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RESEARCH PAPER

Improved Degradation of Lignocellulosic Biomass Pretreated by Fenton-like Reaction Using Fe_3O_4 Magnetic Nanoparticles

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Abstract The ability of Fe_3O_4 Fenton-like reaction to produce glucose from lignocellulosic biomass was investigated. Fe_3O_4 magnetite nanoparticles were chemically synthesized from iron salts (a mixture of 1 M $FeCl_2$ and 2 M $FeCl_3$) using an ammonia solution (30% NH_4OH). The synthesized Fe_3O_4 nanoparticles were further characterized by X-ray photoelectron spectroscopy, energy dispersive X-ray spectroscopy, scanning electron microscopy, and transmission electron microscopy. Reed stems and rice straw biomasses pretreated with optimized Fenton-like reagents (Fe_3O_4 and H_2O_2) increased glucose production by 177 and 87%, respectively, compared to the control without the catalysts.

Keywords: lignocellulosic biomass, Fe_3O_4 nanoparticles, Fenton-like reaction, cellulase, glucose

1. Introduction

Metal nanoparticles have played an important role in basic research and in a variety of applications [1,2]. Compared to bulk counterparts, they possess proprietary physical and chemical properties [3]. The production of ultra-fine, uniformly dispersed nanoparticles is becoming increasingly important due to the exceptional properties [4,5]. As a result of their high surface area to volume ratio, nanosize, and magnetic properties, magnetite nanoparticles (Fe_3O_4 NPs) are useful in many scientific and industrial applications such as magnetic resonance imaging, immunoassays, bioseparation, and drug delivery [6-9]. Their usefulness as catalysts [10] and catalyst supports [11,12] has been studied in recent years. Gao *et al.* [13] demonstrated the efficacy of Fe_3O_4 NPs as a self-supporting catalyst for Fenton-like reaction. Ozonation of *para*-chlorobenzoic acid was also achieved due to the catalytic nature of Fe_3O_4 NPs, which is complemented by a large surface area, basic sites on surface, and nanosize [14].

The recoverable nature of the Fe_3O_4 NPs through the magnetic approach has made it advantageous to produce chemical precursors from renewable resources through the immobilization of catalysts containing active functional groups [15,16]. Such catalysts with magnetic cores are becoming a replacement for catalysts commonly used in the treatment of biomass [17,18]. They are useful for the synthesis of other chemicals such as 2,5-furandicarboxylic acid [19], 5-hydroxymethylfurfural [20,21], and 5-ethoxymethylfurfural [22] from sustainable biomass.

Lignocellulose is one of the most abundant renewable resources available on the planet. Lignocellulose is mainly composed of cellulose, hemicellulose, and lignin [23]. Cellulose and hemicellulose can freely hydrolyze to fermentable sugars, but lignin has a negative impact on cellulose availability and must be removed or modified by pretreatment. Therefore, choosing the appropriate pretreatment method is essential to increase the proficiency of saccharification technology and realize the process economically [24]. Pretreatment of lignocellulosic biomass is usually achieved *via* two ways: acidic and enzymatic [23,25]. Acidic processes generally inhibit bacterial growth and interfere with downstream fermentation processes. Enzymatic hydrolysis is another approach to biomass conversion that can extract large amounts of sugar with low levels of inhibitors. A major obstacle to the implementation

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of economically feasible lignocellulosic biorefinery is the overly high cost of the enzyme. The Fenton reaction does not require extreme conditions such as high temperature, high pressure, or high concentration of chemicals. It is therefore considered an environmentally friendly process. Since the Fenton reaction is effective in destroying wood in nature, it can be applied to pretreatment of lignocellulose to increase enzyme digestibility [26].

