

CALCINATION TEMPERATURE EFFECT ON SnO_2 NANOPARTICLES FOR THE ENHANCED PHOTOCATALYTIC PERFORMANCE OF MALACHITE GREEN DYE MINERALIZATION UNDER NATURAL SOLAR LIGHT

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ABSTRACT

The rapid use of organic dyes for industrial purposes has led to water pollution, which has sparked a lot of interest towards photocatalytic applications. The most affordable, green and widespread method of treating aquatic wastewater is by breakdown of the dye molecules with photocatalysts in the presence of daylight. Therefore, it is necessary to create photocatalytic materials that, when exposed to natural light, can produce reactive oxygen species. So, keeping in mind the aforementioned point, sol gel technique was used to synthesize Tin oxide (SnO_2) nanoparticles at three distinct temperatures such as 350 °C, 450 °C and 550 °C respectively. This article reports the significant degradation application of SnO_2 nanoparticles against Malachite Green (MG) dye under direct sunlight illumination. The removal of dye concentration found to be escalating with the increase in calcination temperature, as it repress the electron hole recombination process. The enhanced dye remediation rate of the as-synthesized nanoparticles achieved at 550 °C of 88.9% can be ascribed due to the lower energy bandgap value.

KEYWORDS: *Malachite green; Tin oxide; Photocatalysis; Temperature; Bandgap*

INTRODUCTION

The ecosystem has been severely contaminated by the rapid growth of industrialization and widespread usage of chemicals for different purposes[1]. Numerous dyes used in the textile and other sectors polluted the soil and aquatic bodies at an alarming rate. Organic dyes such as crystal violet, malachite green, methyl orange, methylene blue, and Congo red, are extremely toxic and pose major threats to both environment and human health[2]. Among them, malachite green is one of the most popular dye for colouring cotton, jute, wool, leather, and other materials, which is also utilised in the food industry as an antimicrobial and antifungal agent. The presence of MG dye in water reduces appetite, damages the liver and kidneys, induces heart failure, lowers the rate of conception, and exhibits teratogenic, carcinogenic, and mutagenic effects on human cells[3]. Therefore, the removal of dyes present in marine bodies becomes the key challenge for researcher community. An affordable and well-liked technique for treating water is the breakdown of these dyes with photocatalysts in the presence of sunlight. It is well known that the optical band gap and photocatalytic properties are directly correlated. The introduction of different defects act as the trapped centres which results in decrement of e^-h^+ pair recombination rate. Therefore, the precise control on bandgap and size characteristics plays a pivotal role in elevating the catalytic degradation performance[4]. Among different literature reviewed metal oxide semiconductors, particularly, Tin oxide, a wide bandgap material has gained considerable attention in the field of photocatalysis[5,6]. This work discusses the degradation activity of malachite green, an organic dye, under direct solar light conditions.

EXPERIMENTAL PROCEDURE

Sol-gel derived SnO_2 nanoparticles at different temperature (350°C-550 °C) were synthesized by previously reported protocol and their microstructural, optical and morphological characteristics have also analysed using different tools such as XRD, FESEM-EDAX and UV-Vis spectrophotometer [7]. The decomposition efficiency SnO_2 nanoparticles was studied under direct sunshine exposure against malachite green dye. The photocatalytic experiment was performed between 10:00 am to 3:00 pm at 37 °C (average recorded temperature). The stock solution of MG dye was prepared with concentration C=10 mg/l. For degradation reactions, 50 mg of SnO_2 photocatalyst was dispersed with 50 ml of MG dye solution. The procured solution was then put in the black chamber with continuous stirring for about 25 minutes to obtain the absorption-desorption equilibrium. After

