

Photocatalytic Degradation of Malachite Green Dye by Plant-mediated Biosynthesized Zinc Oxide Nanoparticles

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Abstract. Photocatalytic activity of ZnO-NPs was tested by degradation of Malachite Green dye under UV light irradiation. The ZnO-NPs were biosynthesized using *Punica granatum* (pomegranate) fruit peels extract as the stabilizing agent. Simple sol-gel method and calcination in different temperatures (400, 500, 600 and 700°C) were carried out to obtain pure ZnO-NPs with high photocatalytic properties. In the degradation studies, 20 mg ZnO-NPs were used to degrade Malachite Green dye of 10 ppm initial concentration for a total period of 50 minutes in a 100 ml reaction volume. Results obtained shown that ZnO-NPs calcined in 700°C had the highest removal efficiency at about 99% in 40 minutes. This proves that biosynthesized ZnO-NPs have a high potential to be used as a photocatalyst to degrade textile dyes in a short time for wastewater treatments.

1. Introduction

In the field of catalysis and water treatment, nanomaterials have been gaining much interest because of their unique physico-chemical properties, high surface area to volume ratio, and strong interaction with other materials [1]. Several types of nanomaterials such as copper oxide [2], titanium dioxide [3], magnesium doped zinc oxide [4], silver doped titanium dioxide [5] and iron [6] have been reviewed for their potential in wastewater treatments. Zinc oxide (ZnO) is one of the most extensively studied semiconductors with a large band gap of about 3.3 eV. At room temperature, ZnO is known to have a high excitation binding energy of about 60 meV with stable hexagonal wurtzite structure [7]. Upon irradiation of ZnO-NPs semiconductor with UV light, electrons from its valence band travels to the conduction band and generate hole-electron (h/e) pair which in turn causes the production of hydroxyl radicals and reactive oxygen species (ROS) [8]. These hydroxyl radicals and ROS will oxidize pollutant molecules from dye compounds in the photocatalytic process.

A major pollutant in our water resource comes from the textile industry which discharges large amounts of dye effluents into the water streams daily [9]. These dye effluents have been proven toxic to the environment and human health thus proper treatments to reduce and degrade them has to be developed. Degradation and removal of various types of dyes such as Gentian Violet dye [7], Methyl Orange [10], Basic Violet 3 dye [11] and Methylene Blue [12] by numerous nanomaterials have been studied and reported before. Extensive studies have also been done to investigate the efficiency of ZnO-NPs as catalysts to degrade various textile dyes thanks to their high surface area, non-toxicity, photosensitivity and cost-effectiveness [9]. Malachite Green is one of the most commonly used dyes in the industrial field. Degradation of Malachite Green dye in particular is more difficult due to the



presence of complex aromatic ring in their triphenylmethane structure [13]. Malachite Green dye has also been reported to be highly resistant to light and oxidizing agents, and previous studies to remove them using biological treatment and chemical precipitation were not that efficient [13].

This present study reports the successful production of ZnO-NPs mediated using *Punica granatum* (*P. granatum*) fruit (F.) peels extract as reducing and stabilizing agents for the sol-gel and combustion methods. We will investigate the effect of different calcination temperature on the morphology of ZnO-NPs as well as their effectiveness to degrade Malachite Green dye under UV light irradiation.

2. Experimental

2.1 Plant collection and materials

Fruit peels of *P. granatum* were collected from “Green Farm” in Fars province, city of Neyriz, Iran. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98 %) of analytical grade was purchased from R&M Chemicals, United Kingdom and used as metal salt precursor. Deionized (DI) water was used to prepare all aqueous solutions. Glassware used in this study were thoroughly cleaned with DI water and dried before use.

2.2 Fruit peel extract preparation

Fresh *P. granatum* F. peels were cleaned using tap water and DI water consequently to remove visible dirt before dried in the oven at 45 °C. The dried peels were ground into fine powder and stored at room temperature for further use. *P. granatum* F. peel extract was produced by extracting the peel powder in DI water at 65 °C for 1 hour in the ratio of 1:10. The extract were then filtered and further centrifuged at 10,000 rpm for 10 min to completely remove any leftover particles. The *P. granatum* F. peel extract was kept at 4 °C for future experiments.