This study suggests the use of Fe_3O_4 NPs as a catalyst to convert lignocellulosic biomass to glucose. Jung *et al.* [26] recently applied a homogeneous Fenton reaction to pretreatment of lignocellulose. However, the use of environmentally friendly and easily recoverable Fe_3O_4 NPs as a catalyst for sugar production from lignocellulosic biomass has not yet been reported as far as we know. The catalytic activity of Fe_3O_4 NPs as a catalyst in the sugar production was evaluated and compared with the control experiment without the catalyst. The reusability of Fe_3O_4 NPs was also tested through several recycling experiments.

2. Materials and Methods

2.1. Chemicals and reagents

D-glucose, iron (II) chloride tetra-hydrate ($FeCl_2 \cdot 4H_2O$, 98%), iron (III) chloride hexa-hydrate ($FeCl_3 \cdot 6H_2O$, ACS reagent grade), and sulfuric acid (H_2SO_4, 99.999%, HPLC grade) were procured from Sigma-Aldrich (St. Louis, MO). Cellulase (Celluclast 1.5L) was obtained from Novozyme, USA. Ammonium hydroxide (NH_4OH) was purchased from Samchun chemicals, Korea. Hydrogen peroxide (H_2O_2) was obtained from OCI, Korea. All other chemicals used were high purity and ultra-filtered Milli-Q water (Millipore, USA) was used for all experiments.

2.2. Synthesis of Fe_3O_4 NPs

Typically, 100 mL of 1 M $FeCl_2$ was added to 100 mL of 2 M $FeCl_3$ solution in an Erlenmeyer flask. To this mixture, 100 mL of 30% NH_4OH was added dropwise using a buret. The reaction took place at room temperature in a magnetic stirrer at 200 rpm for 30 min. After the reaction, neodymium magnets were used to separate the black particles. The synthesized particles were thoroughly washed 3 ~ 4 times with deionized water and dried overnight under ambient conditions before use for further experiments.

2.3. Characterization of Fe_3O_4 NPs

The synthesized and dried powders of Fe_3O_4 NPs were further analyzed using energy dispersive X-ray spectroscopy (EDS, Philips XL-30) and X-ray photoelectron spectroscopy (XPS, ESCALAB 210) equipped with Al X-ray source (1486.6 eV) and analyzer. Scanning electron microscopy (SEM, Philip Model CM 200) was performed to investigate the morphology of the particles. The particles were also analyzed by energy filtering transmission electron microscopy (TEM, JEM-2100 F, HR, Jeol Ltd.) operating at 200 kV.

2.4. Catalytic reactions with Fe_3O_4 NPs

Two lignocellulosic biomasses (reed stem and rice straw) were used in this study. Reed stem was harvested from Musimcheon riverside (Cheongju, Korea). Rice straw was collected from Chungbuk National University campus (Cheongju, Korea). The biomass was uniformly crushed to a size of 1 mm or less using a mill (MF10, IKA). The pulverized biomass was stored in a sealed container at room temperature.

The conversion reaction experiment was carried out in a 250 mL Erlenmeyer flask. In a characteristic experiment, a mixture of different ratios of H_2O_2 and Fe_3O_4 NPs was added to a 10% (w/v) biomass in a separate flask and stirred at a rate of 200 rpm at 30°C for 24 h. The product was filtered using filter cloth (22 ~ 25 μm pore size) and washed with deionized water until pH reached 6 ~ 7. Enzymatic digestion was performed by adding 1.0 mL Celluclast 1.5 L (Novozyme 60 FPU/g) and 10 mL citrate buffer to pretreated biomass (1% w/v) followed by reaction at a rate of 150 rpm at 55°C for 24 h. Analysis to confirm the identity and concentration of the product was performed by high pressure liquid chromatography (HPLC, YL 9100, YOUNG-LIN Inc., Anyang, Korea) after cooling the reaction product at room temperature. Control experiments were also carried out without the use of catalysts. All experiments were done in triplicate. The mean and standard deviation values of the results obtained are reported.

2.5. Recycling of Fe_3O_4 NP catalyst

Fe_3O_4 NPs was removed from the reaction solution using a magnet and washed three to four times with deionized water. After recovery, the catalyst was dried in air at 80°C for 1 h and then reused in subsequent reactions.

