PHOTOCATALYTIC ACTIVITIES OF SYNTHESIZED TIN(IV) OXIDE NANOPARTICLES BY USING AQUEOUS EXTRACT OF *CITRUS AURANTIFOLIA* LEAVES

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Abstract

Citrus aurantifolia leaves aqueous extract was used to synthesize tin(IV) oxide nanoparticles utilizing a straightforward, environmentally friendly, and inexpensive approach. Aqueous leaves extract of *C. aurantifolia* was utilized as a reducing agent, while tin(II) chloride dihydrate was utilized as the starting material. SnO_2 NPs were produced at 600 °C, according to an X-ray diffractogram (XRD) examination, and their crystallite size was 28.7 nm when they were made with an aqueous leaf extract. The distinctive peak of SnO_2 was visible in the 450–790 cm^{-1} range according to the results of the FT IR investigation. SEM examination revealed SnO_2 NPs with very minor agglomerations. The average crystallite size of SnO_2 NPs was determined by TEM examination to be consistent with the XRD results. For the commercial dye, methyl violet, which serves as a representative organic dye pollutant, the produced SnO_2 NPs demonstrated outstanding degrading efficiency. The ideal conditions for the photocatalytic degradation of 10 ppm of methyl violet were achieved using 0.5 g of SnO_2 NPs in the sunlight for 8 h.

Keywords: *Citrus aurantifolia*, tin(IV) oxide nanoparticles, methyl violet, photocatalytic degradation

Introduction

Water pollution is one of the biggest problems today, which increases every year causing serious and irreparable damage to the planet (Luquea *et al*., 2020). Water pollution is a serious threat to human health and aquatic life all over the world (Paramarta *et al*., 2017). Among various industrial effluents, the effluents are one of the most toxic by-products of the textile industry. These toxic effluents are responsible for many hazardous health effects such as cancer, skin irritation, and allergic response. Industrial wastewater may contain poisonous chemicals such as insecticides and organic dyes. Dyes cause allergies, dermatitis, skin irritation, cancer, etc, in humans. Methyl violet (MV) is a water-soluble dye, used in textile industries, paper dyeing, paints, and printing ink. MV is also used as a disinfectant and is found very poisonous to animals (Archita *et al*., 2015). Methyl violet dye is a highly toxic, carcinogenic dye. Contamination with water causes long-term adverse effects on the aquatic environment and is a real threat to aquatic life (Bhattacharjee *et al*., 2014). These organic dyes can be degraded photochemically by the use of nanostructure semiconductor oxide which acts as an excellent photocatalyst in the degradation process. The SnO_2 is an important n-type semiconductor having a bandgap of 3.6 eV, exhibits unique size and shape-dependent properties including optical, electronic, electrochemical, and catalytic properties (Fu *et al*., 2015).

Using plant parts to synthesize nanoparticles is known as green synthesis. These nanomaterials are advantageous due to easy handling, non-toxic, environment-friendly, and economical nature. Leaves extract of *Citrus aurantifolia* was used in the present work for preparation of SnO_2 NPs. The extract obtained from plants serves the purpose of reducing agents. Photocatalytic degradation of the dyes namely methyl violet in the presence of synthesized SnO_2 NPs acts as a catalyst. This method does not cause secondary pollution and has attracted increasing attention as cleaner and greener technology for the removal of toxic organic and inorganic pollutants in water and wastewater. The synthesized SnO_2 NPs using aqueous extract of *Citrus*

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aurantifolia leaves were characterized by XRD, FT IR, TG-DTA, SEM, and TEM. Then these NPs were used for photocatalytic degradation of the methyl violet dye.

Materials and Methods

Materials

The *C. aurantifolia* leaves were collected from Moattama village, Mawlamyine Township, Mon State. Ethanol and 98 % pure tin(II) chloride ($SnCl_2$. $2H_2O$) from BDH were used. To evaluate the photocatalytic activity, methyl violet was obtained from Sigma- Aldrich.

Preparation of the Leaves Aqueous Extracts of *C. aurantifolia*

The collected *C. aurantifolia* leaves were washed thoroughly with deionized water to remove the dust particles. Next, 10 g of the sample was mixed with 100 mL of deionized water and the mixture was ground by using a motor and pestle. Eventually, the solution was filtered with Whatman filter paper to obtain the green-colored leaves extract.

