



Article

Preparation MnO₂ NPs by Sol-Gel method and Study Antioxidant Properties

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Abstract

Manganese dioxide nanoparticles (MnO₂ NPs) is a well-known pseudocapacitive substance that has been widely discovered. It has been studied and greatly appreciated, especially for its antioxidant and antibacterial activities. The current study aims to manufacture manganese dioxide nanoparticles, characterize them, and study their properties as antioxidants. In this work, Nano of MnO₂ was created using the sol-gel method, which involved dissolving manganese nitrate in distilled water to create a solution, adding urea, heating the solution for three hours at 100 C to create a gel, and drying the gel for an additional hour at 280 °C to create manganese oxide powder. The resultant substance was examined using SEM and X-ray diffraction methods, and compared with JCPDS card number 00-044-0141. The material was discovered to be a quaternary crystal system. Using the Debye-Scherrer equation, the crystal size was determined to be **37 nm**. The highest free radical scavenging activity is by MnO₂ NPs compared to standard, with estimates of 92.51 ± 1.3%, and 81.44 ± 2.1%. The results of the current study indicate the antioxidant effect of MnO₂-

NPs, which indicates their promising medical applications and opens new horizons for their use in further applications.

Keywords: Anti-oxidant , Manganese dioxide nanoparticles, Physical Properties, Sol-Gel method.

Introduction

Manganese is a transitional element that has three distinct valence states and is predicted to have very complex oxides(1). Manganese oxide II is an inorganic compound with a blackish or brown color that is found in pyrolidusite, a form of manganese ore found in nature (2). Manganese oxides, such as MnO, MnO₂, and Mn₃O₄, are interesting composites with a range of applications in wastewater treatment, biosensors, supercapacitors, and batteries because of their distinct physical and chemical properties (3). Nowadays, harmful diseases are controlled by the drugs prepared by the nano-biotechnology method. Usually, metal oxide receives more attention in nanotechnology due to the huge requirements in industries, pharmaceuticals such as disinfectants, catalysts, and antimicrobial drugs (4). Various crystal structures of Manganese dioxides (MnO₂) have more attention because of their physical and chemical properties and its broad applications in catalysis, biosensors, water treatment, electrochemical supercapacitors, and others (5). One of the most significant inorganic materials is MnO₂, and its electromagnetic properties and efficacy have been investigated carefully (6). It has many applications as antioxidants, antibacterials, and anti-inflammatory.

Several approaches, such as thermal breakdown, co-precipitation, sol-gel, simple reduction, solid-phase process, hydrothermal method, microwave process, etc., have been used to manufacture MnO₂ thus far (7, 8). The shape of the materials used in hydrothermal and sol gel processes is what draws most researchers to them, whereas precipitation method is preferred by others due to its simplicity,

low cost, quick preparative method, and ability to control particle size and composition easily [14].

Using a hydrothermal method, Singh and colleagues first created manganese oxyhydroxide (γMnOOH) nanowires, which they then converted into $\beta\text{-MnO}_2$ by calcining at 300°C [15].

Using a hydrothermal process, Feng *et al.* created two different types of $\alpha\text{-MnO}_2$ crystals: one that is caddice-clew-like in neutral conditions and urchin-like in acidic ones(9). MnO_2 was effectively produced by Zadeh et al. using sol-gel and hydrothermal processes. The findings showed that $\alpha\text{-MnO}_2$, βMnO_2 , and $\delta\text{-MnO}_2$ nanorods were all produced via a hydrothermal method, whereas $\gamma\text{-MnO}_2$ was produced via a sol-gel method (10). Using two distinct anions salts (sulphate monohydrate and oxalate), Kumar et al. and Balamurugan produced manganese oxide nanoparticles with a tetragonal shape through co-precipitation (11).

