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PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE DYE BY CARBON DOPED TITANIUM DIOXIDE

Nikita. S. Gupta[1] and Susmita A. Mandavgane[2]
[1]Lady Amritbai Daga College & Smt. Ratnidevi Purohit College, Nagpur
[2]DRB Sindhu Mahavidyalaya, Nagpur
Corresponding Email Id: susmitamandavgane@gmail.com

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ABSTRACT:
The simple Sol-gel method was adopted to synthesize carbon-doped TiO_2 nanophotocatalysts that worked better in visible light. For carbon doping, microcrystalline cellulose (MCC) was used. The prepared carbon-doped TiO_2 samples were calcined at 400–600 °C. Carbon-doped nanophotocatalysts were analyzed using XRD and SEM. The image obtained from the SEM shows that C-doped TiO_2 synthesis in the presence of MCC also restricted TiO_2 nanoparticle development and regulated the size and aggregation of nanoparticles. In contrast to pure nanoparticles, carbon doping enhanced the photocatalytic activity of the TiO_2 photocatalyst in the degradation of methylene blue dye. Carbon-doped TiO_2 attained an efficiency of 98% and 60% under UV and visible lights, respectively.

Keywords:- Carbon-doped TiO2; Methylene blue; Microcrystalline cellulose; Photocatalytic degradation; Sol–gel.

INTRODUCTION :

The most prevalent, renewable, biodegradable, and easily accessible biopolymer a linear polymer of beta-D-glucose is microcrystalline cellulose, which is utilized to create a range of safe, biocompatible, and useful products. TiO_2 is a broad-band gap semiconductor with a number of intriguing characteristics, including a low absorption coefficient, a high refractive index, high photo stability, transparency to visible light, and non-toxicity. Because of its ability to decompose organic molecules by photo catalysis, it finds extensive utility in environmental applications such as the purification of wastewater.TiO_2's Photocatalytic behaviour is heavily influenced by its structural characteristics, including its crystalline phase, specific surface area, porosity, and particle size and shape. Despite all of its benefits, TiO_2's comparatively wide band gap (3.0 eV for the rutile phase and 3.2 eV for the anatase phase) limits its use in visible light. Doping various metal and non-metal ions has been used to modify the photo catalyst's band gap. The elements most often utilized for this purpose are carbon[1], nitrogen, sulphur, fluorine, boron[2], phosphorus[3], and iodine[4]. Of these, carbon is the element that can penetrate TiO2's lattice structure the best, allowing carbon-doped TiO2 to absorb a broad spectrum of visible wavelengths [17]. However, the incorporation of carbon elements in the TiO_2 lattice and its Photocatalytic activity are limited by the inclusion of exogenous carbon precursors [28]. One of the most common biopolymers on the planet, cellulose, polymer of beta-D glucose, cellulose typically consists of several fibres joined by intra- and intermolecular hydrogen bond networks [30, 31]. It is inexpensive and easily accessible [29]. Metal oxide nanoparticles can develop on the OH groups found in the cellulose molecule. A linear polymer of beta-D glucose, cellulose typically consists of several fibres joined by intra- and intermolecular hydrogen bond networks [30, 31]. It's an intriguing option for a variety of functional materials because of its renewability, biodegradability, and biocompatibility. Microcrystalline cellulose (MCC) is hydrophilic, which makes it a suitable substrate for the sol–gel production of -TiO_2

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nanoparticles. TiO_2/cellulose composites were created by Hamad and colleagues [35] by dissolving MCC in HNO_3 or H_3PO_4, followed by the solar impregnation of TiO_2. More TiO_2 loading and a greater active photocatalyst were the results of the pre-treatment procedure. This work used the simple sol-gel approach to produce carbon-doped TiO_2 nanoparticles. MCC was utilized to dope carbon ions in the TiO_2 crystalline structure, which reduced the aggregation of the nanoparticles and increased the Photocatalytic activity of the samples. Since cellulose is mostly composed of carbon, it is an appropriate agent for carbon doping in metal oxide semiconductors. Based on this, the morphological, structural, and optical characteristics of the samples were examined, along with the impact of annealing temperature on the stability of carbon ions doped in the TiO_2 structure. Ultimately, the produced samples' Photocatalytic activity was examined using the photo degradation of methylene blue (MB) in the presence of UV and visible light.

EXPERIMENTAL :

Materials :

Titanium tetrabutaoxide [Ti $(OBu)_4$] were purchased from Sigma Aldrich used as a precursor in the catalyst synthesis, dopant- MCC ,Methylene blue Dye, H_2SO_4, HNO_3, Ethanol. All chemicals are AR graded and prepared with double distilled water at 25° C.

Synthesis of microcrystalline cellulose using Conc HCl :

Four grams of cotton were placed in eighty 80mL of HCl and left for a 24 hours. The next day, the cotton was placed in ice cold water and filtered and dried at room temperature. It broke down, yielding pure cellulose.