Preparation of SnO_2 NPs

The desired SnO_2 NPs were prepared by mixing 40 mL of $SnCl_2.2H_2O$ (0.02 M) with 100 mL of aqueous extract of *C. aurantifolia* leaves sample solution in a 250 mL beaker and then mixed thoroughly by a magnetic stirrer at 80 ˚C. The greenish gel was washed with deionized water and ethanol. The residue obtained was then collected in a porcelain crucible and heated in air at 80 ˚C. The grey-colored powder was obtained for *C. aurantifolia* leaves. It was cooled at room temperature and was calcined at a temperature of 600 ˚C in the muffle furnace for 3 h. SnO_2 NPs were carefully collected and packed for characterization purposes.

Characterization of SnO_2 Nanoparticles

The prepared SnO_2 nanoparticles were characterized by powder X-ray diffraction (XRD) method using MultiFlex 2kW Type, Rigaku. D/max 2200, Japan diffractometer with CuK_α radiation of wavelength 1.5418 Aº. The surface morphology of the prepared SnO_2 NPs was studied by Scanning electron microscope. The surface morphology and particles size distribution of each of the prepared sample was studied by transmission electron microscope (TEM, JEOL TEM-3010). An infrared spectrum was recorded in the wavenumber range of 400 to 4000 cm^{-1} by using an FT IR spectrometer.

Photocatalytic Activity of Synthesized SnO_2 Nanoparticles

The photocatalytic potential of the prepared SnO_2 NPs was investigated by the decomposition of methyl violet dye under sunlight. Effects of contact time, the dosage of SnO_2 NPs, and the initial concentration of methyl violet dye on the photocatalytic degradation of dye were studied. Briefly, to 25 mL of 50 ppm methyl violet solution in separate 150 mL capacity of clean and dry conical flasks, 0.05 g of the prepared SnO_2 NPs was added. The solution mixture was stirred for 30 min in dark for the equilibrium of the adsorption and desorption process of methyl violet with nanoparticles. After stirring, the conical flasks were placed in sunlight. After stirring for 1, 2, 3, 4, 5, 6, 7, and 8 h under sunlight, the conical flasks were taken out and filtered off the filtrate. Afterward, the absorbance values of filtrates were measured at 590 nm by using a spectrophotometer.

Results and Discussion

Characterization of the SnO_2 Nanoparticles Prepared by Green Synthesis Method

SnO_2 nanoparticle was prepared by using aqueous leaves extracts of *C. aurantifolia* by reaction with $SnCl_2.2H_2O$. The formation of black Sn $(OH)_2$ gel was observed at 80 ˚C. The grey-colored powder was obtained for *C. aurantifolia* leaves. It was cooled at room temperature and was calcined at a temperature of 600 ˚C in the muffle furnace for 3 h.

XRD studies

The X-ray diffraction pattern of the NPs obtained by means of the green synthesis is presented in Figure 1. The XRD pattern was recorded in order to investigate the crystal structure, purity, and crystalline nature of synthesized SnO_2 nanoparticles. The XRD pattern of SnO_2 nanoparticles at 600 ˚C shows the diffraction peaks at 2θ values of 26.12˚, 33.40˚, 37.49˚, and 51.30˚ which correspond to the (110), (101), (200), and (211) planes respectively. The diffraction peaks of SnO_2 were indexed to the tetragonal structure with lattice parameters a= 4.8207 Å and c= 3.2250 Å (JCPDS Card No. PDF 99-0024). From the XRD data, pure and crystallite SnO_2 NPs become gradually sharper and the full width at half maximum (FWHM) is reduced by increasing in calcination temperature to 600 ˚C. The average crystallite size was estimated by using the reflections of characteristic planes (110), and the average crystallite size was 28.7 nm in aqueous leaves extract for samples prepared at 600 ˚C. There is the absence of some other phase that does not correspond to SnO_2 NPs confirming the purity of the sample.

