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DEVELOPMENT AND APPLICATION OF GREEN SYNTHESIZED α MnO_2 USING THE PLANT EXTRACT *CENTELLA ASIATICA* FOR THE DEGRADATION OF MALACHITE GREEN IN WASTE WATER TREATMENT

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ABSTRACT

In the present work αMnO_2 nano particle was synthesized using green method, the plant extract used for the synthesis was *Centella asiatica*. The synthesized material was characterized using XRD, SEM, FTIR and UV/V is absorbance spectroscopy. The study investigates the applicability of αMnO_2 nano particle for the photo catalytic degradation of the dye Malachite green. The green synthesized material used as a good candidate for the removal of dyes.

KEY WORDS : Photo catalysis, Green synthesis, Nanomaterial.

INTRODUCTION

Different types of harmful dye effluents are discharged into water bodies by industries like pharmaceutical, food, printing and textiles (Rajeshkannan, 2011; Ali *et al*., 2016; Khan *et al.,* 2011 and Ali, 2006). Fluoresce in dyes have been reported to be highly cytotoxic for mammalian tissues and they produce morphological and genetic alterations (Culp, 2002) therefore the removal of harmful organic dyes from water bodies is a matter of concern. Malachite green (MG), a cationic dye is extensively used as a dyestuff in many industries and also in aquaculture to control parasites and diseases because of its easy preparation and low manufacturing cost. The various conventional methods have been employed for the degradation of dyes from industrial water. These include biological treatment, advanced oxidation process (AOPS), adsorption and photo catalysis (Chandran, 2017; Ali, 2012; Ali *et al*., 2017; Ali, 2014; Khan *et al*., 2017).

Of these, photo catalysis has been considered as the cost effective method for the purification of dye containing waste water. Of the various transition metal oxides, Manganese oxides have generated considerable interest in various fields like catalysis, energy storage, magnetic data storage, drug delivery and biomedical imaging (Armstrong *et al.,* 1996; Khulood, 2019). Herbal plants and their extracts possess several medicinal properties which have been used in the development of new drugs *Centella asiatica* commonly named as kudangal, a clonal, perennial herbaceous creeper belonging to the family *Umbellifere* (*Apiceae*) is found throughout India growing in moist places up to an altitude of 1800 m. It is found in most tropical and subtropical countries growing in swampy areas, including parts of India, Pakistan, Sri Lanka, Madagascar, and South Africa and South pacific and Eastern Europe. About 20 species related to *Centella asiatica* grow in mostparts of the tropic or wet pantropical areas such as rice paddies, and also in rocky, higher elevations] It is a tasteless, odourless plant that thrives in and around water. It has small fan-shaped green leaves with white or light purple-to-pink or white flowers

and it bears small oval fruit. The phenolic compounds present in *Centella asiatica* is a good reducing agent and exhibits good antioxidant property (Rashed Taleb Rasheed, 2020). Thus, the present investigation was aimed to synthesis MnO_2. α MnO_2 synthesized by the above method was well characterized and used as a catalyst in the photo catalytic degradation of malachite green dye.

MATERIALS AND METHODS

A R grade $KmnO_4$ Obtained from Merk and the plant extract of *Centella asiatica* were used for the preparation of nano MnO_2.

Malachite green ($C_{23}H_{25}N_2Cl$), dye which is mainly used in textile industries was procured from Merck, India. The molecular weight of malachite green is 364.90 g/mol and it absorbs at a maximum wavelength of 620 nm. The chemical structure of the dye is shown in Figure 1.

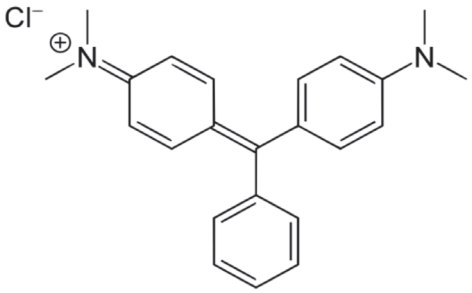

Fig. 1. Chemical structure of Malachite green

Preparation of *Centella asiatica* Leaf extracts

Fresh leaves were collected and thoroughly washed the leaves with distilled water for 3–4 times. The leaves were chopped into fine pieces and boiled it with 200 ml of distilled water at 60 ^{0}C for 10 min. The extract was filtered and stored at 4 ^{0}C and then used for nano particlesynthesis.