2.3 Biosynthesis of ZnO-NPs

The ZnO-NPs were synthesized using a simple sol-gel and combustion method consequently. In the ratio of 1:10, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was added to *P. granatum* F. peel extract under vigorous stirring. The solution was stirred at 90 °C until the aqueous solvent is completely removed, leaving a gel-like product. The product was then calcined at different temperatures (400, 500, 600, and 700 °C) for 1 hour until it turned into fine white powder form. All ZnO-NPs powder were kept in room temperature and used in the experiments.

2.4 Characterization methods and instrumentation

To evaluate the purity and crystallinity of ZnO-NPs, X-ray diffraction (XRD, Philips, X'pert, Cu Ka) at the small angle range of 2 θ (10°- 90°) was used. High Resolution Transmission electron microscopy (HRTEM) (model JEM-2100F) was used to observe and capture images of all biosynthesized ZnO-NPs. The shapes and sizes of ZnO-NPs were then analysed in this study. Information on surface area, pore volume and pore radius were obtained using BET surface analyzer (NovaTouch) by measuring nitrogen adsorption-desorption isotherm at 77 K. All ZnO-NPs were degassed for 2 hours at 150 °C. For photocatalytic experiments, Ultraviolet-visible (UV-vis) spectroscopy (UV-2600, SHIMADZU) was used to measure absorbance values in the wavelength range of 220 to 900 nm.

2.5 Photocatalytic studies

The efficiency of all biosynthesized ZnO-NPs was evaluated by its ability to degrade Malachite Green dye. 20 mg of ZnO-NPs photocatalyst was mixed with Malachite Green dye solution of 10 ppm concentration in a 100 ml reaction volume. The mixture was stirred in dark for 30 minutes to obtain adsorption and desorption equilibrium. After that, the mixture was exposed to UV light irradiation and small amount of samples were taken every 10 minutes for absorbance reading using UV-vis spectrophotometer. The photocatalytic studies were carried out for 50 minutes until complete

degradation of the dye. Results were analyzed to investigate the effectiveness of all ZnO-NPs as a photocatalyst.

3. Results and discussion

To confirm the successful production of ZnO-NPs, XRD analysis was carried out for all samples. Figure 1 shows the Miller indices peaks of all four samples of ZnO-NPs, which can be indexed to hexagonal wurtzite phase structure as supported by JCDPS Cardno. 89-1397 data [14]. As no other foreign peaks can be seen, it is confirmed that the biosynthesized ZnO-NPs are highly pure and crystalline. Calcinating in higher temperatures produce ZnO-NPs with increasing crystallinity as the diffraction peaks become more intense and narrower.

