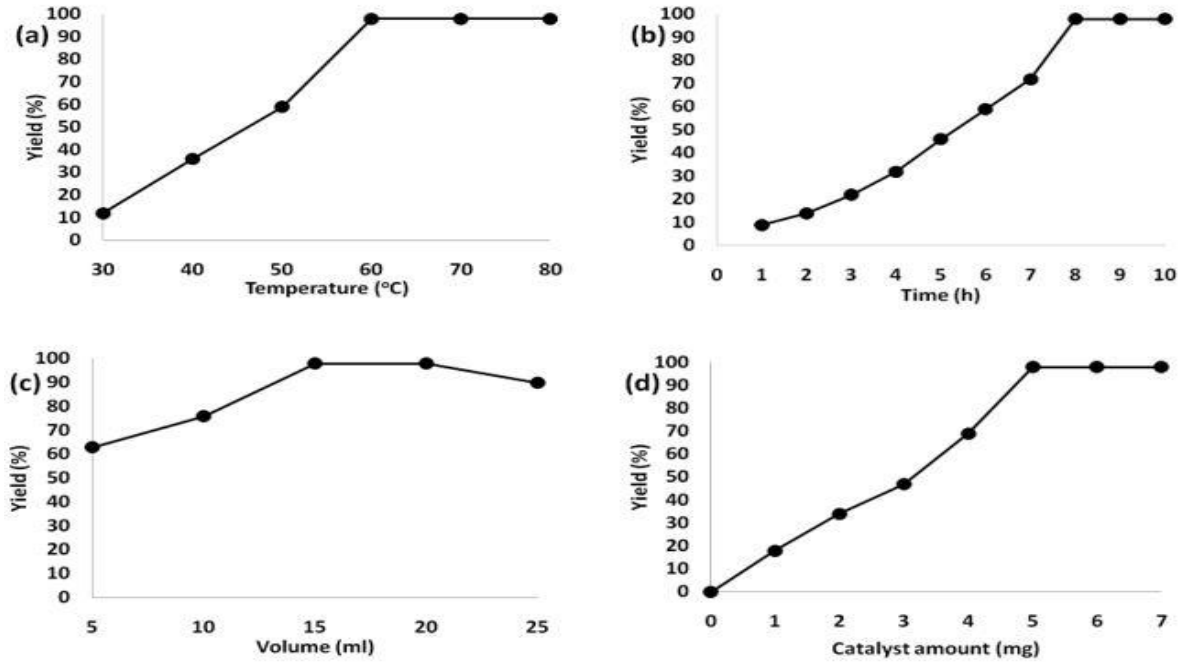

Fig 5. The effect of (a) temperature; (b) time; (c) volumes of water; and (d) catalyst amount on the depletion of CO_2.

Pressure alteration was examined by converting the minor pressure of both carbon dioxide and H_2. The pressure of 10 bar of H_2 (5 bar) and CO_2 (5 bar) led to the yield of 55%. The pressure increase to 25% by employing 11 bar resulted in a 77% efficiency. Doubling the pressure using the total partial pressure to 36 bar increased the efficiency to 97%. In the cases of different pressure ratios of hydrogen and carbon dioxide, the efficiency was reduced. The constant pressure of H_2 and reduced pressure of CO_2 resulted in the depletion of CO_2 conversion and efficiency (58%). This was because one mole of CO_2 form one mole of formate. Correspondingly, the depletion of H_2 gas pressure led to the depletion of efficiency. This could be due to the insufficient partial pressure of the H_2 gas to create the hydride and enhance the CO_2 hydrogenation (Figure 6).

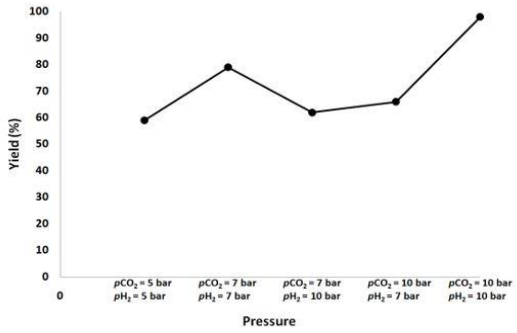

Fig 6. Influence of pressure (Reaction circumstances: catalyst (5 mg) and KOH solution (1M, 15 mL), 60 °C, 8 h).

Moreover, formates were generated with a yield of 3% when employing chemically synthesized heterogeneous ZnO catalysts under similar

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reaction situations. For instance, ZnO nanoparticles produced by chemical vapor deposition (cZnO NP) and Zn on activated carbon (ZnO/C) both formed formate at 19 % efficiency, which increased to 26 % for cZnO NP. This fascinating finding demonstrated a unique characteristic of nanoparticle biosynthesis in D. alaskensis that is suitable for the production of highly active heterogeneous ZnO catalysts.

