Green Synthesis and Photocatalytic activity of Manganese oxide Nanoparticles using *Illicium Verum* Extract

A. Emi Princess Prasanna

Department of Chemistry
Pope's College (Autonomous), Sawyerpuram 628 251, Tamilnadu
Affiliated to M.S University, Tirunelveli – 627 012, Tamilnadu, India

***Abstract*- An efficient methodology of manganese oxide nanoparticles were synthesised through green synthesis using illicium** verum **extract. The prepared nanoparticles were characterized by UV-Vis, FT-IR, AFM and SEM studies. UV-Vis spectroscopy of manganese oxide nanoparticles shows the maximum absorption around 250 nm and 300 nm. This is because of n → π^* and π → π^* transitions. The FT-IR spectrum of manganese oxide shows Mn–O vibrational peaks centered at 580 cm^{-1}, while other one pronounced peaks centered around 1627 cm^{-1} are O–H stretching vibrations on Mn atom. The surface morphology was characterized by AFM and SEM. The photocatalytic activities for the dye degradation of Manganese oxide nanoparticles were evaluated using Methylene Blue as an organic contaminant.**

***Keywords:* Manganese oxide, UV-Vis, SEM, Photocatalytic activity, Methylene Blue**

1. Introduction

Green synthesis is an environmentally friendly method presenting a different way of thinking in chemistry intended to eliminate toxic waste, reduce energy consumption, and to use ecological solvents water, ethanol, ethyl acetate, etc. Nanomaterials have appeared as novel antimicrobial agents containing a high-surface area to volume ratio and the inimitable physicochemical properties [1]. Manganese oxide NPs are widely used in contaminant sensing, drug delivery, data storage, catalysis and biomedical imaging. Green synthesis of NPs is important due to increased concern of environmental pollution. Green chemistry based synthesis of NPs is preferred due to its ecofriendly nature. Manganese oxide NPs have engrossed consideration due to their extensive applications in several field such as catalysis, ion- sieves, rechargeable batteries, chemical sensing devices, microelectronics and optoelectronics. [2-9] In this study, manganese oxide NPs were prepared through the green method and characterised by ultraviolet-visible, Fourier-transform infrared, and n scanning electron microscopy analysis methods. Synthesised manganese oxide NPs exhibit photocatalytic activities for the dye degradation in the visible light region.

2. Experiments

2.1. Preparation of Manganese oxide nanoparticles

In a typical reaction procedure, 3.2 g of manganese sulphate and 1.0 g of polyethylene glycol were dissolved in 50 mL of water. Then the solution was heated until to dissolve. Add 6.56 g of sodium acetate and 50 mL of freshly prepared star anise extract (*Illicium verum*) solution and then the mixture was stirred vigorously for 3 hr at room temperature. The resulting solution was filtered. The nanoparticles were washed, separated and dried in a vacuum oven at 90°C for 12 hr, and stored for further studies.

2.2. Preparation of *Illicium verum* Extract

About 10 g of fresh Illicium Verum was taken and washed thoroughly with distilled water to remove dust particles. These washed Illicium Verum were cut into small pieces and boiled in 100 mL of distilled water for 1 hr in a round-bottom flask with a water condenser. The extract was filtered using Whatman No.41 to obtain the pure extract.

2.3. Photocatalytic activity `

In the present study, methylene blue the well-known dye was used as a probe molecule to evaluate the photocatalytic activity of synthesized nanoparticles in response to direct sunlight. The characteristic optical absorption peak of methylene blue at 665 nm was chosen to monitor the photocatalytic degradation process. The experiment was carried out according to the following procedure.

2.4. Procedure `

For each measurement, 0.05 g of the sample was added into 100 mL of methylene blue aqueous solution having the concentration of 0.0031g/L. The suspension was stirred in the dark for about one hour to ensure the establishment of adsorption and desorption equilibrium of methylene blue on the nanoparticles surface. Then the solution was exposed to sunlight. At constant time interval of 10 minutes after equilibrium, 3 mL of the suspension was extracted and then centrifuged to separate the nanoparticles from the supernatant. UV-Vis absorption spectra of the supernatant were measured with a JASCO V650 UV-Vis spectrophotometer.
The percentage of dye degraded has been calculated using the following equation

$$\text{Percentage of degradation} = \frac{C_o - C_t}{C_o} \text{ X } 100$$

where C_o is the initial concentration of the dye solution and C_t is the final concentration of the dye solution at time t.

2.5. Characterization

Computer controlled JASCO V-600 was used to the study the absorption characteristics. Fourier transformed infrared spectra were recorded on Thermo Fisher Scientific, USA, Model - Nicolet iS5, iD3 ATR spectrometer.

3. Results and Discussion

3.1. FT-IR analysis

FTIR spectrum of manganese oxide is given in Fig.1. The peaks around 580 and 667 cm^{-1} denote the Mn-O stretching mode [10]. Mn-O mode of stretching 580 cm^{-1} indicates asymmetric stretching [11]. The FT-IR spectrum shows characteristic Mn–O vibrational peaks centered at 580 cm^{-1}, while other one pronounced peaks centered around 1627 cm-1 are O–H stretching vibrations on Mn atom, as reported previously [12].