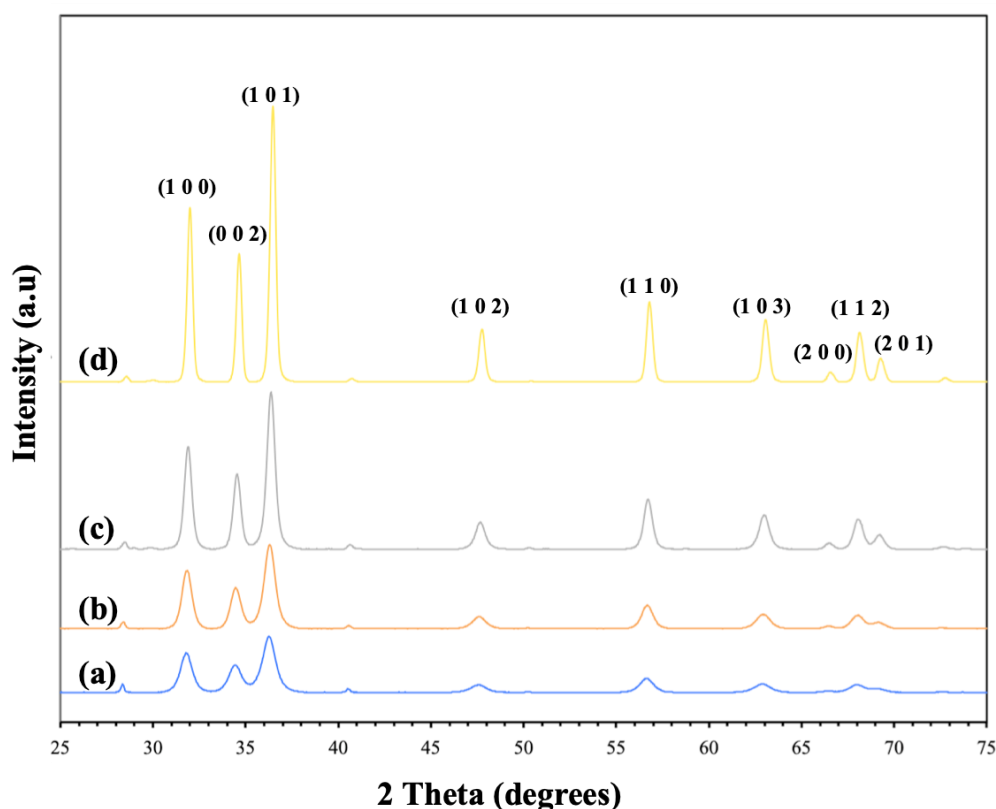


Figure 1. XRD patterns of (a) ZnO-NPs 400, (b) ZnO-NPs 500, (c) ZnO-NPs 600 and (d) ZnO-NPs 700 respectively.

The morphology of all biosynthesized ZnO-NPs was observed using TEM imaging. Figure 2 shows the shapes and sizes of all ZnO-NPs samples. Irregular shapes of ZnO-NPs with slight agglomeration were produced for all calcination temperatures. In lower calcination temperature, mostly spherical particles were synthesized but as calcination temperature increases, more irregular shapes of ZnO-NPs can be observed. This might be due to aggregation of small primary particles to form secondary or even tertiary particles [15]. Therefore, in higher calcination temperature, larger and irregularly shaped ZnO-NPs were produced as can be seen in Figure 2(c,d) as compared to Figure 2(a,b). Particle sizes of ZnO-NPs 400 and ZnO-NPs 500 were measured to less than 50 nm while ZnO-NPs 600 and ZnO-NPs 700 were in the range of 40-70 nm.