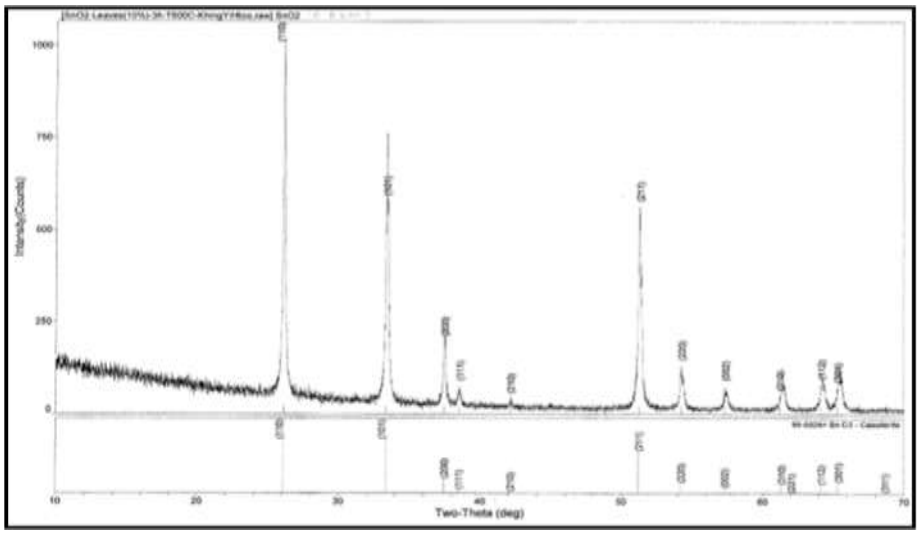

Figure 1 X-ray diffractogram of SnO_2 NPs by using aqueous extract of *C. aurantifolia* leaves at 600 ˚C

TG-DTA analysis

The thermal stability of the prepared SnO_2 NPs sample before calcination was investigated by TG-DTA. The thermogram of SnO_2 NPs is shown in Figure 2 and the corresponding thermal data are presented in Table 1. Two endothermic peaks and one exothermic peak were observed in the thermogram of SnO_2 NPs obtained by using an aqueous extract of *C. aurantifolia* leaves. The first endothermic peak was due to the removal of physically adsorbed water. The second endothermic peak was due to the removal of chemisorbed water. The exothermic peak appeared at 504.89 ˚C in SnO_2 NPs by using aqueous leaves extract was due to oxidation of SnO to SnO_2. Thus, thermal analysis data confirmed the calcination temperature of 600 ˚C for the preparation of SnO_2 NPs.

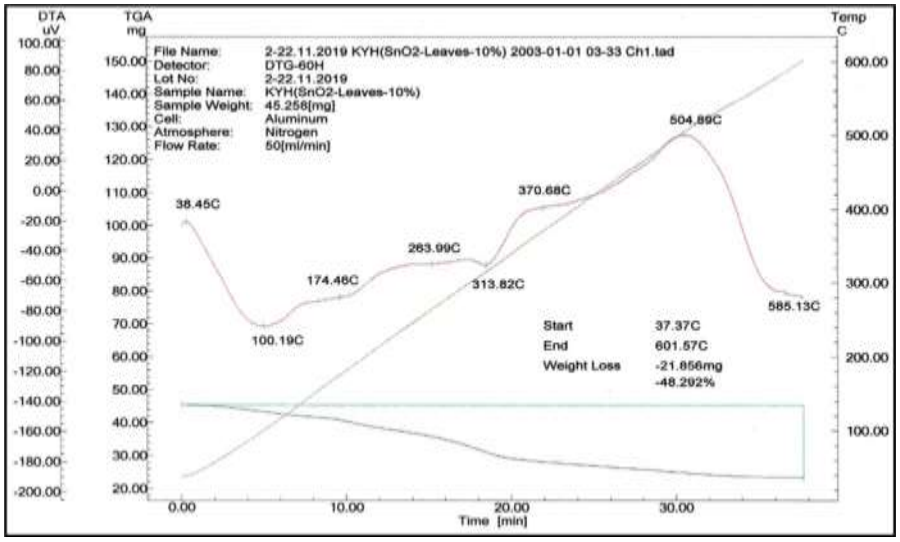

Figure 2 TG-DTA thermogram of SnO_2 NPs prepared by using aqueous extract of *C. aurantifolia* leaves (before calcination)

Table 1 TG-DTA Data of SnO_2 NPs prepared by Using Aqueous Extract of *C. aurantifolia* Leaves (before calcination)

No.	Temperature range (˚C)	Weight loss (%)	Break-in temp: (˚C)	Nature of peak	Remark
1.	36.45-200	12.779	100.19	Endothermic peak	Desorption of physically adsorbed water molecules
2.	200-400	19.885	313.82	Endothermic peak	Removal of chemisorbed water
3.	400-601.57	6.628	504.89	Exothermic peak	Oxidation of SnO to SnO_2

FT IR analysis

The structural information was further evidenced by the FT IR spectrum for the prepared SnO_2 NPs obtained at 600 ˚C (Figure 3). The characteristic peaks of SnO_2 due to stretching vibration were observed at 479 cm^{-1} and 609 cm^{-1}. The absorption peaks between 450-790 cm^{-1} were attributed to the vibration of SnO_2 stretching and indicated the formation of SnO_2 NPs.