2.6. HPLC analysis

Major biomass components were analyzed by HPLC using the National Renewable Energy Laboratory method [27]. Reaction products were also analyzed by HPLC. Prior to each analysis, the test product was first centrifuged and filtered through a 0.2 μm polytetrafluoroethylene syringe filter (VWR, Radnor, PA) to remove the remaining catalyst. The product was identified and quantified in the filtrate using an Aminex HPX-87H (Bio-Rad Laboratories, Inc., Hercules, CA) column with a differential refractometer. The mobile phase used was 5 mM sulfuric acid at a flow rate of 0.6 mL/min. The temperature of the column and the detector were adjusted to 55 and 35°C, respectively. The calibration curve for quantification of reaction products was prepared using glucose in water as standard. Theoretical amount of glucose production by enzymatic digestion was expressed based on the measured cellulose content in the biomass.

3. Results and Discussion

3.1. Synthesis and characterization of Fe_3O_4 NPs

The co-precipitation process of the reactants used in the reaction (1 M $FeCl_2$, 2 M $FeCl_3$, and 30% NH_4OH) produced a black product, which was attracted to the magnet. This showed a successful synthesis of Fe_3O_4 NPs (Fig. 1A). An image of the synthesized and dried Fe_3O_4

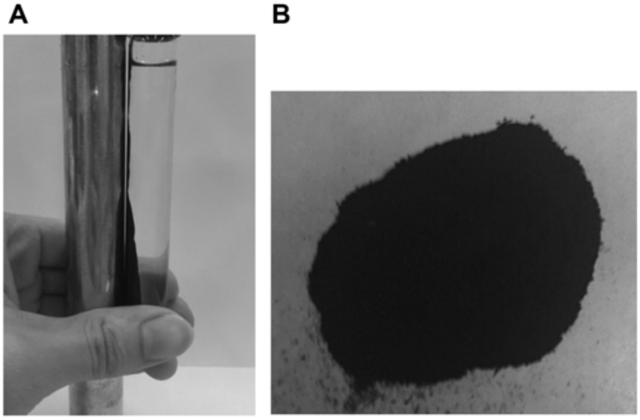

Fig. 1. (A) Attraction between magnetic Fe_3O_4 NPs and neodymium magnetic stick. (B) Dried powder of Fe_3O_4 NPs.

