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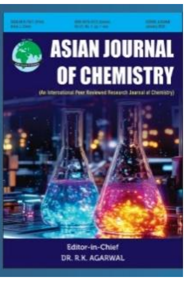

Green Synthesis of Magnetite Nanoparticles and Catalytic Activity on Hydrogen Production

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In this study, magnetite (Fe_3O_4) nanoparticles were synthesized *via* a green route using *Cucurbita pepo* leaf extract as a bioreducing and capping agent and their catalytic efficacy in hydrogen production from aqueous formaldehyde under alkaline conditions was investigated. The biosynthesized Fe_3O_4 nanoparticles exhibited a strong UV-Vis absorption peak at 200-300 nm and characteristic Fe-O stretching vibrations in the FTIR spectrum, confirming successful nanoscale magnetite formation with biofunctional surface groups enhancing stability and catalytic activity. Hydrogen evolution experiments, performed through the downward displacement of water to ensure CO- and CO_2-free collection, revealed a 350-folds increase in hydrogen production rate from formaldehyde compared to the non-catalyzed system at 60 ºC. The hydrogen generation rate was directly proportional to catalyst loading, with a threefold increase in Fe_3O_4 quantity (0.005 g $\rightarrow$ 0.015 g) resulting in a substantial enhancement of H_2 yield (from 30 $\rightarrow$ 48 mL h^{-1}). Mechanistic insights suggest a magnetite-facilitated Cannizzaro-type pathway, where formaldehyde and water each contribute a hydrogen atom to form molecular hydrogen, while sodium formate is generated as a recyclable byproduct. This green, low-temperature and CO-free hydrogen production process highlights the potential of biofunctionalized Fe_3O_4 nanoparticles as efficient and sustainable catalysts for on-demand hydrogen supply in proton exchange membrane fuel cells (PEMFCs) applications.

Keywords: Magnetite nanoparticles, Cannizzaro reaction, *Cucurbita pepo* leaf extract, Catalytic activity, Hydrogen production.

INTRODUCTION

Recently, the use of proton exchange membrane fuel cells (PEMFCs) has attracted a great deal of attention since it offers more efficient, environmental and operational benefits than the conventional technologies [1]. However, the success of the application of PEMFCs depends largely on the hydrogen supply [2-8]. Unfortunately, most hydrogen production methods cannot satisfy the criteria of size, cost, safety and purity for PEMFCs, especially for a mobile PEMFC. For example, efficiency of the fuel cell is seriously affected by carbon monoxide in hydrogen gas from hydrocarbons reforming [9-12]. In general, this hydrogen generation method requires the external heat supply and operation at higher temperature, which baffles its miniaturization, simplification and on-line applications [13-17].

For hydrogen production from the electrolysis of water, fermentation of mass or other renewable sources, problems of discontinuity and relatively high-energy costs have to be resolved. Recently, hydrogen generation from hydrolysis of chemical hydrides has also been reported [18-23]. Although this method has many merits compared with others for providing pure hydrogen in PEMFCs at room temperature, the price of chemical hydrides is a considerable barrier for large-scale application. Hence, it is highly desirable to develop an efficient and low-cost method for production CO-free hydrogen at low temperature. Under highly basic aqueous conditions at room temperature, formaldehyde and water could quantitatively generate hydrogen, each contributing one hydrogen atom to H_2 formation. However, compared with other costly hydrogen sources such as sodium borohydride ($NaBH_4$) and hydrazine hydrate, formaldehyde offers a more economical and widely

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available alternative due to its lower cost and large-scale industrial production. Consequently, it represents a promising and efficient route for hydrogen generation through hydrogen atom extraction from water. Moreover, the byproduct sodium formate (HCOONa) can be readily recycled *via* a simple acidification process, enhancing the overall sustainability of the method. Moreover, certain metallic nanoparticles exhibit strong catalytic activity toward hydrogen generation from formaldehyde solutions, leading to a significant enhancement in the hydrogen production rate under atmospheric pressure conditions [24-27], henceforth, in this work, magnetite (Fe_3O_4) nanoparticles were found to be effectively synthesized using *Cucurbita pepo* leaf extract via a green synthesis approach and demonstrated notable catalytic activity in enhancing hydrogen production from formaldehyde solutions under ambient conditions.

EXPERIMENTAL

All analytical-grade compounds used in this study were purchased from Central Drug House (CDH) Pvt. Ltd., India. Ferrous chloride tetrahydrate ($FeCl_2\cdot 4H_2O$), ferric chloride hexahydrate ($FeCl_3\cdot 6H_2O$) and sodium hydroxide (NaOH) were used as main constituents for synthesising magnetite nanoparticles (Fe_3O_4) through precipitation method. To ensure purity and uniformity throughout the synthesis process, deionized water was employed as the solvent for both the reaction and washing stages.

