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ENHANCED PHOTOCATALYTIC METHYLENE BLUE DYE DEGRADATION WITH MANGANESE OXIDE NANOPARTICLES FROM *Ziziphus Oenopolia (L.) MILL* FRUIT EXTRACTS FOR WASTEWATER TREATMENT

Kavica Sathasivam, Rajesh Pattulingam✉, Vignesh Nagarajan and Syed Illiyas Syed Maqbool

Department of Chemistry, Government Arts College, Coimbatore-641018, Tamil Nadu, India
✉Corresponding author: gacchemistryrajesh@gmail.com

ABSTRACT

The ecologically safe synthesis of manganese oxide nanoparticles from sodium hydroxide solution was achieved by using *Ziziphus oenoplia* fruit extract as a bio-reductant. The synthesis of manganese oxide nanoparticles was confirmed by the characteristic SPR bands observed in the bio-fabricated nanostructures. Powder X-ray diffraction studies reveal the tetragonal phase. The distinct spherical shapes of manganese oxide nanoparticles was demonstrated by scanning electron microscopy. With oxygen and manganese peaks, the corresponding Energy Dispersive X-ray spectra confirm the elemental composition. Manganese oxide nanoparticles were also used to perform the Methylene blue dye breakdown by photo-catalysis. The effects of concentration, time, pH, and catalyst dosage was investigated in this study. Degradation slows down as dye concentration rises. The dye began to deteriorate at 10ppm as a result of concentration. Within sixty minutes, the dye colour deteriorated. At pH 9, the degradation percentage was 90, indicating a successful outcome. When the catalyst dosage was increased from 0.005 to 0.013, the percentage of degradation also increased from 49% to 93%. Consequently, the generated Manganese Oxide nanoparticles functioned as a photo-catalyst in the purification of polluted wastewater.

Keywords: *Ziziphus Oenopolia (L.) Mill* Fruit Extract, Manganese Oxide Nanoparticles, Methylene Blue Dye, Photocatalytic Activity.

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INTRODUCTION

The most common contaminants that can be released into water and endanger both human life and the environment are organic wastes, notably dyes.[1] In worldwide based on the calculation each year, nearly $5x10^3$ tons of coloring substances are released.[2] Furthermore, humans face a lot of health consequences, like accelerated heartbeat, nausea, jaundice, tissue necrosis, and quadriplegia, when consumed through contaminated water from the dyes.[3,4] For Humans, animals, the major health problems have been created mainly due to the industrial dye is methylene blue dye(MB).[5] A shortage of clean water supplies has caused the environment in emerging markets to be at severe risk over the last few years. The World Health Organization (WHO, 2014) reports that water-related contamination led to over 10 million individuals getting various ailments.[6] About 15% of the colors generated worldwide are wasted throughout the dying procedure and end up in textile effluents.[7] One of the main causes of water contamination is the release of unregulated textile effluents into the environment.[8] The Hydrosphere is mainly threatened due to the dyes that cause pollution for the living things, and people inside the environment.[9-11] The textile, soil waste, pharmaceutical, food, and cosmetics industries are polluted in the soil and water.[11] The main source of pollution in the chemical sector, which includes the production of textiles, leather goods, paper, and paint, is dye.[12] Dye's complex geometries increase their stability, making it more difficult to extract or degrade these complex compounds from wastewater. A variety of methods, including chemical, biological, and physical remediation, have been used to eliminate dyes from wastewater.[13-14] However, these methods have certain drawbacks.[15] However, the complete elimination of pollutants from the environment may result from the use of nano-catalysts in conjunction with a photocatalytic technique for dye degradation.[16-17] Photocatalytic degradation is a well-known and dependable technique for fully decomposing organic substances in wastewater that has been polluted.

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Using the suitable radiation from light and a photo catalyst, this method produces highly hydroxyl (OH) radicals. Water pollutants can be converted by these radicals into CO_2, H2O, and other inorganic ions.[18-19] The transformation ensures both human and environmental safety. Compared to other traditional methods, photocatalytic degradation has an array of perks. Furthermore, synthetic organic dyes are completely degraded and are reasonably priced.[20] Methylene blue (MB) is a synthetic that is commonly used for silk, paper, and wool.[21]

EXPERIMENTAL

Materials and Chemicals

From Merck, the chemicals sodium hydroxide (NaOH) and Manganous Sulphate monohydrate ($MnSO_4.H_2O$) were purchased. Fruits of *Ziziphus Oenopolia* were collected in the Erode district of Tamil Nadu from Sathyamangalam.

Preparation of Fruit Extract

To remove any impurities, the *Z. Oenopolia* fruit was cleaned with tap water, followed by distilled water after collection. After being cleaned, the fruits were collected and left to dry at room temperature for fifty days. The fruits were dried and then powdered into a fine powder. 250 ml of distilled water and 25g of powdered fruit was mixed for four hours using a magnetic stirrer. After filtering, the solution was used for synthesis.