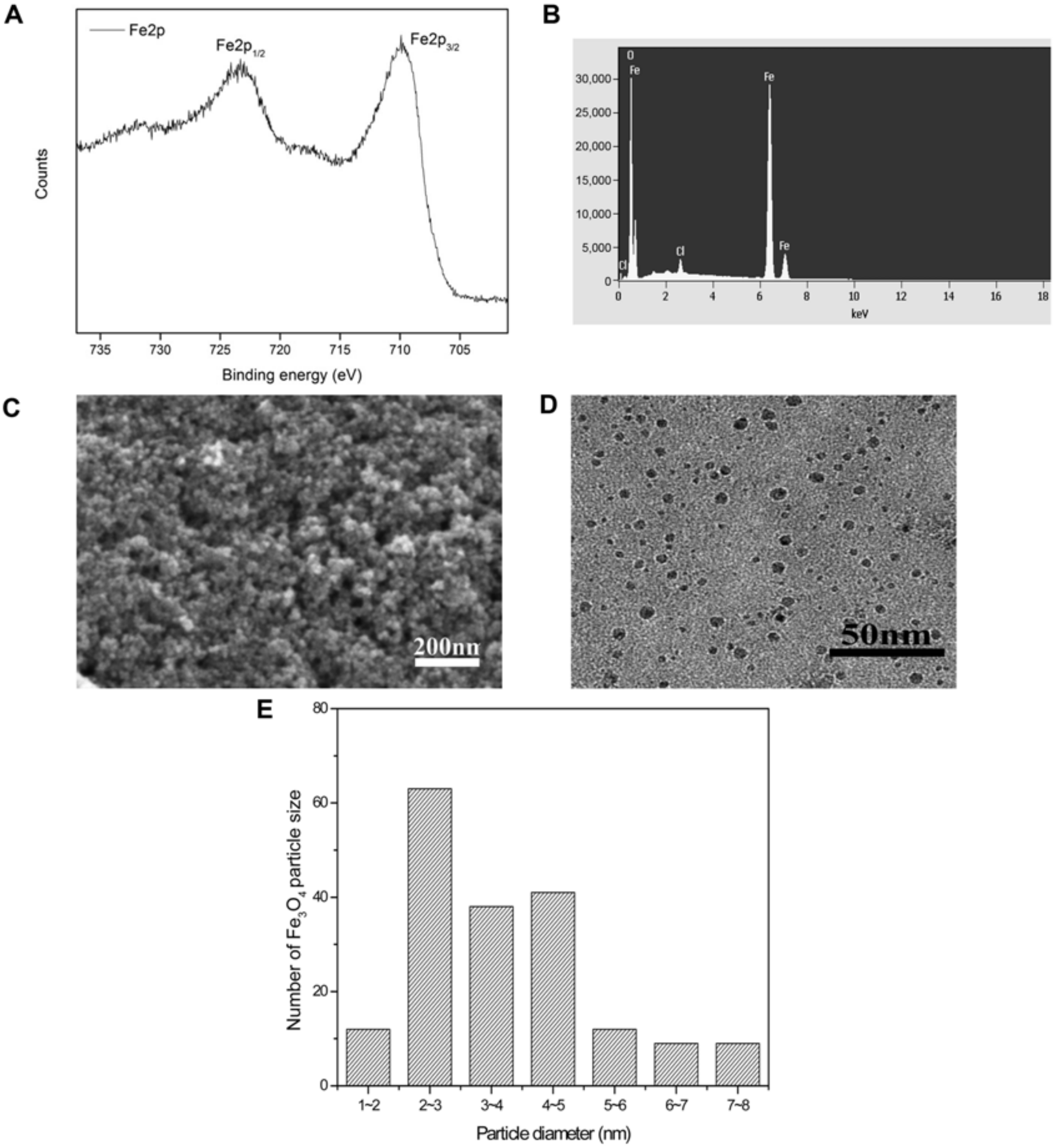

Fig. 2. (A) XPS, (B) EDS, (C) SEM, (D) TEM, and (E) particle size analysis of Fe_3O_4 NPs.

NPs is shown in Fig. 1B. XPS analysis revealed $Fe2p_{1/2}$ and $Fe2p_{3/2}$ core level binding energy for Fe_3O_4 NPs at 724 and 710 eV, indicating the presence of metallic Fe in the sample (Fig. 2A). EDS analysis indicated the presence of Fe and O peaks in all samples (Fig. 2B). The elemental compositions of atomic % and weight % of Fe were 44.65 and 73.79%, respectively, and the atomic % and weight % of O were 55.35 and 26.21%, respectively. SEM showed the presence of spherical nanoparticles (Fig. 2C). TEM micrographs of synthesized Fe_3O_4 NPs showed spherical particles ranging in size from 1 to 8 nm (Figs. 2D and 2E). More than 60 particles showed a diameter of 2 ~ 3 nm (Fig. 2E). Observations on the characterization of Fe_3O_4 NPs in this study are similar to previous reports [28-30].