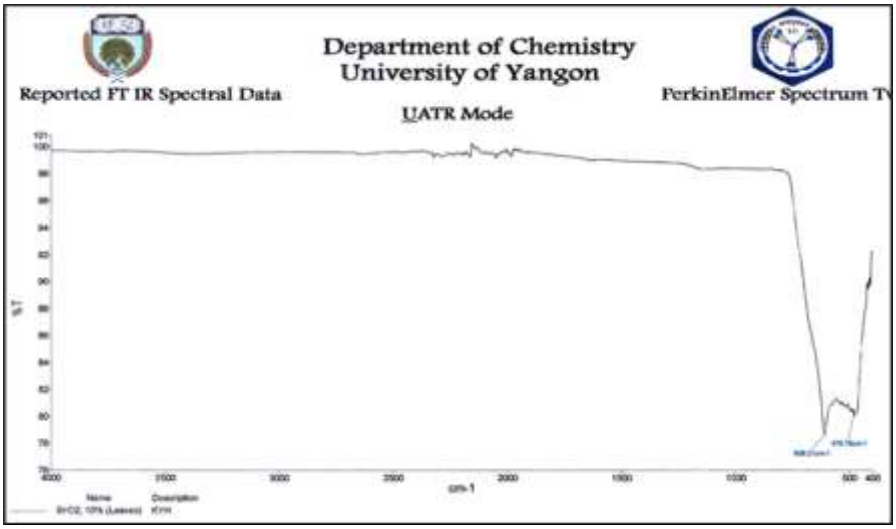

Figure 3 FT IR spectrum of the prepared SnO_2 NPs by using aqueous extract of *C. aurantifolia* leaves

Surface morphology of the prepared SnO_2 NPs by scanning electron microscopy

The surface morphology of the prepared SnO_2 NPs was studied by using SEM. SEM image of the prepared SnO_2 NPs by using aqueous extract of *C. aurantifolia* leaves.is depicted in Figure 4. The SEM images showed slightly agglomerated particles with a tetragonal shape was observed in SnO_2 NPs using an aqueous extract of *C. aurantifolia* leaves.

Surface morphology of the prepared SnO_2 NPs by transmission electron microscopy

TEM images are used to study the shape and size of the nanoparticles. Figure 5 shows the TEM picture of the SnO_2 NPs sample and it was mainly consisting of tetragonal shaped along with large agglomerated particles with an average diameter of around 28.1 nm. These values are well-matched with the grain size calculated from XRD results and confirm the SnO_2 nature with a tetragonal rutile type structure.

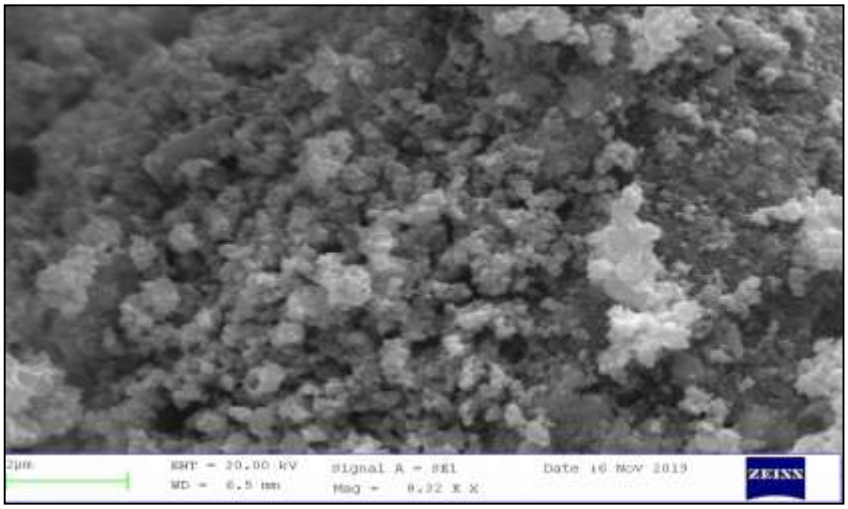

Figure 4 SEM image of the SnO_2 NPs prepared by using aqueous extract of *C. aurantifolia* leaves