Synthesis of MnO_2 Nanoparticles

Manganese oxide Nanoparticles were synthesized by the co-precipitation method. The fruit extracts of *Z. Oenopolia* served as an impeccable sealant that assisted in the production of MnO_2 -NPs. 1M aqueous solution of 60 ml of manganese sulphate was added to a beaker containing around 40 ml of fruit extract, which had been agitated with a magnetic stirrer. Lastly, NaOH was added gradually until the pH of the mixture reached. The resultant solution was centrifuged at 10,000 rpm to produce MnO_2 nanoparticles. After that, distilled water was used to rinse the pellet in order to get rid of any impurities. The precipitate was dried using a hot air oven that was kept at 70°C. Characterization was done using the dried nanoparticles.

Photo Degradation of MB using MnO_2 Nanoparticles

MnO_2 NPs were employed to study MB dye breakdown when exposed to UV light.[22] To make the solution, 250 ml of distilled water was added to the dye MB (0.0025 g) in a standard flask. MB dye solutions were made at a range of concentrations (10, 20, 30, and 40 ppm). A beaker was filled with 100 mL of each prepared solution, and 0.05 g of nanoparticles was added. Every solution has been placed under the sun for an hour at a time. The reduction percentage was computed using the various pH medium concentrations (5,7 and 9). Before being kept in the sunlight, 0.1M HCl and NaOH was added. In several glass containers, 20ml of methylene blue dye and several grams (0.005,0.007,0.009,0.011,0.013) of synthesized nanoparticles was added and kept in the sunlight. At different time points (0,5,15,30,45,60), the following studies was carried out.

Evaluation of Photocatalytic Breakdown using UV-Visible Spectrophotometer

With the use of UV-visible spectroscopy, the photocatalytic dye degradation for the different parameters employing a Methylene blue dye was investigated. The percentage of dye degradation was calculated using the following formula,

$$\text{Degradation rate (\%)} = (C0 - C / C0) \times 100 \quad (1)$$

$$\text{Degradation rate (\%)} = (A0 - A / A0) \times 100 \quad (2)$$

Characterization Techniques

UV, XRD, SEM, and EDX examinations have to be obtained to study the generated MnO_2 nanoparticles. UV-visible spectroscopy was used to record the absorption data of the produced nanoparticle. X-ray diffraction was used to analyze the crystal formations. Using a scanning electron microscope, the surface morphology of MnO_2 nanoparticles was examined. The elemental makeup of the produced nanoparticle was ascertained via EDX analysis.

RESULTS AND DISCUSSION

Ultra Violet-Visible spectroscopy

The UV-Vis spectrum of MnO_2 nanoparticles may absorb light with wavelengths ranging from 300 to 600 nm. At 347 nm, the MnO_2 nanoparticle that was produced for the fruit extract exhibits a high absorption. Figure-1, which results in the UV-Vis spectrum of MnO_2 nanoparticles.

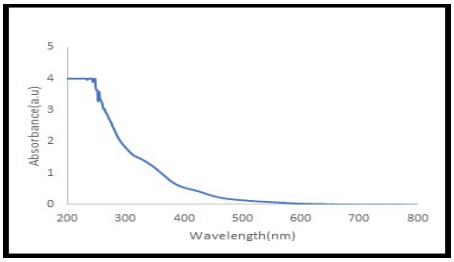

Fig.-1: UV-visible Graph of Synthesized MnO_2 Nanoparticles

X-ray Diffraction

Figure-2 depicts the MnO_2 nanoparticle X-ray diffraction pattern. To determine the crystalline structure, XRD analysis was conducted. The study revealed that the lattice planes of (020), (200), and (211) matched the significant peaks at Bragg's angles 32.1°, 35.8° °, and 44.0°. When compared to the standard data from the JCPDS card (File no: 14-644), the patterns are allocated to the tetragonal phase.[23] The Debye-Scherer formula was utilized to ascertain the NP size. The synthesized MnO_2 NPs had an average particle size of 28 nm.

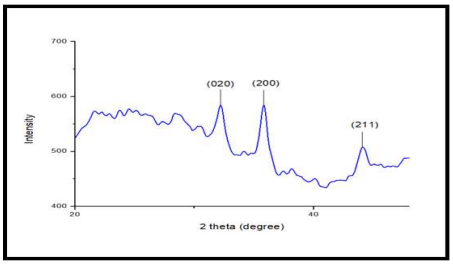

Fig.-2: X-ray Diffraction Analysis for the Synthesized MnO_2 Nanoparticles

SEM and EDX Analysis

The synthetic nanoparticle's surface shape and comprehensive picture are displayed by the SEM, while the elemental composition of the targeted samples is displayed by the EDX. As a result of smaller particles overlapping and grouping, large particles have been observed. According to the SEM image, the particles are spherical and irregularly distributed, with smaller diameters. The energy dispersive X-ray analysis was used to examine the elemental composition of the synthesized MnO_2 nanoparticle for *Ziziphus Oenopolia* fruit extract. In the EDX spectra, there were two prominent peaks, Mn and O has were found.