3.2. Catalytic activities of Fe_3O_4 NPs on the conversion of biomass to glucose

The effect of pretreated biomasses on the enzymatic digestibility by different concentrations of Fe_3O_4 NPs and H_2O_2 was investigated (Figs. 3 and 4). The enzymatic digestibility (% theoretical glucose) was calculated based on the cellulose content in the dry biomass. The compositions of cellulose, hemicellulose, and lignin of reed stem were 34.2 ± 2.1, 10.0 ± 0.9, and 34.0 ± 0.9%, respectively. For 2 g/L Fe_3O_4 NPs, glucose production was not increased compared to the untreated group even after increasing the H_2O_2 concentration (Fig. 3A). For 4 g/L Fe_3O_4 NPs, enzymatic digestibility increased from 9.01 to 13.5% theoretical glucose at H_2O_2 concentrations above 1.2 M (Fig. 3B). For 6 g/L Fe_3O_4 NPs, the highest enzymatic digestibility of 25% theoretical glucose was obtained at 2.5 M H_2O_2 (Fig. 3C). When H_2O_2 concentration was fixed at 10 M, higher concentrations of Fe_3O_4 NPs did not increase glucose production. Therefore, optimum concentrations of Fe_3O_4 NPs and H_2O_2 were 6 g/L and 2.5 M, respectively, in pretreatment of reed stem biomass. Similarly, optimum conditions for rice straw pretreatment were 10 g/L Fe_3O_4 NPs and 4 ~ 4.5 M H_2O_2 concentrations (Fig. 4). Under these conditions, enzymatic digestibility was 43% theoretical glucose, which was higher than 23% theoretical glucose of untreated rice straw. The enzymatic digestibility of rice straw (43% theoretical glucose) was higher than that of reed stem (25% theoretical glucose) because of less lignin content of rice straw (17.5%) than reed stem (34.0%).