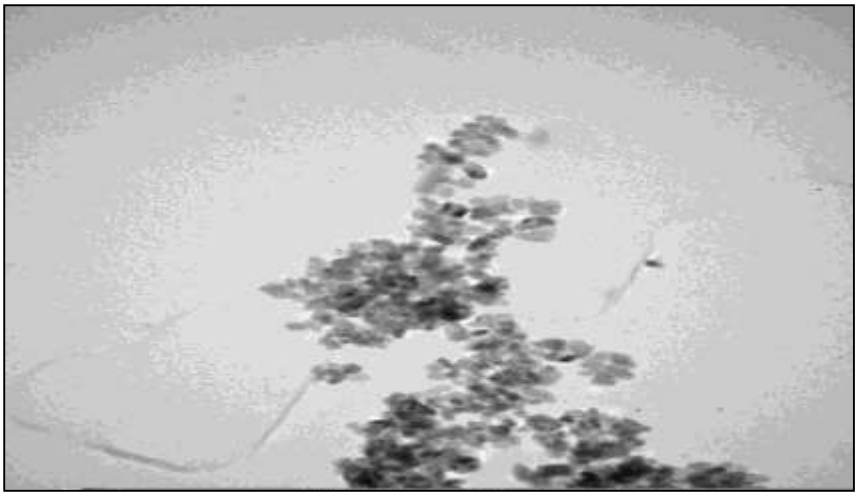

Figure 5 TEM image of the SnO_2 NPs prepared by using aqueous extract of *C. aurantifolia* leaves

The wavelength of Maximum Absorption of Methyl Violet Solution and its Calibration Curve

In quantitative analysis of substance by spectroscopic method, the standard plot techniques require the Lambert-Beers' law to be obeyed in the first place. In this work, the absorption spectra of methyl violet were recorded in the wavelength range of 400-800 nm, and was found that the wavelength of maximum absorption occurred at 590 nm (Figure 6). The standard calibration curve for methyl violet was plotted using five different concentrations (10, 30, 50, 70, and 90 ppm) at a fixed wavelength (λ_{max}) at 590 nm. The curve became a straight line and passed through the origin, which indicated Beer's Law was well obeyed (Table 2 and Figure 7).

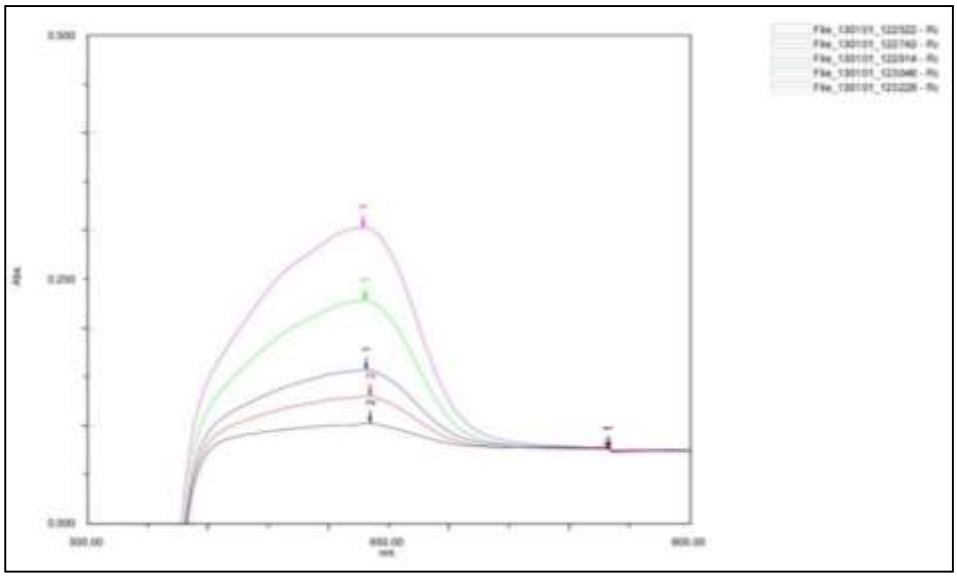

Figure 6 Overlay absorption spectra of various concentrations of methyl violet dye solution