Synthesis of α MnO_2 nanoparticles

The leaf extract was taken in a 500 ml Erlenmeyer flask and placed in the magnetic stirrer and1mM solution of potassium permanganate was prepared. The plant extract was mixed with 1:1 ratio of 1mM potassium permanganate solution using a burette and stirred for 6hours. The formation of red colour was observed The solution is stored in room temperature for 24h for the complete settlement of nanoparticles. After 24h discard the supernatant. Washed several times with distilled water. Finally the product obtained was dried and calcinated in a muffle furnace at 600 ^{0}C for 3 hour.

Characterization of α MnO_2 nanoparticle

The structural identity and phase purity of the prepared material were verified by powder X-ray diffraction technique (XRD) using a Bruker AXS D8 Advance model diffracto meter with Cu Kα radiation. FT-IR spectrum was recorded with Fourier transform infrared (FT-IR) spectrometer of Thermo Nicolet, Avatar 370 model. Surface morphology of the sample was analyzed by SEM of JEOL Model JSM - 6390LV.

Photo catalytic Degradation of Malachite Green Dye

Photo catalytic degradation efficiency of nano α $MnO_2$was studied by measuring the absorbance of MG dye solution.

1000 ppm concentration of MG was prepared and the desired concentrations were taken and used as dye samples. The degradation experiments were performed in sun light. The degradation efficiency of the prepared catalyst was optimized by varying experimental parameters such as pH, concentration of dyes and weight of the catalyst taken. The photo catalyst was mixed with 300 ml of the dye solution. The solution was stirred in the dark for 30 min to establish an adsorption/desorption equilibrium. Samples were taken out periodically after irradiation by sun light and the change in concentration of the dyes in liquid phase were determined by UV-Visible spectro photometer.

The percentage of degradation was determined by using the following equation,

$$\text{Removal (R \%)} = \left[\frac{(C0 - Ce)}{C0}\right] * 100 \qquad .. (1)$$

RESULTS AND DISCUSSION

XRD analysis

XRD peaks give the phase purity, structural identity and particle size of the prepared nano material. The powder XRD pattern of the synthesized product (Fig. 2) matched well with JCPDS Card No. 44-0141 and all diffraction peaks were indexed. Particle size calculated using Debye-Scherer equation was found to be 14 nm. No peaks from other phases were found, suggesting the high purity of the synthesized α MnO_2 nanoparticles.