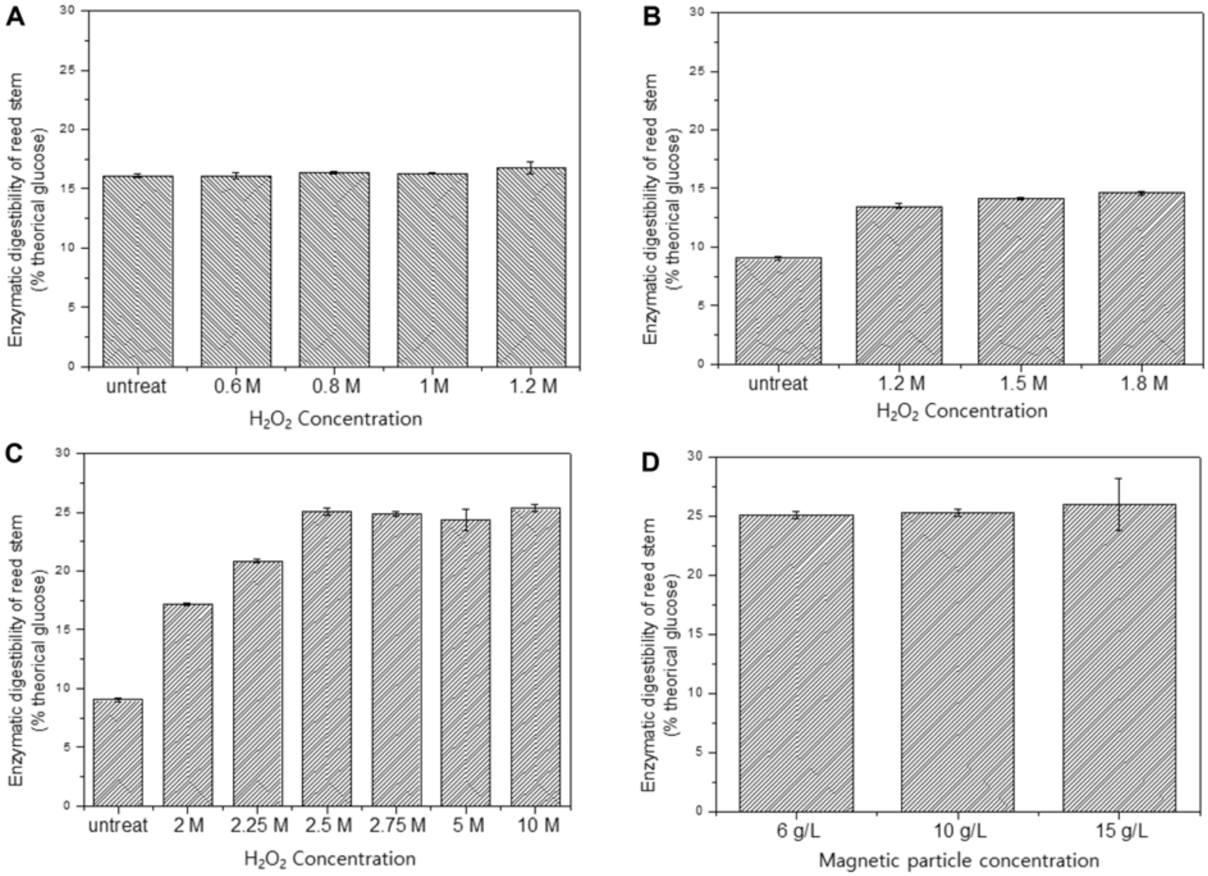

Fig. 3. Effect of Fe_3O_4 NPs and H_2O_2 concentrations on enzymatic digestibility of reed stem pretreated with (A) 2 g/L Fe_3O_4 NPs, (B) 4 g/L Fe_3O_4 NPs, (C) 6 g/L Fe_3O_4 NPs, and (D) 10 M H_2O_2.