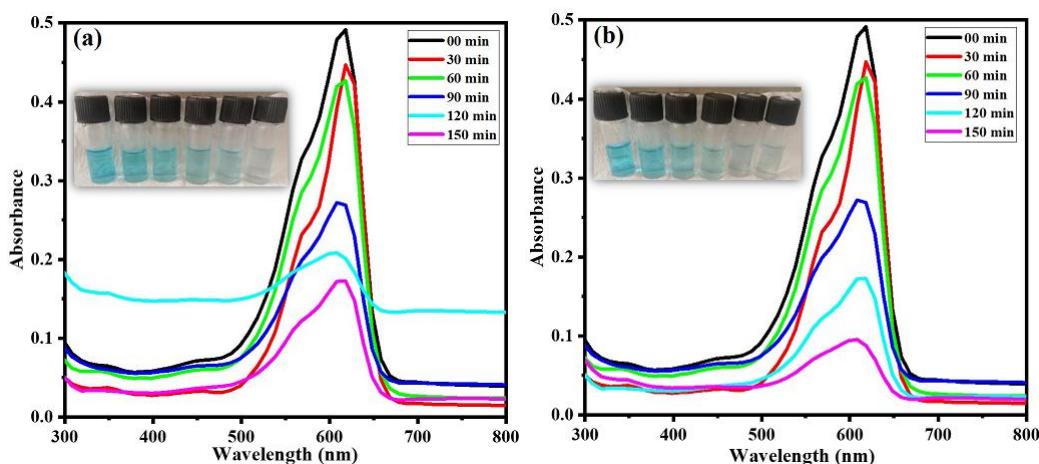
that uniformly pour the mixture in different glass bottles and then exposed under solar light. During the experimentation, monitor the decolourization of dye by taking off the bottles from sunlight irradiation at specific time span. The extracted dye solutions for each sample were tested from 300 nm–800 nm wavelength range using UV–VIS spectrophotometer. The catalytic efficiency was determined by using following equation:

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \dots \dots \dots \text{(i)}$$

Where, C_0 represents the initial concentration of the dye solution and C_t be the dye concentration at specific time slots.

RESULTS & DISCUSSION

Figure 1 (a-c) represents the UV-Vis absorption plots of MG dye for SnO_2 samples calcined at different temperature i.e. 350 °C, 450 °C and 550 °C. The photocatalytic measurements were recorded at regular intervals for all samples respectively and displayed the λ_{max} characteristic absorption wavelength at 620 nm. The peaks of the dye for all samples found to be declined with regular time span. For each sample, the dye solution almost turns transparent in 150 minutes. It was noticed that the SnO_2 photocatalysts calcined at highest temperature exhibited superior dye decomposition performance in contrast to other ones. The cause of comparatively lower degradation rate is due to its larger bandgap energy value. It is observed from the Table 1 that the highest degradation efficiency is 88.9% within 150 min of time frame. The enhanced photocatalytic activities could be due to the separation of charge carriers by the introduction of more defects at the SnO_2 lattice sites[8]. The overall obtained outcomes depicted that SnO_2 nanopowder calcined at 550 °C is ideal for the decomposition of MG dye molecules. Further, two different set of experiments were carried out one without solar light and other in the absence of nanopowder resulted in no degradation of dye molecules. Hence, it revealed that the light illumination and photocatalysts are necessary for the efficient decolourization of the MG solution. The estimated degradation efficiencies in respective time intervals with different temperature were decipher in Table 1.



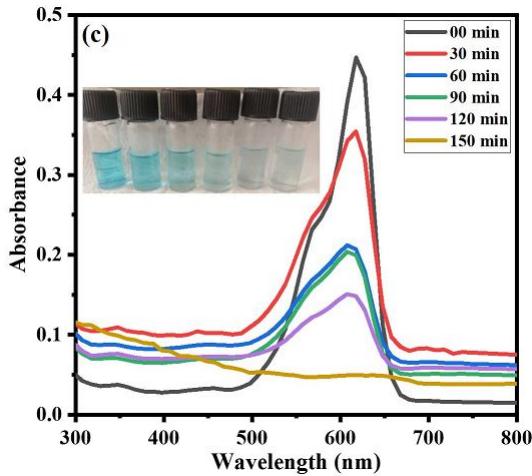


Figure 1.Dye absorption spectrum of SnO_2 nanoparticles (a) $350\text{ }^{\circ}\text{C}$, (b) $450\text{ }^{\circ}\text{C}$ & (c) $550\text{ }^{\circ}\text{C}$.