Table-1: Manganese Oxide Composition as Evaluated by EDX

Element	Mn	O
Wt.(%)	69.24	30.76

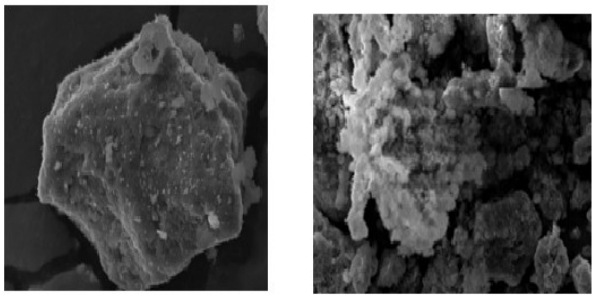

Fig.-3: Scanning Electron Microscope Image for the Synthesized MnO_2 Nanoparticles

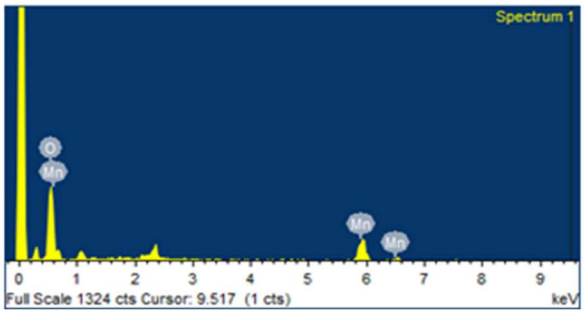

Fig.-4: EDX Spectrum of Synthesized MnO_2 Nanoparticles

Effect of MnO_2 Nanoparticle Dye Concentration on Photocatalytic Dye Degradation

At concentrations between 10 and 40 ppm, the dye used for photo-catalysis breakdown MB dye was first investigated. Over 60 minutes, the dye degradation conduction was investigated. When the dye concentration rose to 20 ppm, 30 ppm, and 40 ppm, the colour and intensity of the dye were more concentrated than when it was at 10 ppm. With an increase in dye concentration, the rate of disintegration slowed. By raising the dye concentration, photons reduced path length leads to inadequate absorption and photo degradation, according to Beer-Lambert's law. The corresponding percentage degradation over 60 minutes for 10, 20, 30, and 40 ppm is 89, 75, 67, and 52%.

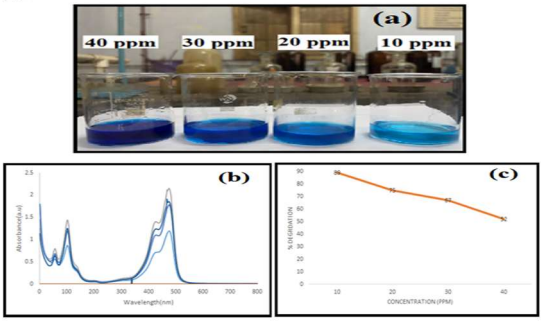

Fig.-5: (a) Dilution Photos Taken at Various Dye Concentrations, (b) UV-Visible Graph Showing the Degradation of MB Dye after 60 Minutes at 10, 20, 30, and 40 ppm Dye Solutions, (c) MB dye's % Deterioration over 60 Minutes

Effect of MnO_2 Nanoparticle Dye Duration on Photocatalytic Dye Degradation

Manganese oxide nanoparticles were used to break down the dye in a solution with 10 parts per million for the MB dye solution over time. The dye's gradual immersion shows that the MB dye molecule is continuously breaking down. At 5, 15, 30, 45, and 60 minutes, the dye degradation percentage was 47,59,72,82,91% respectively. The dye molecules were continuously breaking down, which confirms the increase in the degradation percentage in the photocatalytic reaction of MB dye molecules. The colour was degraded at 60 minutes compared to the initial time, which was represented in Fig.-6(a).