Table 2 Relationship between Absorbance and Concentration of Methyl Violet Solution

No.	The concentration of methyl violet (ppm)	Absorbance at 590 nm
1.	10	0.148
2.	30	0.403
3.	50	0.618
4.	70	0.828
5.	90	1.021

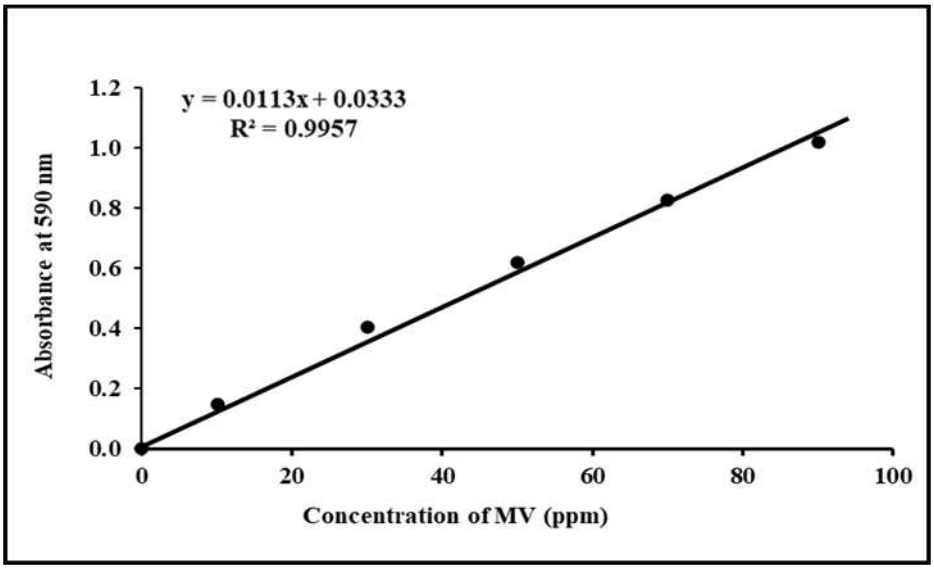

Figure 7 Calibration curve of methyl violet solution

Photocatalytic Degradation of Methyl Violet by the Prepared SnO_2 NPs under Sunlight

Effect of contact time for degradation of methyl violet solution

The effect of optimum contact time on photodegradation was performed with varying contact times ranging from 1-8 h, as shown in Table 3 and Figure 8. After 1 h of contact time, the degradation percent of methyl violet was 39.95 % by using prepared SnO_2 NPs in the presence of aqueous leaves extract. As the contact time increased, the degradation percentages of dye solution were also found to increase. After 8 h, it was observed that the degradation percent was found to be 99.13 % using SnO_2 NPs. Then, degradation processes proceed gradually and became nearly constant. This hindrance in further degradation of methyl violet may be due to the fact that the surface of the nanoparticles gets saturated so no active site is available for further photodegradation of methyl violet. Therefore, the optimum contact time for the degradation study was chosen as 8 h for these dyes.

Table 3 Degradation Percentage of Methyl Violet by the Prepared SnO_2 NPs Using Aqueous Leaves Extract of *C. aurantifolia* with Different Contact Times

No.	Contact time (h)	Absorbance after degradation	Degradation percent (%)
1.	1	0.481	39.95
2.	2	0.380	52.55
3.	3	0.289	63.92
4.	4	0.188	75.52
5.	5	0.149	81.39
6.	6	0.068	91.51
7.	7	0.019	97.62
8.	8	0.007	99.13