Proposed Malachite Green dye photocatalytic degradation mechanism

The photocatalytic decomposition mechanism of selected dye under natural solar light irradiation is presented in the Figure 3. When incident light with energy higher or equivalent to the band gap range an electron –hole pair generates on the surface of photocatalysts. These electron-hole pairs frequently recombine quickly, making them incapable of participating in photocatalytic processes. Superoxide anionic radicals are produced when the electrons (e^-) produced in the conduction band act as a reducing agent and are absorbed by the physisorbed oxygen molecule on the surface of the SnO_2 photocatalyst. By reacting with water, the holes (h^+) created in the valence shell either directly oxidise the pollutant or produce hydroxyl radicals (OH^\cdot). Hydroxyl radicals were produced when superoxide anionic radicals and hydrogen (^+H) interacted. After $-\text{OH}$ and MB reacted, carbon dioxide and water molecules were created as by products. The reaction mechanism[5] involved is depicted in the Figure

2:

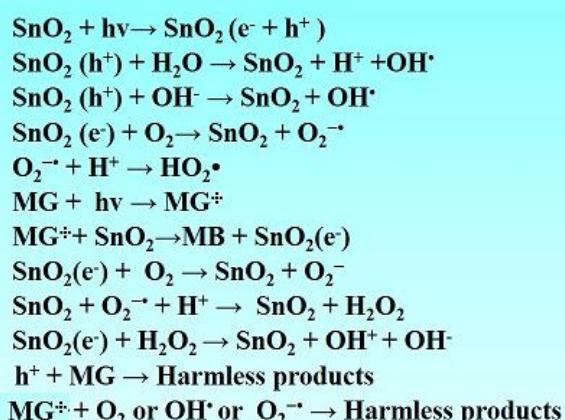


Figure 2.Proposed mechanism steps involved in decomposition of MG dye molecules

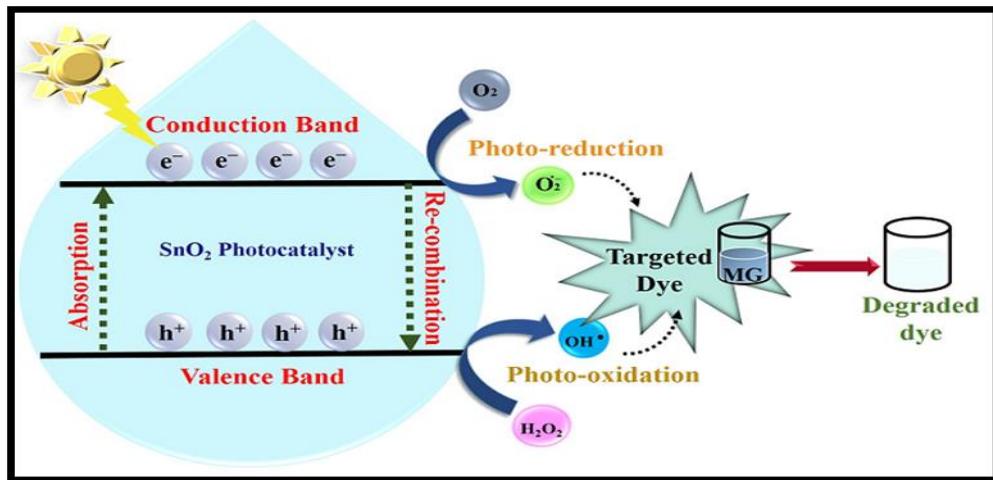


Figure 3. Proposed catalytic degradation mechanism of MG dye molecules

CONCLUSION

Nanopowders of SnO_2 were successfully prepared at three distinct temperatures such as 350 °C, 450 °C and 550 °C via sol-gel method. This present study revealed that the photodegradation properties under direct solar light can be tuned by varying calcination temperature which could be further used for different applications. The obtained outcomes showed that SnO_2 nanopowder calcined at 550 °C is ideal for the decomposition of MG dye molecules with efficiency of about 88.9%. The cause of comparatively higher degradation rate is due to its smaller bandgap energy value which further suppress the recombination of generated electron-hole pairs.

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Table 1: Degradation efficiency w.r.t illumination time of synthesized nanopowders

Calcination Temperature (°C)	Illumination time (min)	Degradation Efficiency (%)
350	150	64.9
450	150	82.1
550	150	88.9

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