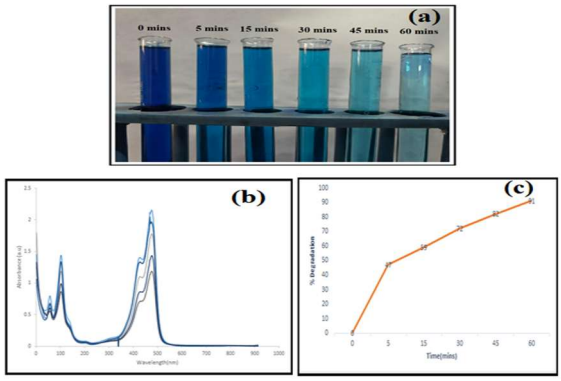

Fig.-6: (a) Photographs showing the MB Dye's Dilution and Catalytic Activity During Degradation at Various Intervals of 0, 5, 15, 30, 45, and 60 Minutes. (b) UV-Visible Graph Showing the Breakdown of MB Dye Over Time (c) % Showing the Breakdown of MB Dye at Various Time Points

Effect of MnO_2 Nanoparticle pH on the Breakdown of Photocatalytic Dyes

The photocatalytic degradation for the effect of pH was carried out for 5,7,9. Figure-7(a) shows the photographic image of dye without degradation and after degradation in the photocatalytic activity. The colour of the dye has diminished when exposed to sunlight. Because increased pH produces OH radicals, this suggests that the molecules in the methylene blue dye are breaking down. The proportion of deterioration and the colour of the solution both decrease when the medium's pH rises. The degradation rate for pH 5,7,9 was 59,73,90 %.

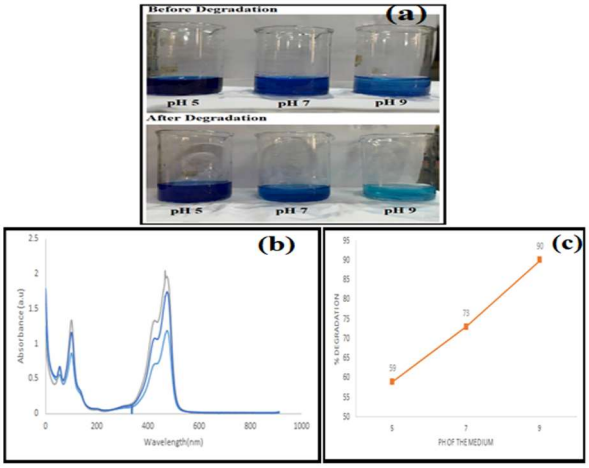

Fig.-7: (a) Photographs of Dye with and Without Degradation (b) The Ultraviolet-Visible MB Dye Degradation Graph at Various pH Levels after 60 Minutes (c) % of MB Dye Degradation at Various pH Values

Effect of MnO_2 Nanoparticle Catalyst on Photocatalytic Dye Degradation

The catalyst dosage study was carried out for the different dosages (0.005,0.007,0.009,0.011,0.013g) that contained 20 ml of methylene blue dye with a period of 60 minutes. Within one hour, the solution has been degraded for all dosages. For the effect of catalysts 0.005,0.007,0.009,0.011,0.013, the degradation percentage is 49,65,78,85,93%. Figure-8(a) shows the colour deterioration photos taken with the catalyst dosages. Enhanced catalyst interaction is achieved by increasing surface area at a higher catalyst dosage, which increases the dye removal percentage.

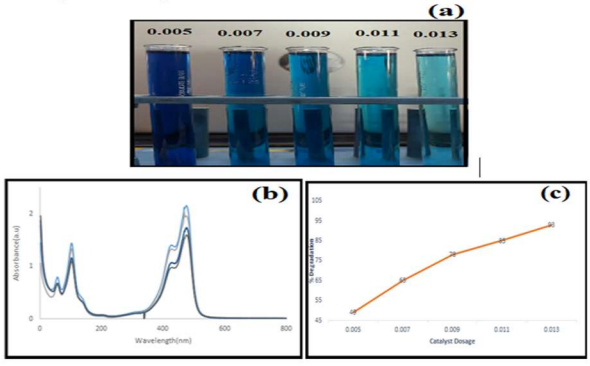

Fig.-8: (a) Photographs Showing Dilutions at 0.005g, 0.007g, 0.009g, 0.011g, and 0.013g Catalyst Doses. (b) UV-Visible Graph Showing the Breakdown of MB Dye Over 60 Minutes with Varying Photo Catalyst Concentrations (c) % of MB Dye Degradation after 60 Minutes

CONCLUSION

The current study found that MnO2 nanoparticles with strong photocatalytic activity were able to destroy methylene blue dye. Experiments were carried out at four dye concentrations: 40 ppm, 30 ppm, 20 ppm, and 10 ppm. At 10 ppm, 91% of the dye was effectively removed within 60 minutes. The degradation was most effective at pH 9. It was further shown that using higher concentrations of the catalyst enhanced the degradation of methylene blue dye by breaking down 93% of the dye using 0.013 g of the photo catalyst over 60 minutes.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6: Clean water and sanitation*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

Kavica Sathasivam https://orcid.org/0009-0005-3333-0887
Rajesh Pattulingam https://orcid.org/0000-0003-1527-623X
Vignesh Nagarajan https://orcid.org/0009-0009-5137-0996
Syed Illiyas Syed Maqbool https://orcid.org/0009-0001-0541-1162

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