FT-IR spectroscopy

The FT-IR spectrum was used to identify the

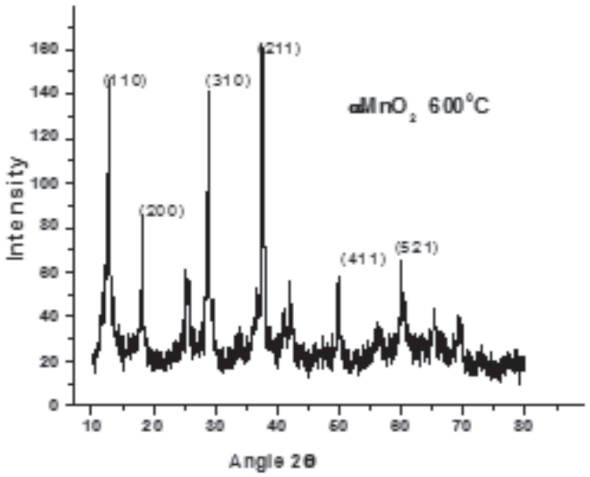

Fig. 2. XRD of α MnO_2

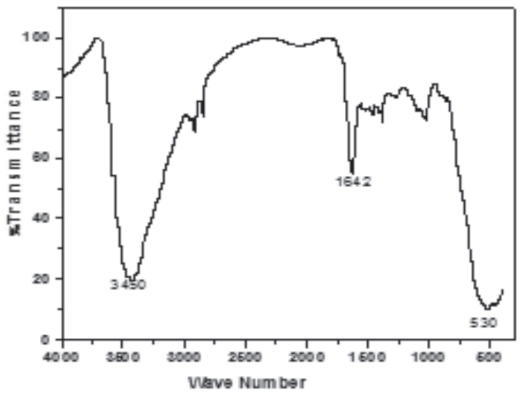

Fig. 3. FTIR Spectrum of MnO_2

functional groups and other impurities present in the final product. Fig. 3 represents the spectrum of α MnO_2 nano powder prepared by green method. The broad band at 3450 cm^{-1} is believed to be associated with the stretching vibrations of hydrogen-bonded surface water molecules and hydroxyl groups. Additionally, the bands at 1642^{-1} correspond to the existence of large numbers of residual hydroxyl groups, which imply the O-H vibrating mode of traces of adsorbed water. The band located at 530 cm^{-1} can be ascribed to the Mn-O vibrations of MnO_2 nano powder. The FTIR analysis presented here is consistent with the results reported in the literatures

UV-Visible spectroscopy

UV-Visible absorption spectrum of αMnO_2 given in Figure 4 (a & b). UV-Visible spectrum is usually used to obtain the band gap of semi conductor materials. The absorption bands at 280 nm are attributed to the $^+$ charge transfer transitions of Mn

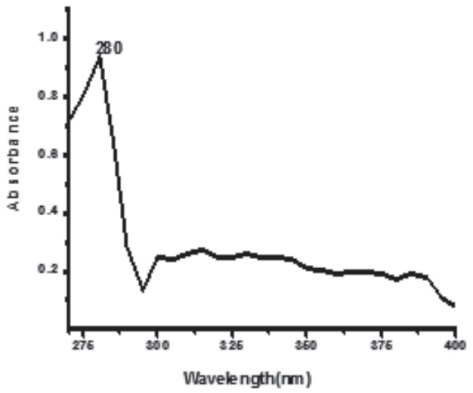

Fig. 4a. UV/Vis Absorption spectrum of α MnO_2

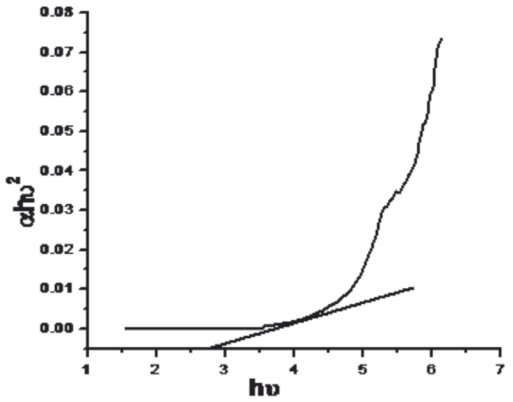

Fig. 4b. Tauc Plot of α MnO_2

and O respectively. The optical band gap of the material determined from the absorption spectrum using Tauc'srelationwas 2.78eV. Due to large value of the optical band gap, the material is most suited in many applications in modern electronic industries.

The SEM image (Figure 5) shows a well-defined thread like morphology for the prepared αMnO_2 nanoparticles

The photo catalytic degradation of MG in aqueous solution using α MnO_2catalyst was studied under visible light. MG is usually resistant to

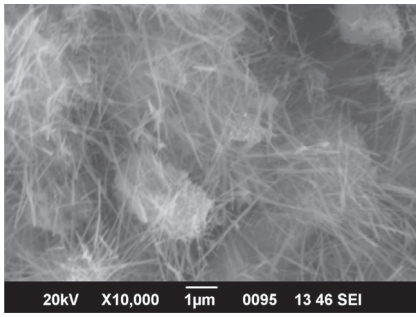

Fig. 5. SEM image of α MnO_2

biodegradation and resists photolysis. The photo catalytic activity depends on many factors like crystallinity, band gap energy and morphology of the nano structured material. The absorption spectrum of MG in aqueous solution under visible light illumination in the presence of catalyst αMnO_2 for different interval times (0 - 180 min) is shown in Figure 6. MG shows a strong characteristic absorption at 620 nm and the absorption maximum steadily decreases as the exposure time of visible light increases. The intense blue colour of the initial solution disappears gradually and becomes almost colourless as the irradiation time increases, indicating the degradation of the dye. Experiments were conducted also using different amount of catalyst.