The functional groups in *Cucurbita pepo* leaf extract and the synthesized magnetite nanoparticles were analyzed using a Fourier-transform infrared (FTIR) spectrometer (Nicolet IS10, Nicolet Corporation, USA) over a spectral range of 400–4000 cm^{-1}. The UV–visible spectrophotometer (Perkin-Elmer Inc., USA) was used for the analysis of biogenic synthesized magnetite nanoparticles periodically as a function of time in the wavelengths ranging from 200-700 nm.

Preparation of plant extract: *Cucurbita pepo* leaves were collected from roadside trees near Mody University of Science and Technology, Laxmangarh, India. The leaves were thoroughly washed with Milli-Q water to remove dust and impurities, then dried in indirect sunlight for 10 days to prevent thermal degradation. The dried leaves were finely ground into powder using an electronic blender. For extraction, 10 g of powder was mixed with 100 mL of Milli-Q water and heated at 60 ºC in a water bath for 20 min. After cooling in the shade, the mixture was filtered through Whatman filter paper to obtain a clear extract, which was stored at 4 ºC.

Preparation of magnetite nanoparticles: In a 250 mL Schott Duran beaker, 100 mL of double-distilled water was combined with 0.53 g of $FeCl_2\cdot 4H_2O$ and 1.11 g of $FeCl_3\cdot 6H_2O$, and the salts were dissolved with gentle stirring. The resulting solution was heated to 80 ºC. After 10 min, 5 mL of *C. pepo* leaf aqueous extract was added dropwise to the heated mixture. Separately, 0.8 g of NaOH was dissolved in deionized water to prepare a 1 M solution, which was then introduced dropwise over 5 min under continuous stirring. The formation of magnetite nanoparticles was evidenced by the gradual color change of the solution from dark red to green and the appearance of a black precipitate, confirming the reduction and nucleation processes.

Estimation of hydrogen from aldehydes: The catalytic potential of synthesised magnetite nanoparticles (Fe_3O_4) was observed by measuring volume of hydrogen (H_2) using different aldehyde resources by studying downward displacement of water *via* graduated measuring cylinder. In brief, the hydrogen generation reaction was carried out by mixing 100 mL of formaldehyde (0.48 M) solution with NaOH (1 M) and a predetermined amount of catalyst in a sealed flask. Vigorous stirring initiated the reaction and then the volume of hydrogen produced was measured *via* downward displacement of water using a graduated measuring cylinder. Observations indicated that, in the absence of a catalyst, only 0.1 mL of hydrogen was generated from HCHO within 60 min, whereas the addition of magnetite nanoparticles significantly increased the hydrogen evolution rate. Notably, hydrogen production became appreciable within 10 min of catalyst addition and the final volume was recorded after 1 h in each case.

RESULTS AND DISCUSSION

UV-Vis spectral studies: The UV-Vis absorption spectrum of the synthesized magnetite (Fe_3O_4) nanoparticles was recorded in the 200-300 nm range, revealing a prominent absorption peak at 2.332 absorbance units. Magnetite nanoparticles typically exhibit a characteristic absorption band between 280 and 350 nm, attributed to $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer transitions. The observed peak in the 200-700 nm region suggests the presence of smaller nanoparticles, likely below 10 nm, due to quantum size effects, as bulk Fe_3O_4 absorbs around ~350 nm (Fig. 1). The blue shift confirms the nanoscale dimensions of the synthesized particles. This absorption band, arising from $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer, is a key feature of the inverse spinel structure of Fe_3O_4 and distinguishes it from the oxidized form, which absorbs at slightly higher wavelengths, thereby verifying the formation of the magnetite phase.

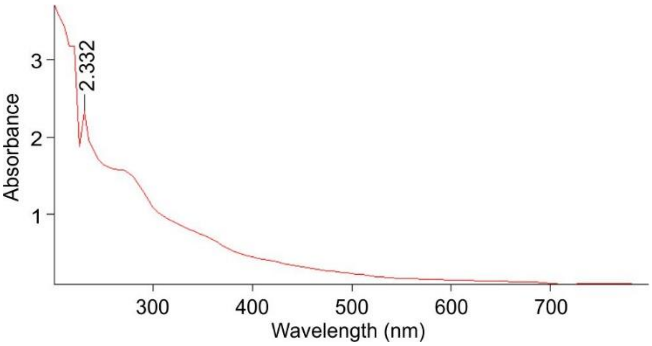

Fig. 1. UV-Vis of the *Cucurbita pepo* leaf extract mediated magnetite nanoparticles