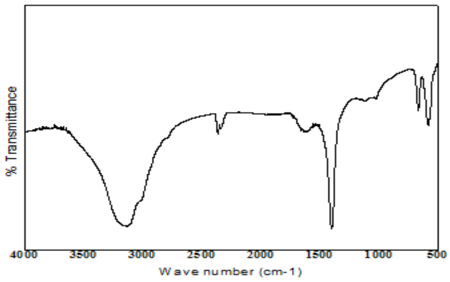

Fig.1. FTIR spectra of Manganese oxide NPs

3.2. UV analysis

UV-Vis spectroscopy of manganese oxide nanoparticles shows the maximum absorption around 250 nm and 300 nm. This is because of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

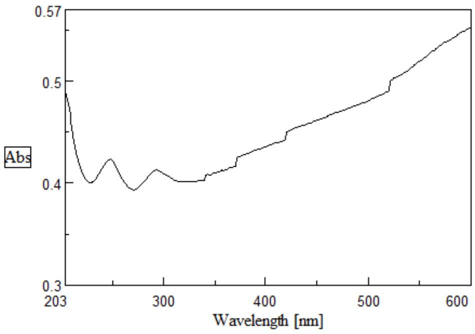

Fig.2. UV-Vis spectrum of Manganese oxide NPs

3.3. AFM studies

AFM images of manganese oxide NPs are given in Fig.3.The surface looks like Spongy granular like structure. Small spherical shaped particles were seen in the topography of the compound. Both 3D view of the metal oxides topography showed small valleys in between the spherical shaped particles.

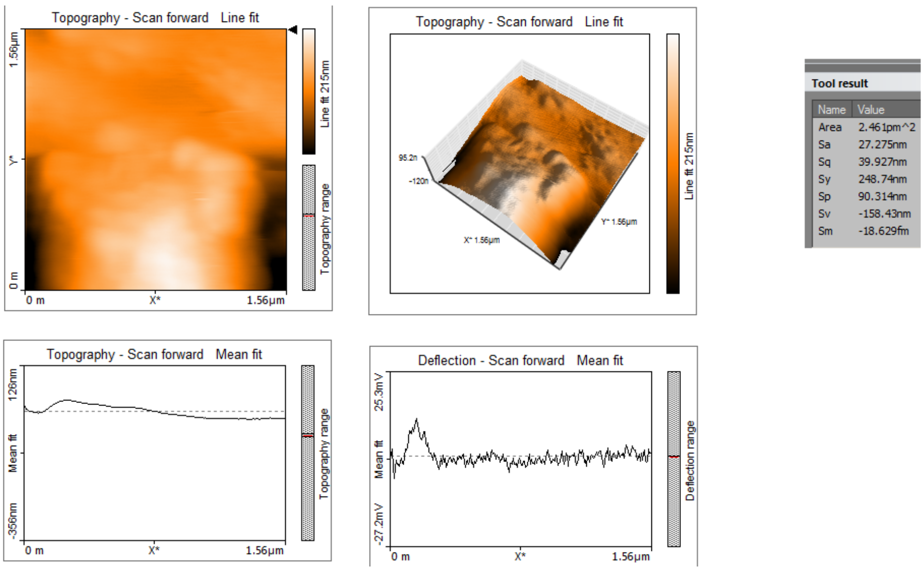

Fig.3. AFM topography of Manganese oxide NPs

3.4. SEM studies

The SEM image of manganese oxide is given in the Fig. 4. Aggregated structure with spherical shaped particles was seen in the SEM image of the nanoparticles. It shows formation of aggregate porous layers of metal oxide nanoparticles. Clusters of spherical particles and layered pattern can be seen. The morphology of NPs shows that there are apparent aggregations of manganese oxide particles.

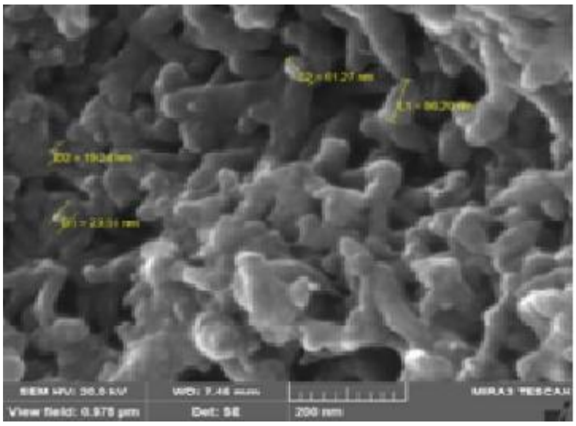

Fig.4. SEM image of Manganese oxide NPs

3.5. Photocatalytic activity

Fig.5. shows the change in the absorbance spectra MB in the presence of manganese oxide nanoparticles as photocatalyst on irradiation with sun light. The decrease in the concentration of methylene blue dye after its reaction with the manganese oxide photocatalyst under visible light was calculated by measuring the absorbance at regular time intervals.

Observation revealed that there is a gradual reduction in the absorbance with increase in irradiation time. About 87.8% of methylene blue dye was degraded within 60 minutes with manganese oxide nanoparticles.

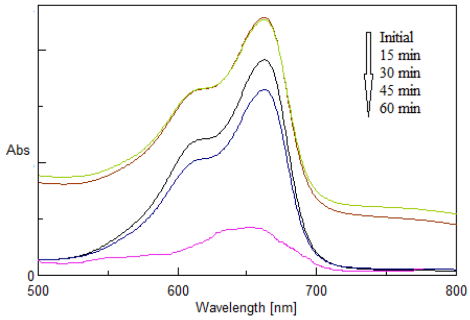

Fig.5. Photocatalytic degradation of MB dye using Manganese oxide NPs as photocatalyst

4. Conclusion

From the investigation it was concluded that the nanoparticles exhibited enhanced photocatalytic activity and can be efficiently used as photocatalyst in the process of removal of organic dyes and used for environmental cleaning and water purification.

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