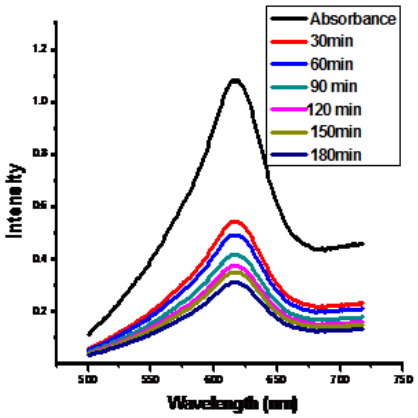

Fig. 6. Time–dependent absorption spectra of MG using α MnO_2

Effect of Amount of αMnO_2

The effect of amount of nano photocatalyst on the rate of dye degradation was examined by varying the amount of catalyst from 0.25 to 0.125 g/200 ml of the dye solution (Figure 7). It was observed that at lower dose of catalyst (0.25 to 0.1 g), the rate of dye degradation increased rapidly with time. But at higher dose (0.125 to higher), the rate of dye degradation was found to decrease. The decreased degradation rate at higher catalyst dose is due to multilayer formation, which causes recombination of electron-hole pair with time.

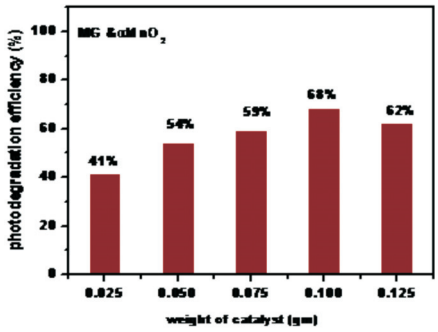

Fig. 7. Effect of catalyst amount on the degradation of MG

Mechanism

On the basis of these observations a tentative mechanism for photo catalytic degradation of malachite green dye may be proposed as:-

$^1MG_0 + hí \rightarrow {}^1MG_1$

$^1MG_1 \rightarrow {}^3MG_1$

$\alpha\ MnO_2 + hí \rightarrow e^-(CB) + h^+(VB)$

$e^- + O_2 \rightarrow O_2^-$

$O_2^- + {}^3MG1 \rightarrow$ Leuco MG

Leuco MG $\rightarrow$ End Products

Malachite green firstly changes to singlet state and then to triplet state by the absorption of radiation of suitable wavelength. The semi conducting αMnO_2 also utilizes the radiant energy to excite its electron from valence band to the conduction band generating superoxide anion radical ($O_2^{-}\cdot$). This anion radical will reduce the dye malachite green to its leuco form, which may ultimately degrade to end products. The biosynthesized α MnO_2 in the present study is a promising photo catalyst for the degradation of dyes like MG using visible light irradiation.

CONCLUSION

A simple, eco-friendly, non-toxic and environmentally efficient green method is explained for preparing α Mn O_2 nanoparticles from *Centella asiatica* leaf extract. The XRD, FT-IR and UV-Visible studies confirm the formation of pure αMnO_2. The SEM studies suggest thread like morphologies for the obtained αMnO_2 nanoparticles with an average particle size of 14 nm. The synthesized material is a good photo catalyst for the degradation of Malachite green dye. The optimum conditions for dye degradation are at 0.1 gm of the catalyst at 20 ppm dye concentration. The results show the excellent photo catalytic performance of α MnO_2 assigned mainly to the formation of oxygen vacancies. The above results suggest the potential applications of α MnO_2in industrial waste water treatment.

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