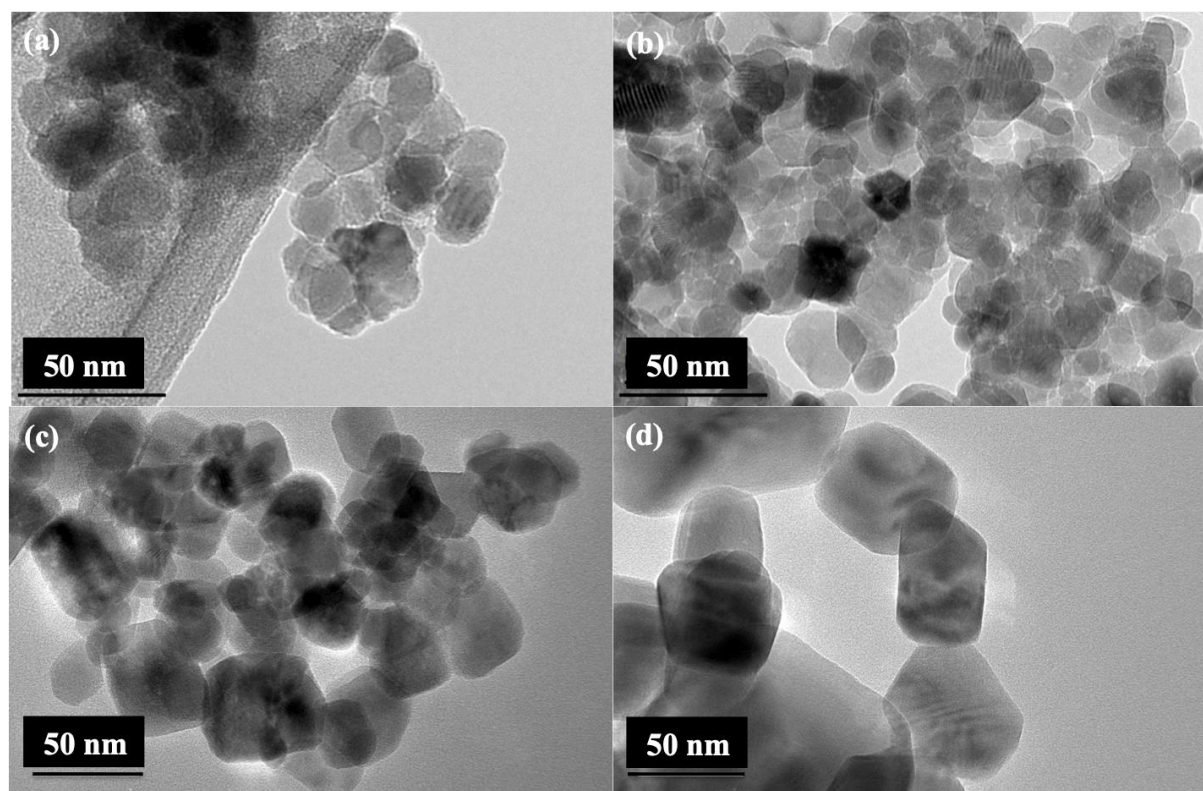


Figure 2. HRTEM images of (a) ZnO-NPs 400, (b) ZnO-NPs 500, (c) ZnO-NPs 600 and (d) ZnO-NPs 700 respectively.

Table 1 lists the surface area, pore volume as well as pore radius of all biosynthesized ZnO-NPs based on BET and BJH analysis. Specific surface area for the biosynthesized ZnO-NPs decreases progressively with increasing calcination temperature. The main factor leading to the reduction of surface area is the increased particle sizes of ZnO-NPs when calcined in higher temperatures, as observed from the HRTEM images in Figure 2. As sizes of ZnO-NPs become larger, pore volume and pore radius also decrease inevitably.

Table 1: Surface area, pore volume and pore radius of all biosynthesized ZnO-NPs.

Sample	Surface area (m ² /g)	Pore volume (cc/g)	Pore radius (nm)
ZnO-NPs 400	52.001	0.158	8.765
ZnO-NPs 500	42.854	0.117	1.245
ZnO-NPs 600	30.444	0.073	1.336
ZnO-NPs 700	17.160	0.021	0.820

The dye degradation activity of all biosynthesized ZnO-NPs samples was carried out against Malachite Green dye under UV light irradiation. The maximum absorbance peak wavelength of malachite green was observed at 617 nm. Figure 3 shows the gradual decrease in maximum absorption peak of Malachite Green with time for all ZnO-NPs samples and a control experiment (without ZnO-NPs photocatalyst). The control experiment as shown in Figure 3(a) shows slow reduction in Malachite Green absorption peak with time. Meanwhile in the presence of ZnO-NPs photocatalyst, upon exposure with UV light, the intensity of absorption decreases until almost zero in about 50 minutes of reaction time signifying a complete degradation of Malachite Green dye for all experiments as plotted in Figure 3(b-e).

Based on Figure 3(d), ZnO-NPs 700 showed the most rapid reduction of Malachite Green dye as the absorption peak reaches almost zero at only 30 minutes of time. Similarly, ZnO-NPs 600 showed high degradation performance as well as the Malachite Green dye is almost completely degraded at around 40 minutes. Despite having larger particles sizes, ZnO-NPs calcined in higher temperatures of 600 and 700°C showed excellent performance in degrading Malachite Green dye compared to ZnO-NPs with smaller particles sizes.