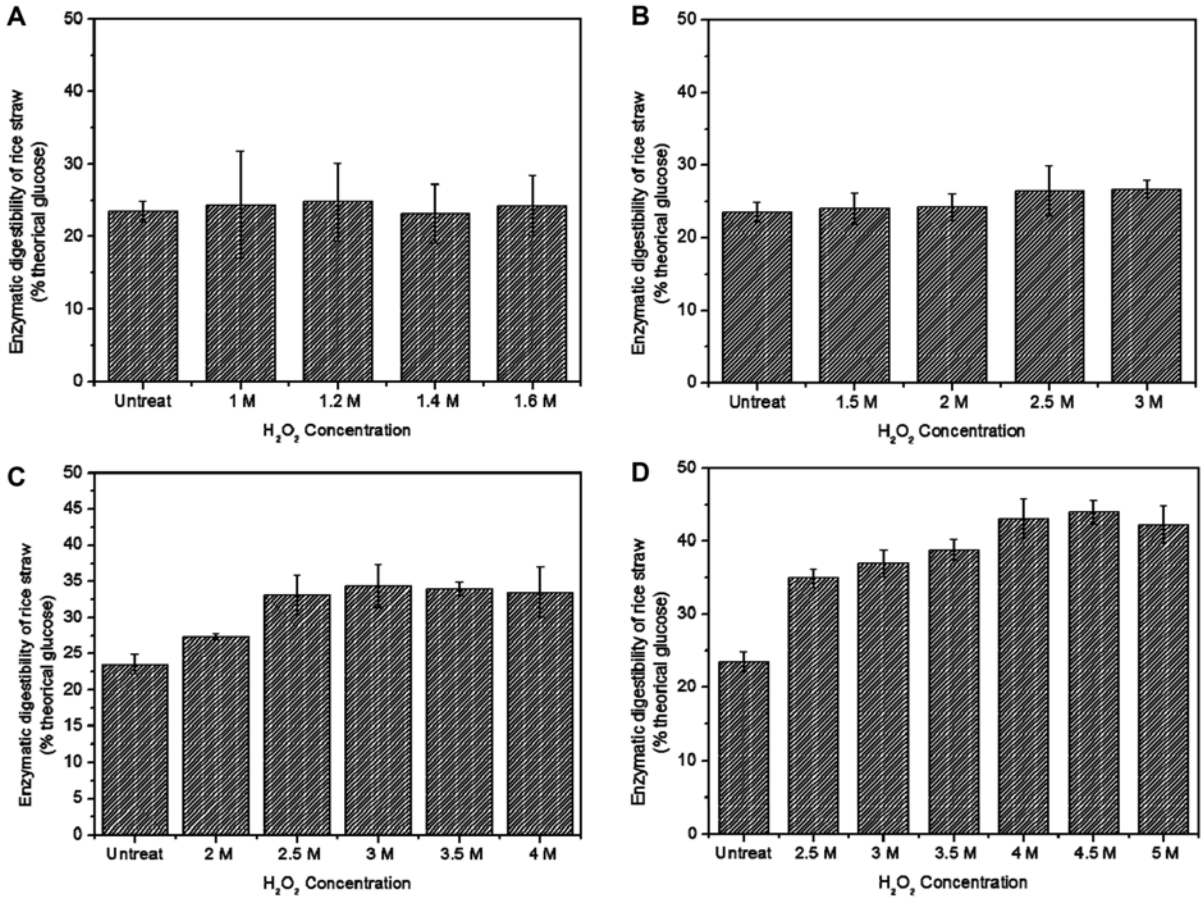

Fig. 4. Effect of Fe_3O_4 NPs and H_2O_2 concentrations on enzymatic digestibility of rice straw pretreated with (A) 4 g/L Fe_3O_4 NPs, (B) 6 g/L Fe_3O_4 NPs, (C) 8 g/L Fe_3O_4 NPs, and (D) 10 g/L Fe_3O_4 NPs.

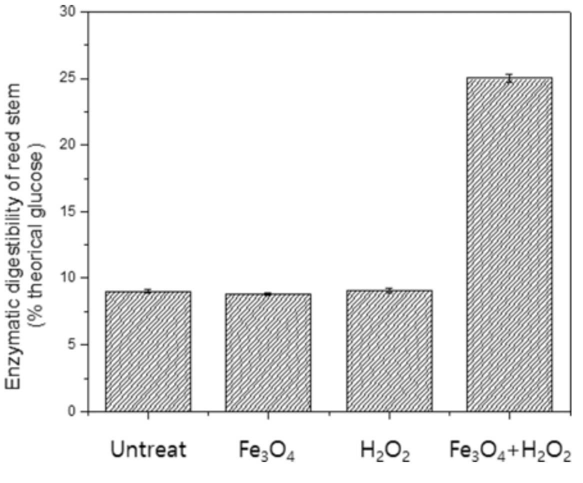

Fig. 5. Comparison of enzymatic digestibility of reed stem untreated and treated with 6 g/L Fe_3O_4 NPs alone, 2.5 M H_2O_2 alone, and combinations thereof.

To clarify the role existing in each compound, 6 g/L Fe_3O_4 NPs and 2.5 M H_2O_2 used in reed stem biomass pretreatment were separately added (Fig. 5). The enzymatic digestibility in the condition of adding Fe_3O_4 NPs and H_2O_2 separately was 8.82 and 9.07% theoretical glucose, respectively, which was not increased compared to 9.01% theoretical glucose in the untreated group. Thus, the individual reagents did not affect the enzyme saccharification but only the treatment of Fe_3O_4 NPs and H_2O_2 together influenced the biomass enzyme saccharification.

$FeCl_2$ and $FeCl_3$ (divalent and trivalent iron salts) have strong Lewis acidity and basicity, which is beneficial for cellulose and hemicellulose degradation studies [31-33]. In this study, the conversion of biomass to glucose was assessed in the presence of Fe_3O_4 NPs. Systems containing cellulose degradation are known to produce a wide variety of products after complete conversion [34,35] In this study, cellulose was hydrolyzed and glucose was identified as the main product of this reaction. Glucose production with the catalyst was 87 ~ 177% higher than in the control experiments without the catalyst, suggesting an important role for Fe_3O_4 NPs when acting as a nanocatalyst to degrade biomass into glucose.