Preparation of carbon doped nano TiO_2

The sol-gel method was used to create carbon-doped TiO_2. Titanium (IV) isopropoxide and ethanol were combined in a beaker at a molar ratio of 1:10, and a magnetic stirrer was used to agitate the mixture vigorously. Drop by drop, this solution was added to the MCC aqueous dispersion to help with the condensation and hydrolysis processes. Using a magnetic stirrer, the liquid was mixed for 30 minutes. HNO_3 was then added to lower the pH to around 2. The precipitates were separated and then allowed to develop at room temperature for a whole day. After that, the samples were calcined at 500°C after being dried for five hours at 100°C in an oven.

RESULT AND DISCUSSION:

Characterization Techniques for the Formation of Carbon Doping

XRD Analysis of carbon-doped TiO_2

The developed nanophotocatalyst's crystalline phase and its size were ascertained using powder XRD analysis. Figure 1 depicts the XRD patterns of sample. The characteristic peaks in the XRD pattern of C-doped TiO_2 assembled as 2θ values of 25.26, 37.8, 48.0, 53.2, 55.0, and 62.8 are assigned to the planes of anatase (101), (004), (200), (105), (211), and (213), respectively, confirming anatase phase (JCPDS No. 21-1272). (23) . Using the Debye-Scherrer equation, the average crystallite sizes of the synthesized compound were determined from the XRD pattern, as seen below.

$D = \frac{k\lambda}{\beta \cos\theta}$ And found synthesized product is a nanomaterial with a size range of 2 nm to 15 nm.

Scanning electron microscopy (SEM) analysis of C-doped TiO_2

Using an accelerating voltage of 5.0 kV, micrographs of the produced material's morphology were recorded using a scanning electron microscope (SEM). The developed nano material's porous shape is evident. The majority of the particles have a consistent size distribution and a nearly spherical shape. It is clear that carbon limits particle development when doping with TiO_2. Upon closer inspection, these figures exhibit a distinct particle-like morphology with a high concentration of spherical-shaped particles and an average agglomerated particle size in the

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1–14 nm range. The spherical form plays a major role in the design of surface area and characteristics as well as in the tuning of the electronic structure, or increasing the activity of the visible light spectrum for improved Photocatalytic activity.

Photocatalytic activity of carbon-doped Nano photocatalyst on Methylene blue dye

Photo degradation experiments were performed with a thermostatic cylindrical Pyrex reactor with a 1000 mL capacity reactor system under the irradiation of a UV lamp and visible light. Methylene blue Dye solution around 500 ml with photocatalyst of 0.5 gram was stirred and added. The mixture was then irradiated with the UV lamp up to 90 min and in visible light 200 mint magnetically stirring was used throughout the experiment. At regular time intervals, 4-5 mL was withdrawn, centrifuged and the absorbance was measured. The quantitative estimation of the environmental pollutants was carried out using a UV-Vis spectrophotometer **(Shimadzu UV)** at their λmax. The results, are presented **in Figure 3 of Methylene blue** which indicate that photo degradation efficiency unequivocally increases with increasing irradiation time.

The percentage of dye degradation was calculated using below Eq.

Dye decolourization (%) = C_o-C_t /Co *100

Where, C_0 is the initial concentration of the dye solution before treatment and C_t is the dye concentration after degradation at time

CONCLUSION:

The incorporation of carbon into TiO_2 nanoparticles using MCC as a carbon source. This carbon doping helps enhance the Photocatalytic activity of TiO_2, making it more effective in degrading the methylene blue dye. This photocatalyst was examined by XRD, SEM analyses, UV-Vis spectroscopy is used to study the optical properties of the photocatalyst, including its absorption of UV and visible light. C-doped TiO_2 shows polyhedral and spherical particles with an average size of 1-15 nm. When it comes to utilizing this photocatalyst for degrading methylene blue dye, its carbon doping enables it to absorb visible light more efficiently. This means it can effectively degrade the dye under both UV and visible light irradiation. During the Photocatalytic process, reactive oxygen species (ROS) are generated, which break down the dye molecules, leading to their degradation and removal from the water. It require more time in visible comparable to UV light. C-doped TiO_2 shows a superb degradation of these pollutants between 98-99% under UV and 60% visible light.