FTIR spectral studies: The FTIR spectrum of *C. pepo* leaf extract revealed several characteristic functional groups indicative of bioactive compounds. A broad peak around 3400 cm^{-1} corresponds to the O–H stretching vibrations, suggesting the presence of hydroxyl groups typical of flavonoids, tannins, and polyphenols. Peaks at ~2923 cm^{-1} and ~2851 cm^{-1} are assigned to C–H stretching vibrations of aliphatic $-CH_2$ and $-CH_3$ groups, indicating lipids or other organic molecules. The peak at ~1567 cm^{-1} corresponds to C=C stretching in aro-

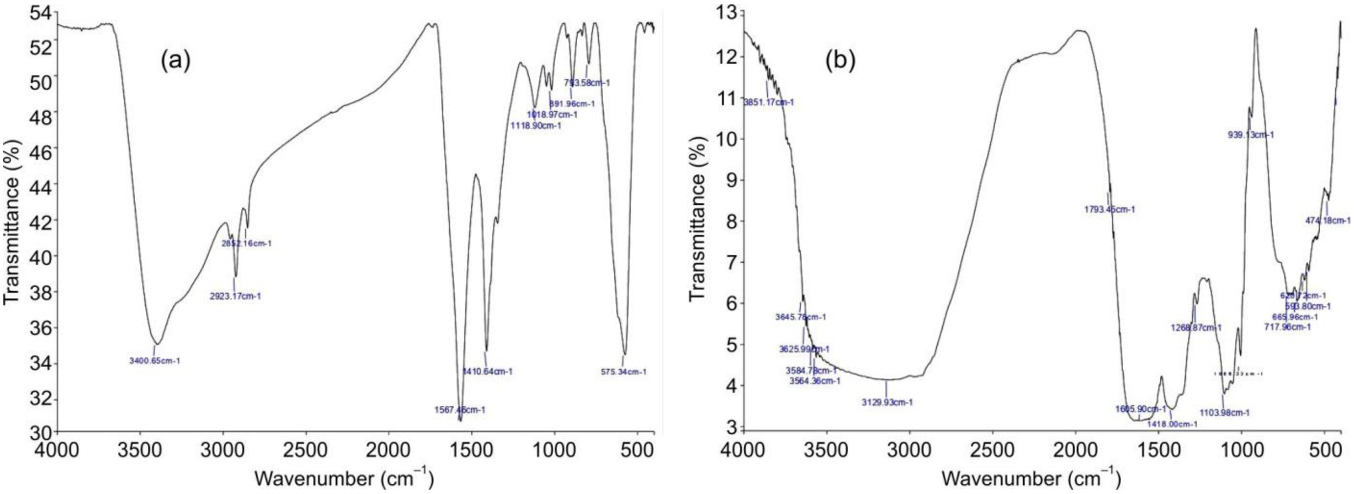

Fig. 2. FTIR spectra of (a) *Cucurbita pepo* leaf extract and (b) magnetite nanoparticles

matic rings, characteristic of flavonoids, tannins and other polyphenolic compounds. The C–O stretching vibrations at ~1410 cm^{-1} suggest carboxylate or phenolic groups, while the range ~1118–798 cm^{-1} indicates C–O–C and C–O vibrations from glycosidic bonds or carbohydrate polymers. A band at ~575 cm^{-1} may reflect metal–oxygen interactions, highlighting possible interactions between biomolecules and Fe^{3+} ions (Fig. 2a). Collectively, these functional groups indicate that the extract contains bioactive molecules capable of acting as reducing and capping agents during nanoparticle synthesis, with C–H vibrations supporting their role in stabilizing the nanoparticles.

The FTIR spectrum of the synthesized magnetite (Fe_3O_4) nanoparticles showed distinctive features confirming their formation and surface characteristics. A broad O–H stretching band from 3851–3564 cm^{-1} indicates surface hydroxylation or adsorbed water, while a peak at 3129 cm^{-1} may arise from surface C–H vibrations due to organic stabilizers. C=O stretching at ~1793 cm^{-1} suggests the presence of surface carboxylate groups, and O–H bending at ~1606 cm^{-1} further confirms adsorbed water. Peaks at 1418 cm^{-1} and 1268-1103 cm^{-1} are attributed to C–O stretching from the surface-bound organic molecules. The Fe–O stretching vibrations at ~939–665 cm^{-1} and ~474 cm^{-1} serve as the characteristic signatures of magnetite, confirming the successful formation of Fe_3O_4 nanoparticles. The observed surface functionalization by hydroxyl, carboxyl and C–O groups likely contributes to nanoparticle stability and potential bioactivity (Fig. 2b). Overall, the FTIR results support both the composition and surface interactions of the synthesized nanoparticles and are consistent with previously reported studies.