Initial absorbance = 0.801

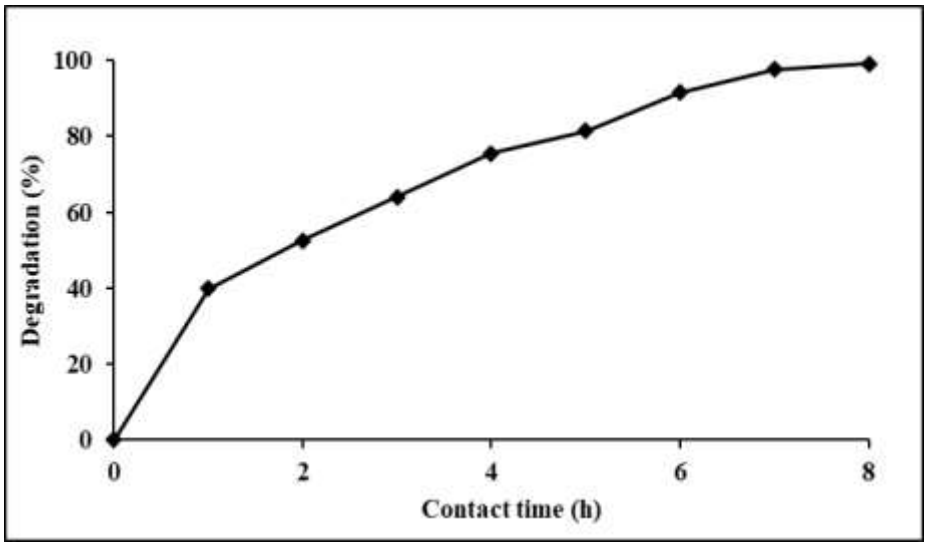

Figure 8 Degradation percentage of dye by the prepared SnO_2 NPs using aqueous extract of *C. aurantifolia* leaves as a function of contact time (dosage = 0.05 g, the volume of dye solution = 25 mL, and dye concentration = 50 ppm)

Effect of dosage of the prepared SnO_2 NPs for degradation of dyes solutions

The degradation percentage of methyl violet dye using the prepared SnO_2 NPs with different dosages ranging from 0.1 to 0.5 g was studied under sunlight and the results are shown in Table 4 and Figure 9. By using 0.1 g of SnO_2 NPs obtained from leaves extract, 94.69 % was degraded, after 8 h of contact time. The maximum percentage of photodegradation was obtained at 0.5 g of SnO_2 NPs, i.e., 99.81 % which can provide the highest absorption of light. At higher dosages loading, the dosages particles also scatter the incident photons, and hence the availability of the photon flux to the solution has increased. Thus, photocatalytic degradation increased.

Table 4 Degradation Percentage of Methyl Violet by the Prepared SnO_2 NPs Using Aqueous Leaves Extract of *C. aurantifolia* with Different Dosages

No.	Dosages (g)	The absorbance of methyl violet after degradation	Degradation percent (%)
1.	0.1	0.015	94.69
2.	0.2	0.007	99.11
3.	0.3	0.007	99.39
4.	0.4	0.005	99.59
5.	0.5	0.003	99.81

Initial absorbance = 0.801

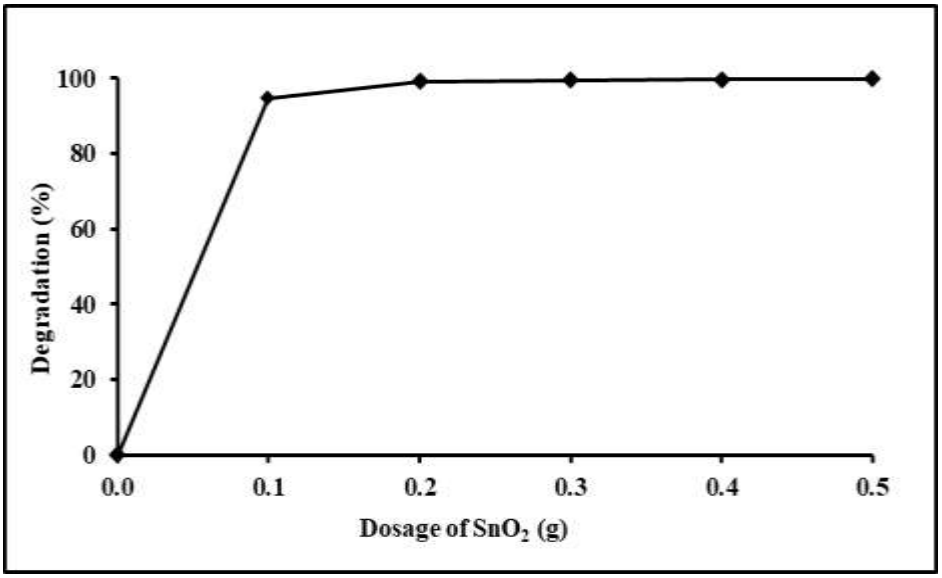

Figure 9 Degradation percentage of methyl violet by the prepared SnO_2 NPs using aqueous extract of *C. aurantifolia* leaves as a function of dosages (contact time = 8 h, the volume of dye solution = 25 mL, and dye concentration = 50 ppm)