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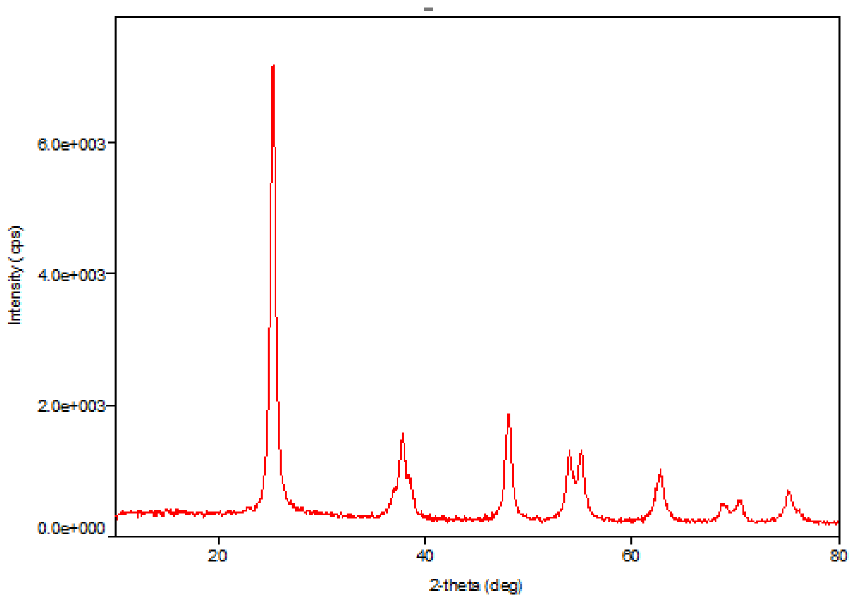

Fig. 1. XRD pattern of C-TiO_2.