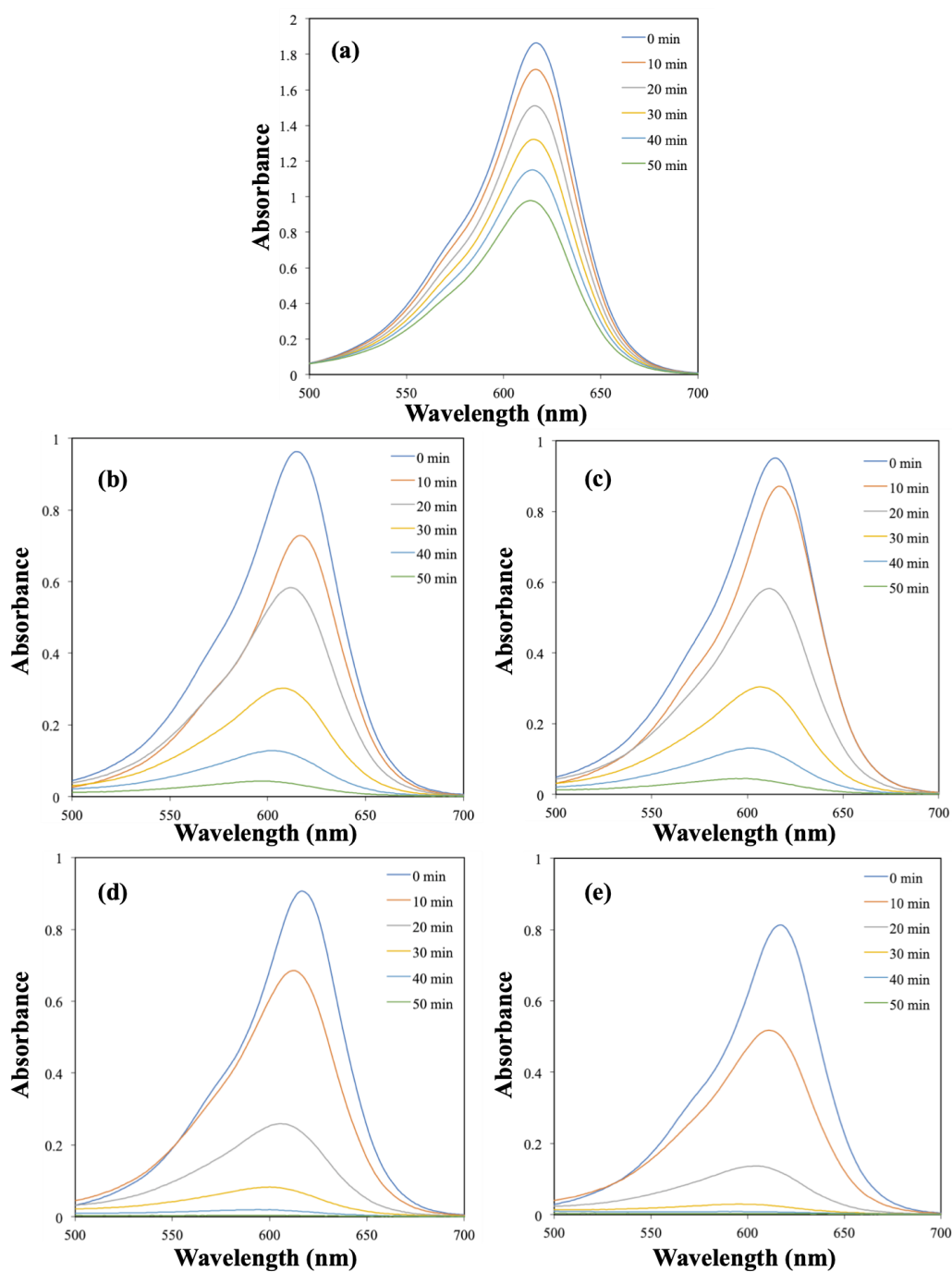


Figure 3. Decrease in absorption peak of Malachite Green dye with time for (a) control (without ZnO-NPs photocatalyst), (b) ZnO-NPs 400, (c) ZnO-NPs 500, (d) ZnO-NPs 600 and (e) ZnO-NPs 700 respectively.