Material and Method

Nano manganese oxide is prepared by (Sol-gel) method by dissolving 35 g of manganese nitrate in 35 ml of distilled deionized water, and then 10 g of urea is added, and after continuous mixing with a magnetic stirrer to obtain the final solution, the resulting solution is filtered using filter paper to get rid of impurities, then after The solution is heated for 3 hours at 100°C to obtain manganese oxide gel, which is dried in the oven at 280°C for one hour to obtain the material (12).

2.1.3. Characterization

X-ray diffraction (Philips, X'pert, Pro-MPD, Cu-K α 40 kV, 20 mA) was employed to assess the phase purity and structural characteristics of the produced MnO_2 nanoparticles. It was conducted at 40 kV and 30 mA, with a scanning rate of $2^\circ/\text{min}$, a sample interval of 0.02, and a range from 20° to 80° . The pattern was obtained utilizing Cu-K α radiation at a wavelength of 1.54060 \AA . A scanning rate

of 2°/min and a sample interval of 0.02 were utilized during a 2-hour span from 20° to 80°. The surface morphology of the nanoparticles was analyzed using scanning electron microscopy (SEM).

2.6 Antioxidant Assay

The antioxidant activity of MnO₂-NPs were estimated using two methods: DPPH and total antioxidant. In these methods Gallic acid (GA) was used as a positive control.

2.6.1 DPPH radical scavenging assay

Antioxidant activities of MnO₂-NPs were calculated using the 1,1-diphenyl-2-picryl-hydrazyl (DPPH) assay with some modifications, as conducted by Villano *et al.*, (13). 1ml of each concentration (100-500 mg in ethanol) of *Musa SP* extract and green synthesized MnO₂-NPs was mixed with an equal volume of DPPH solution. The absorbance of mixtures was measured at λ_{max} =517 nm after being incubated in the dark at room temperature for 1 hour. The formula below (Equation 1) was used to determine the sample's capacity to scavenge DPPH radicals:

$$DPPH \text{ scavenge effect} = \frac{A_{control} - A_{sample}}{A_{control}} \times 100 \dots \dots \text{Equation 1}$$

Where,

A control is the absorbance of the control samples (DPPH solution without samples) and **A samples** is the absorbance of the sample (DPPH solution and samples).

Results and Discussion

1- X-RAY Diffraction

Study of crystal structure the structural characterization is analyzed to obtain information about particle size, crystal structure and surface shape (14). Where x-ray diffraction is considered to be the successful method for determining the structure of crystallized bodies, as a substance is a polycrystallized particle consisting of a large number of particles call a single crystal, which is a group of atoms stacked in a regular manner and described by crystal levels [15]. In this study, the particles were subjected to x-ray diffraction as shows the x-ray diffraction spectrum of MnO₂ nanoparticles, the XRD in figure (1) showed that the prepared material is nano MnO₂ this after matching with JCPDS No. (00-044-0141) and the crystal system is Quadrant, we can see from figure that the obtained peaks at [110], [220], [310], [400], [330], [420], and [510] agree with the brague reflections for the angles (12.7°, 25.7°, 28.8°, 36.6°, 39.01°, 41.2°, and 47.3 °) and the dominant growth trend is (110), the crystallite size calculated to be 37 nm by using Scherer-equations.

$$D = 0.94\lambda / \beta \cos \Theta$$

The results of the current study are consistent with many other studies (15, 16)