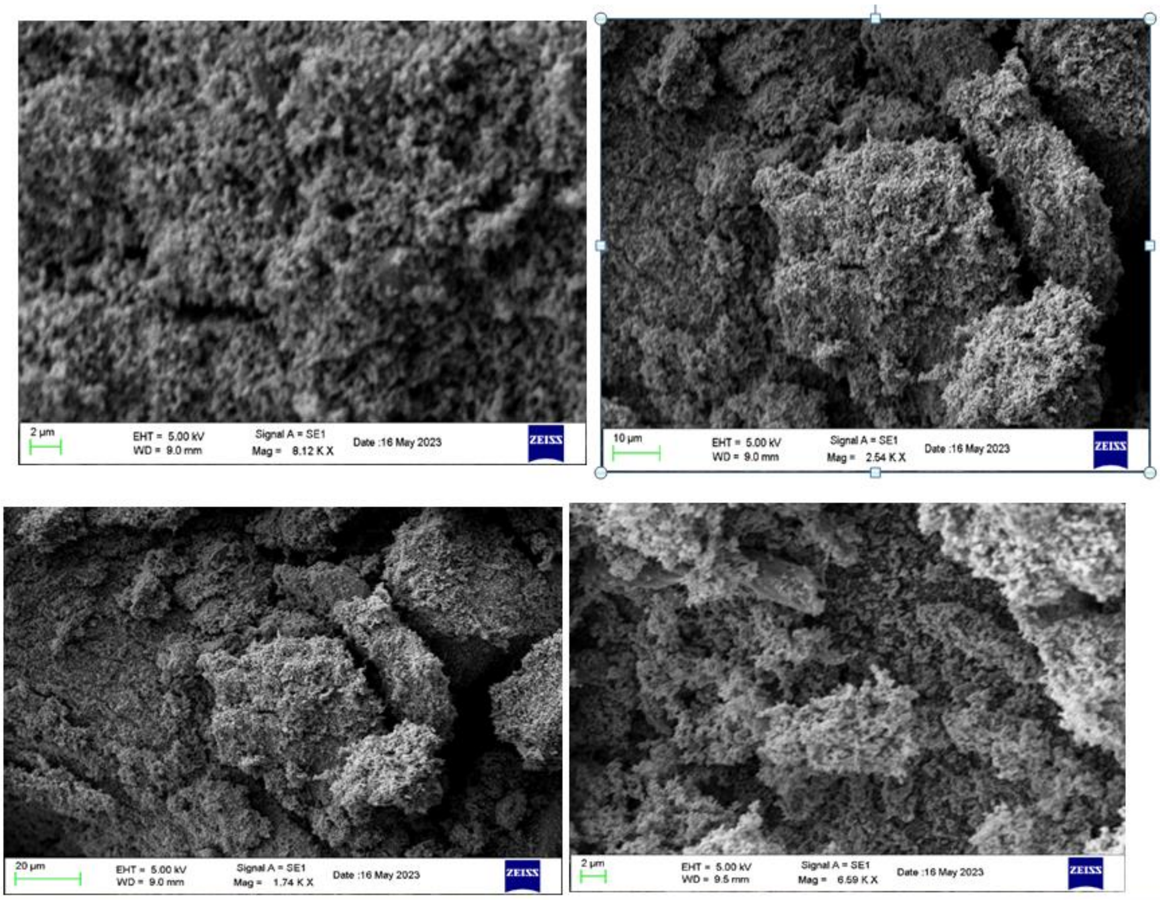

Figure 2 :- SEM images of carbon doped TiO2

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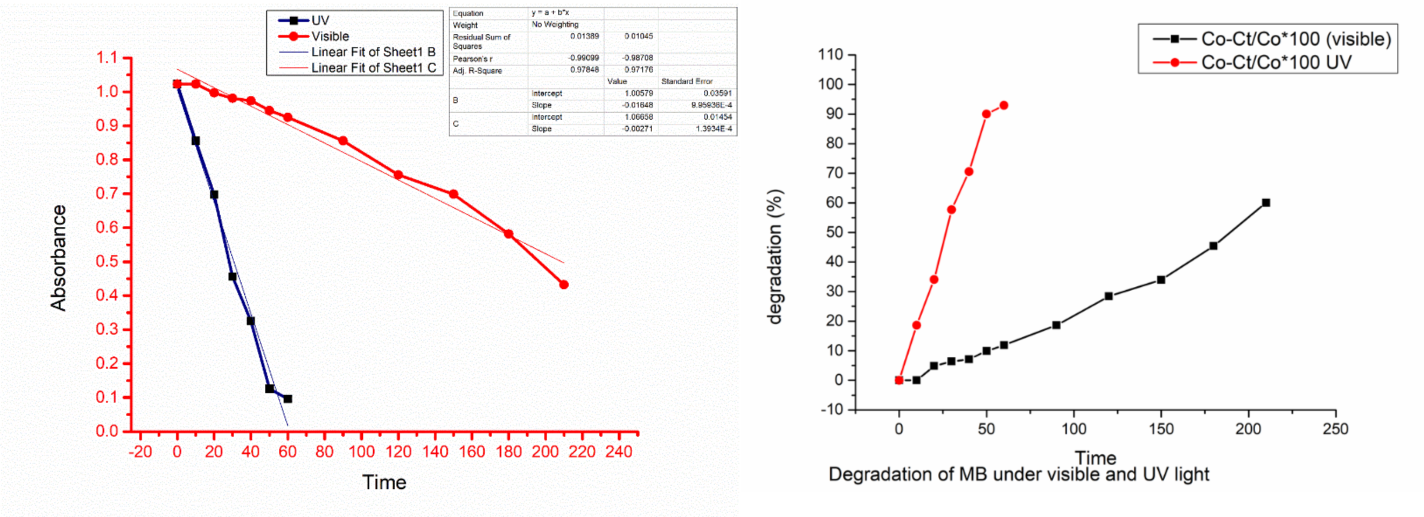

Figure 3- Degradation of methylene blue dye using C-doped TiO_2 under UV and visible light

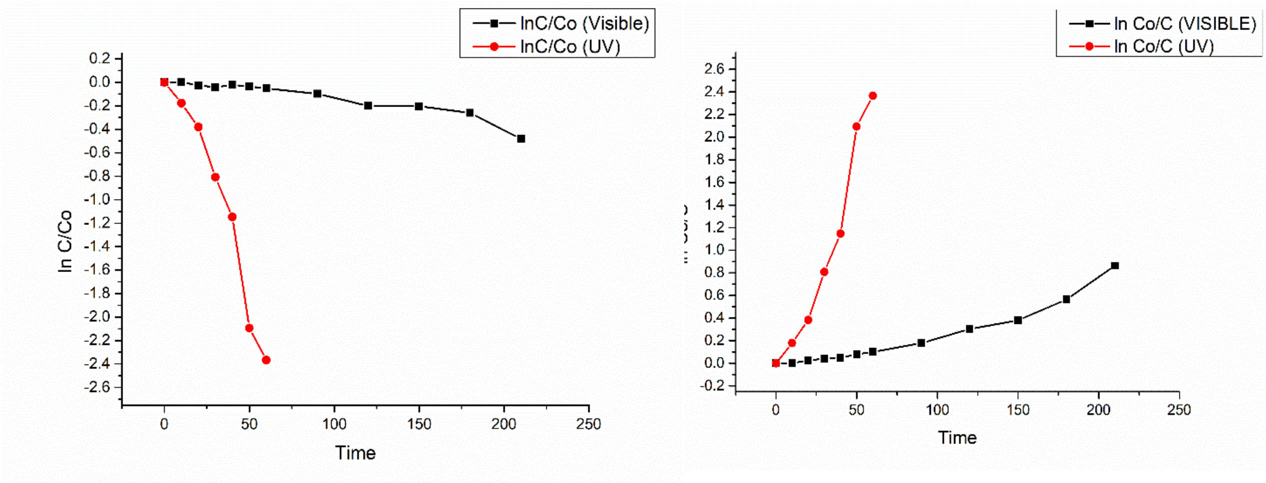

Figure 4- Kinetics of Methylene blue dye follows pseudo order

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