Effect of initial concentration of dye solutions

To investigate the effect of the initial concentration of methyl violet, photodegradation studies were performed with varying concentrations of methyl violet solution of 10, 30, 50, 70, and 90 ppm. The results are described in Table 5 and plotted in Figure 10. For a 10 ppm concentration of methyl violet dye, the degradation percent was 98.80 % by using SnO_2 NPs from an aqueous extract of leaves. When the initial concentration of the dye reached 90 ppm, 96.82 % of methyl violet dye was degraded. The rate of photocatalytic degradation gradually decreased with the increase of the initial concentration dye. This behavior is due to the decrease of the concentration OH^- adsorbed on catalyst surface with the increase of dye concentration, that the active sites are covered the methyl violet dye molecules (Hazin *et al*., 2015). As a result, the degradation percent of the dyes decreased.

Table 5 Degradation Percentage of Methyl Violet by the Prepared SnO_2 NPs Using Aqueous Extract of *C. aurantifolia* Leaves with Different Concentrations of Dye

No.	Concentration (ppm)	The absorbance of methyl violet after degradation	Degradation percent (%)
1.	10	0.009	98.80
2.	30	0.012	98.78
3.	50	0.015	98.70
4.	70	0.015	98.47
5.	90	0.019	96.82

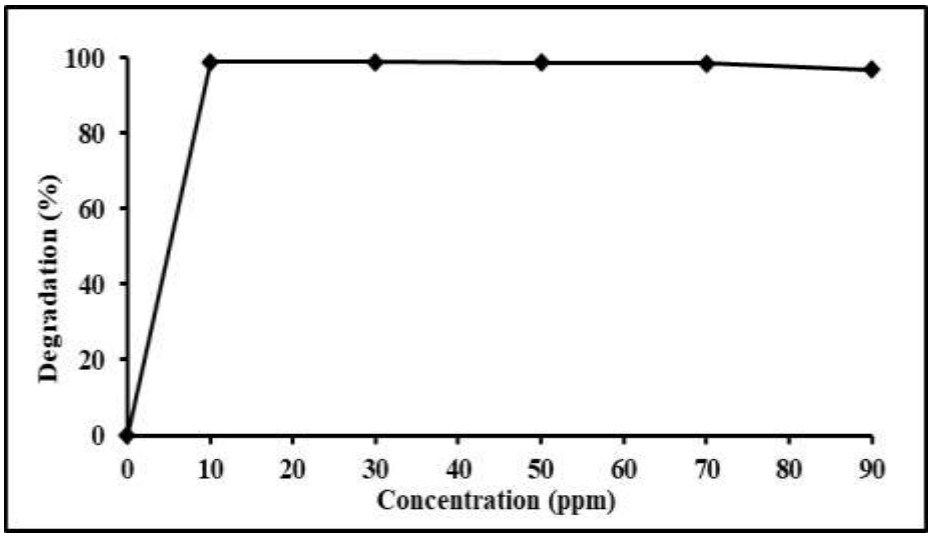

Figure 10 Degradation percentage of methyl violet by the prepared SnO_2 NPs using aqueous extract of *C. aurantifolia* leaves as a function of different concentrations (contact time = 8 h, the volume of dye solution = 25 mL, and dosage = 0.05 g)

Conclusion

A simple, eco-friendly, and efficient synthesis of SnO_2 was conducted by using aqueous leaves extract *C. aurantifolia* with acts as a reducing agent. XRD pattern confirmed the tetragonal structure of prepared SnO_2 NPs using aqueous leaves extract and the average crystallite size was found to be 28.7 nm. The Crystallite size of SnO_2 NPs from leaves was confirmed by the crystallite size and morphology by TEM analysis. SEM images showed slightly agglomerates. Thermal analysis of SnO_2 NPs indicated that SnO_2 was almost thermally stable at 600 ˚C. The purity of SnO_2 NPs was checked through FT IR analysis. Photocatalytic degradation of synthesized SnO_2 NPs was studied using methyl violet dye solution. High degradation percentage of methyl violet was attained at 99.13 % in 8 h contact time. The maximum photocatalytic degradation percent was found to be 99.81 % using a 0.5 g dosage of SnO_2 NPs. The maximum degradation percentage was found to be 98.80 % using a 10 ppm quantity of methyl violet color.

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