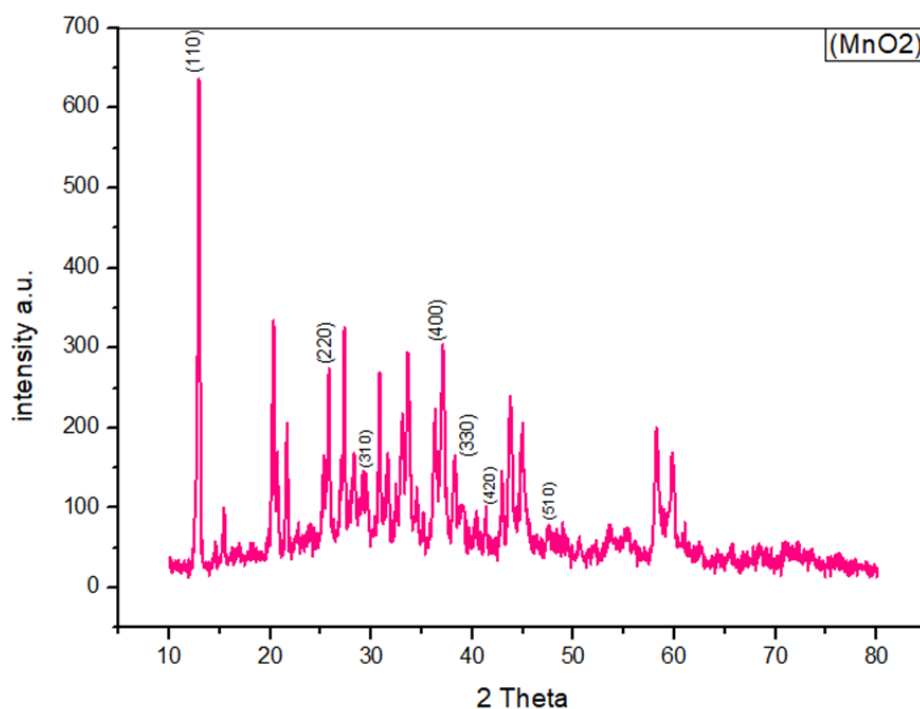


Figure (1) X-ray diffraction of MnO₂NPs

2- Field Emission Scanning Electron Microscopy

The MnO₂-NPs particle size and morphology of particles were evaluated by FE-SEM, the FESEM measurement was used to verify the surface shape of the MnO₂ particles what where chemical synthesized by sol-gel methods and we note from figure 2 that these particles have plate morphology and homogenous without defect and cracks, which can firms the success of the study in achieving good results in reaching nanoparticles with small sized ranging from (29-44) nm as shown in fig 2.