3.3. Recycling of Fe_3O_4 NP catalyst

In addition to the promising catalytic activity of Fe_3O_4 NPs

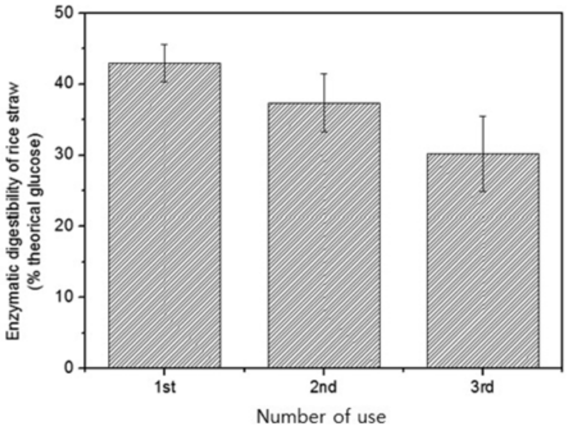

Fig. 6. Effect of multiple use of Fe_3O_4 NPs on enzymatic digestibility of rice straw pretreated with 10 g/L Fe_3O_4 NPs and 4 M H_2O_2.

that convert biomass to glucose, the magnetic properties of the NPs have led to another benefit of easy recovery from the reaction system. The recovery and recyclability of Fe_3O_4 NP catalysts was evaluated by performing three sequential runs with the recovered catalyst. The enzymatic digestibility of rice straw pretreated with 10 g/L Fe_3O_4 NPs and 4 M H_2O_2 was 43% theoretical glucose when first used, and it was 37.5 and 31% theoretical glucose when the Fe_3O_4 NPs was reused twice and three times, respectively (Fig. 6). After each recycle run, the activity of the recycled Fe_3O_4 NP catalysts was slightly reduced with decrease in glucose production. This can occur due to the deposition of reaction by-products on the catalyst surface similar to polymeric humin deposition on the catalyst surface [36]. Nevertheless, the magnetic and XPS patterns of Fe_3O_4 NPs were almost similar after recycle. This observation shows that no noticeable change of the Fe_3O_4 NP catalyst to the other forms of iron oxide occurs and they maintain most activity as the active component in the recycle operation.

3.4. Reaction mechanism of the conversion of biomass to glucose using Fe_3O_4 NP catalysts

Several types of metal nanoparticles such as MnO_2 [37], silver [38], and gold [39] have been used for the degradation of complex molecules. Metal nanoparticles help to speed up the degradation reaction. Fenton's reaction mechanism at the surface of the Fe_3O_4 NPs was reported by Li *et al.* [40], which showed a mechanism similar to the classic Haber-Weiss mechanism. They believe that the in situ formation of surface-bound ferrous ions is thermodynamically beneficial by electron transfer from the iron NP core to the oxide layer surface ($2Fe^{3+} + Fe \rightarrow 2Fe^{2+}$, $\Delta E = 1.21$ eV), which reacts with H_2O_2 to produce hydroxyl radicals (·OH) with strong oxidative ability ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot HO + OH^-$) and thus provides an effective delivery pathway of electrons through the Fe^{3+}-Fe^{2+} surface switch to induce the continuous production of ·HO to degrade biomass. Salunke *et al.* [38] proposed an enhanced degradation of cellulose in the presence of AgNPs as a catalyst by immobilizing the cellulase enzyme on the nanoparticle support. Fe_3O_4 NPs can be immobilized with a catalyst having an active functional group [15,16]. By forming a catalyst with a magnetic core [17,18], they can act as a virtuous catalyst in the treatment of biomass.

4. Conclusion

Pretreatment of biomass by Fenton-like reaction increased cellulase enzymatic degradation activity. Magnetite nanoparticles (Fe_3O_4 NPs) have proven to be effective catalysts for converting lignocellulosic biomass to sugar. At optimum concentrations of H_2O_2 and Fe_3O_4 NPs, the enzymatic digestibility increased by 177 and 87% for reed stem and rice straw, respectively, compared to the control groups. Moreover, Fe_3O_4 NPs can be easily synthesized and separated using the magnetic method and are easily recyclable for this reaction. Therefore, this environmentally friendly catalyst has an excellent potential for glucose production from biomass.

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