Hydrogen production: After 1 h of reaction at 60 ºC with vigorous stirring, measurement of hydrogen generation was done with three different aldehydes *e.g.* formaldehyde, acetaldehyde and benzaldehyde has been tabulated in Table-1. It was observed that on using magnetite, rate of hydrogen production was 350 times more as compared to blank test in case of formaldehyde. The experimental design of hydrogen production from formaldehyde through downward displacement of water in a graduated measuring cylinder. In present study, the unique aspect is the collection procedure of hydrogen gas by downward displacement of water excluding the possibility of presence of CO, CO_2 and NH_3 as impurity with H_2, CO and CO_2 are heavier gases and highly water soluble and NH_3 though lighter is highly water soluble while hydrogen is not.

TABLE-1
THE AMOUNT HAS BEEN RECORDED AFTER 1 h IN EACH CASE USING 0.01 g OF MAGNETITE NANOPARTICLES

Aldehydes	Amount of hydrogen (mL)
Formaldehyde	35
Acetaldehyde	38
Benzaldehyde	45

Effects of amount of magnetite as nanocatalyst: The activity of hydrogen generation against catalyst loading at an elevated temperature (60 ºC) has been performed with different amount of magnetite *e.g.* 0.005 g, 0.01 g and 0.015 g in similar sets of experimental conditions to ensure the surface-mediated catalytic activity of magnetite nanoparticles. Rate of hydrogen production was found directly proportional to amount of magnetite catalyst. On increasing amount of catalyst by three times *i.e.* from 0.005 g to 0.015 g, rate of hydrogen production for HCHO generously increased from 30 to 48 mL in 1 h. Reaction period. It also shows that the catalytic hydrogen generation reaction uses HCHO surface reaction as well and these results combinedly conclude that rate of hydrogen production can be regulated by catalyst loading. The surface mediated magnetite catalyzed hydrogen production has been depicted in Fig. 3.

Mechanism of hydrogen production: The Cannizzaro reaction is a base-induced disproportionation reaction in which aldehydes lacking α-hydrogen atoms undergo simultaneous oxidation and reduction. In present study, this reaction was examined in competition with the conventional Cannizzaro pathway, catalyzed by magnetite (Fe_3O_4) nanoparticles under varying molar ratios of aldehyde and NaOH.

From the obtained results, it can be inferred that aldehydes devoid of α-hydrogen atoms act as key intermediates capable of generating hydrogen. The data indicate that both formaldehyde (HCHO) and water contribute one hydrogen atom each to form molecular hydrogen (H_2). Interestingly, a

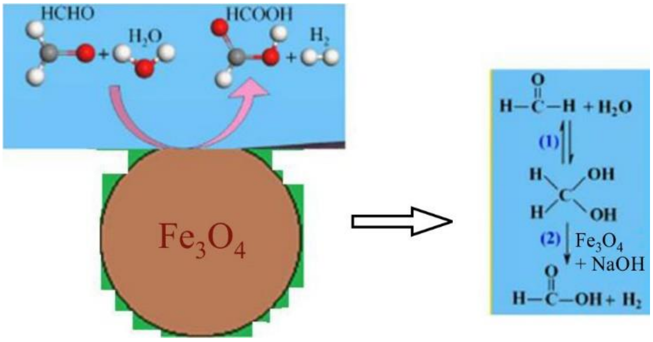

Fig. 3. The surface mediated magnetite catalyzed hydrogen production from formaldehyde

considerable amount of hydrogen was also evolved from acetaldehyde, which contains an α-hydrogen. This observation suggests that an alternative reaction mechanism may govern hydrogen generation from acetaldehyde, differing from the classical Cannizzaro pathway operative for aldehydes without α-hydrogen.

Conclusion

A feasible and efficient pathway for hydrogen generation from aqueous formaldehyde (HCHO) using magnetite (Fe_3O_4) nanoparticles as a catalyst has been demonstrated. The adopted hydrogen collection method effectively minimizes contamination by other gaseous byproducts such as CO and CO_2, which can be readily trapped or eliminated during the process. The pure hydrogen gas obtained *via* downward displacement of water highlights the potential of this approach as a viable alternative for clean hydrogen production. Overall, the use of magnetite nanoparticles as a catalyst offers an eco-friendly and cost-effective route for CO- and CO_2-free hydrogen generation. The involvement of Fe_3O_4 not only enhances the hydrogen evolution rate but also improves the reaction's stability and durability. Given its simplicity, scalability, and economic feasibility, the proposed method presents a promising strategy for sustainable hydrogen production.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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