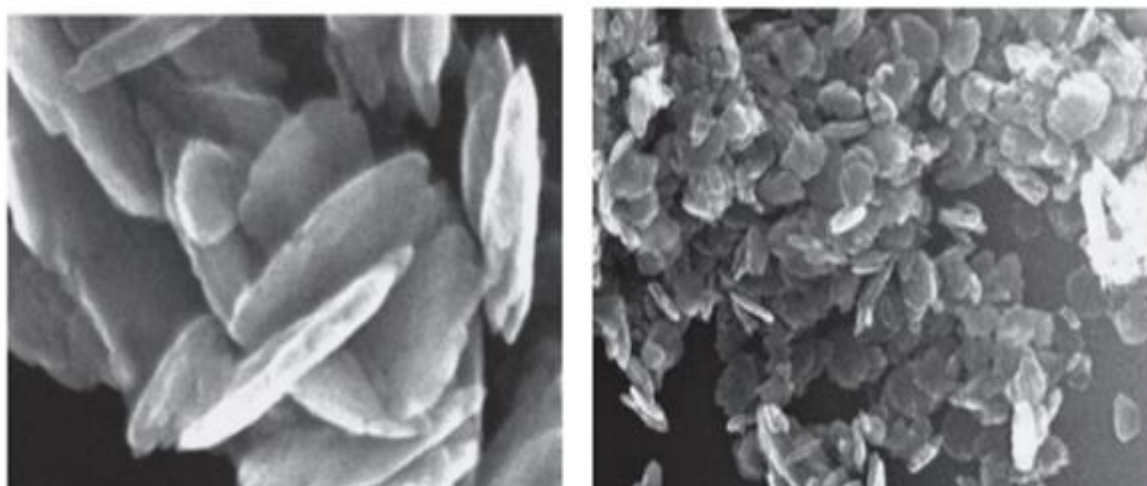


Figure (2) FE-SEM images of MnO₂ NPs

Anti-oxidant activity of green synthesized MnO₂-NPs

This study examined the anti-oxidant activity of MnO₂-NPs using DPPH assay is always used to measure the free radical scavenging ability of compounds found in medical plant extract (17). This assay was also used to assess the anti-oxidant activity of MnO₂-NPs . To confirm anti-oxidant activity, the colour of the DPPH solution should shift from purple to light yellow. This is because the DPPH radical is reduced by hydrogen atom transfer, resulting in a pale yellow solution(18). Figure 3 shows the DPPH radical inhibition of MnO₂ NPs using different concentrations and comparing the results with gallic acid. Although this

method used gallic acid as a positive control, the results showed that the MnO₂ NPs had significant free radical scavenging activity compared to standard. The highest free radical scavenging activity is by MnO₂ NPs compared to standard, with estimates of $92.51 \pm 1.3\%$, and $81.44 \pm 2.1\%$. The results obtained in this study strongly agree with previous studies (19, 20). Notably, various studies indicate that green synthesis enhances the antioxidant activity of MnO₂ nanoparticles in comparison to those produced via conventional chemical procedures. This is attributed to many substances, including polyphenols, flavonoids, proteins, and fatty acids, which are connected with MnO₂ nanoparticles.

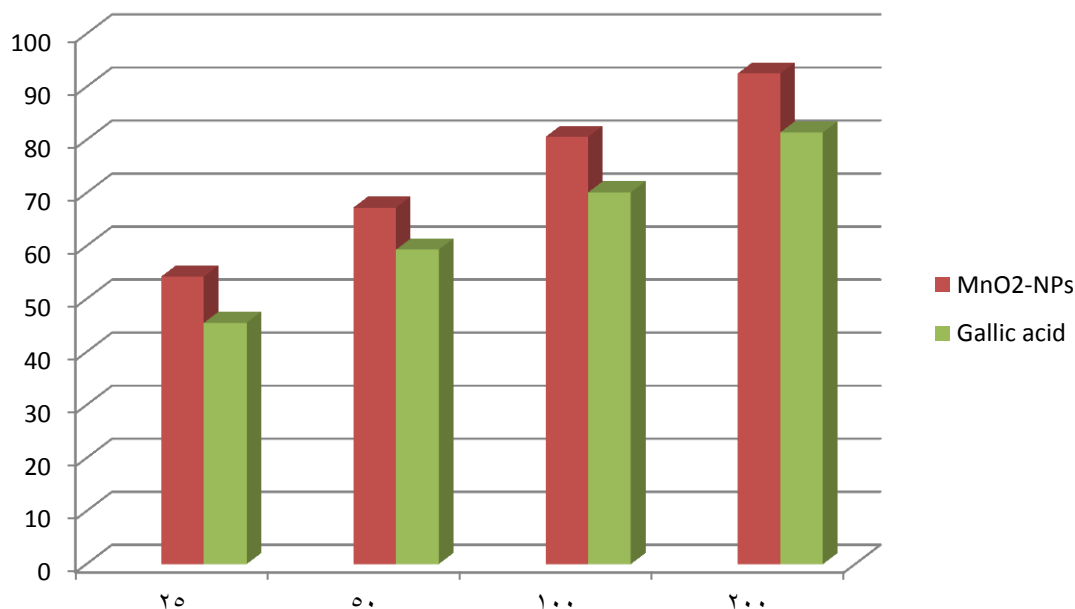


Figure 3: Anti-oxidant activity of MnO₂ NPs using DPPH assay.

Conclusion

The current research highlights that MnO₂ nanoparticles, created through the sol-gel method, exhibit some promising antioxidant properties. These findings suggest that these nanoparticles could serve as safe and effective solutions for combating a range of infections. However, to fully realize their potential in medical applications, further investigation is essential.

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