Table 1. The catalytic activities of ZnO/C, cZnO NP and DaZnO NP.a

Entry	Reaction time (hour)	Yield (%) ZnO/C	cZnO NP	DaZnO NP
1	2	4	10	14
2	4	10	16	32
3	6	14	19	59
4	8	19	26	98

a. Reaction condition: catalyst (5 mg) and KOH solution (1M , 15 mL), 60 °C, 8 h.
b. Isolated yields.

Besides, the heterogeneous nature of the catalyst was specified in a comprehensive investigation. First, the hot filtration test for the hydrogenation of CO_2 to formate showed that the catalyst was removed after 4 hours with 32% efficiency. After 8 hours, the yield reached up to 34%. The results of the reaction proved the heterogeneous nature of the catalyst and there was only an insignificant drain in the reaction. Second, to guarantee the heterogeneity of the catalyst, Mercury toxicity was tested. Mercury (0) severely deactivated the metal catalyst and declined the catalyst activity.

The results of these tests proved the heterogeneity of the catalyst. After four hours of reaction, around 300 molar mercury was conveyed to the reaction composite. The reaction environment was stirred for 8 hours and no further conversion was observed. Figure 7 portraits the kinetics form of the reaction in the presence of Hg (0). Negative findings of heterogeneity tests demonstrated the heterogeneity of the catalyst and the hydrogenation of CO_2 to formate did not lead to leaching of Zn.

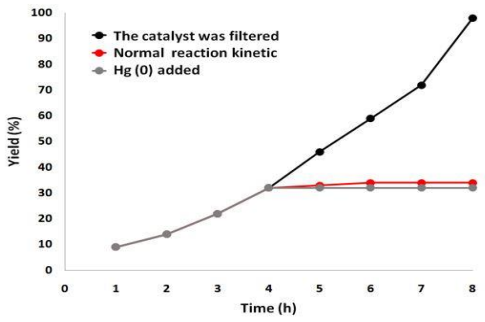

Fig 7. Reaction kinetics, Hg (0) poisoning, and hot filtration tests for the hydrogenation of CO2 to formate.

Convenient recovering and isolation are two crucial attributes of a heterogeneous catalyst. The catalyst recoverability was probed for the fabrication of the product. The DaZnO NPs was eliminated from the amalgam after each run. The DaZnO NPs were eluted with H_2O and EtOH, and vacuum-dried. As Figure 8 depicts, the catalyst preserved its potency after ten continual runs.

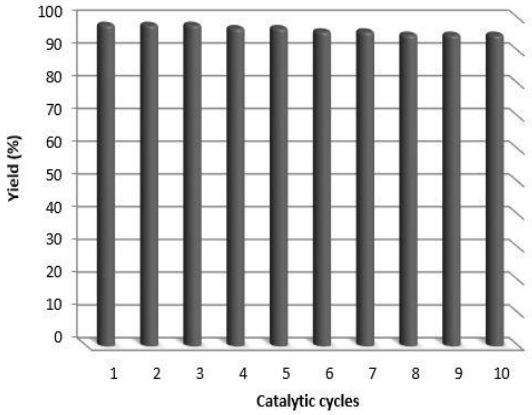

Fig 8. Reproducibility and recyclability of the catalytic system.

CONCLUSIONS

To sum up, we showed that ZnO nanoparticles synthesized by Desulfovibrio alaskensis are very active heterogeneous catalysts for the hydrogenation of carbon dioxide to formate. These biological catalysts can be easily generated from bacterial cell culture employing high-efficiency Zn salts which work better compared to available chemically or biologically-made heterogeneous Zn catalysts.

We demonstrated that the reactions catalyzed by these nanoparticles could be improved by employing designer micelles to co-localize substrates at the cell membrane. The focus of future studies will be on the genetic engineering of D. alaskensis to generate “designer NPs” by increasing reactivity and extending the process to use industrial waste streams as a metal source.

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هیدروژناسیون دی اکسید کربن با استفاده از یک سیستم سبز جدید از نانوذرات اکسید روی زیستی

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چکیده

میکروارگانیسم ها پس از قرار گرفتن در معرض یون های فلزی سمی، نانوذرات فلزی ایجاد می کنند. با این وجود تا به امروز عملکرد کاتالیزوری نانوذرات فلزی بیوسنتز شده با وجود امکان استفاده از این فرآیندهای بیولوژیکی در بهبود پایدار فلزات حیاتی (مانند اکسید روی) مورد بررسی قرار نگرفته است. این استراتژی دارای مزایای فوق العاده ای مانند کارایی اقتصادی بالا و حفظ گروه های عاملی است. ویژگی‌های نانوذرات بیوژن اکسید روی با تکنیک‌های متعددی از جمله تحلیل‌های FT-IR، SEM، TEM، XRD و EDS شناسایی شدند. در این مطالعه، نانوذرات بیوژن اکسید روی توسط Desulfovibrio alaskensis برای کاهش دی اکسید کربن برای تهیه نمک های فرمت در یک محیط آبی تولید شد.

کلید واژه ها

شیمی سبز؛ اکسید روی؛ نانوکاتالیست؛ دی اکسید کربن.

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