From the absorbance data obtained, a degradation study was carried out and a comparative graph shown in Figure 4 was plotted to analyze the different removal efficiency of all ZnO-NPs photocatalysts. When compared to the control experiment, all four samples of ZnO-NPs photocatalysts showed excellent performance as they successfully degraded Malachite Green dye to almost a 100% rate. The percentage degradations Malachite Green dye by ZnO-NPs calcined at 400°C and 500°C are 96%. For ZnO-NPs calcined at 600°C and 700°C, highest removal efficiency of 99% were achieved in a short time of about 40 minutes. ZnO-NPs 700 performed the best as 10 ppm initial concentration of Malachite Green was degraded in only 30 minutes time. This corresponds to the previous analysis and characterization where ZnO-NPs 700 showed highest removal rate compared to those calcined in lower temperatures despite having larger particle sizes and lower surface area value.

Plausible reasons for this analysis have been discussed in previous studies mentioning the effect of surface defects and charge transfer on dye adsorption abilities of ZnO photocatalysts. When calcination temperature of ZnO-NPs increases, more surface defects such as oxygen vacancies are formed on their surface due to crystal structure disorder. This in turn stimulated greater dye adsorptions which influence their photocatalytic performance [16][17]. Crystallinity enhancement of ZnO-700 compared to other ZnO-NPs also plays an important role in decreasing charge transfer resistance. As charge transfer resistance decreases, electron transfer rate increases thus more hydroxyl radicals and ROS can be generated to oxidize the dye compounds [18].

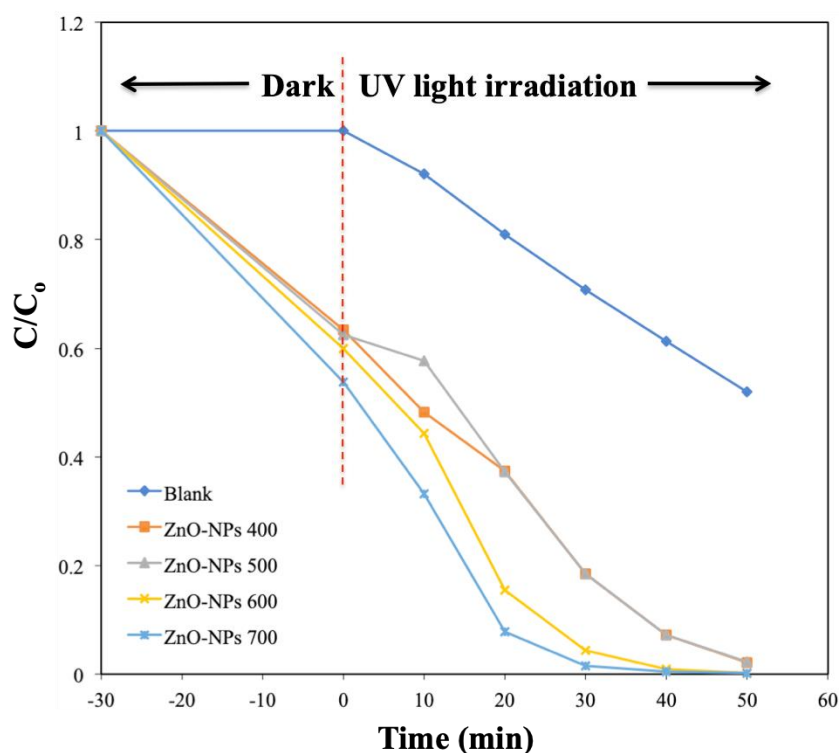


Figure 4. Comparative degradation study of Malachite Green dye with and without the presence of ZnO-NPs photocatalysts.

4. Conclusion

In the present work, plant-mediated biosynthesized ZnO-NPs were successfully produced using a simple sol-gel and combustion method in four different temperatures of 400, 500, 600, and 700°C. The effects of different calcinating temperatures towards the purity, crystallinity, surface area and particle sizes of ZnO-NPs were analysed. Comparative study of degradation efficiency for all biosynthesized ZnO-NPs was also carried out to determine which photocatalyst performed the best. HRTEM imaging showed smaller sized ZnO-NPs when calcined in lower temperatures of 400°C and 500°C with mainly

spherical shapes. Higher calcination temperatures at 600°C and 700°C synthesized larger ZnO-NPs with more irregular shapes. As larger particles are produced in higher calcination temperatures, surface area, pore volume and pore radius of ZnO-NPs also decrease progressively. Photocatalytic experiments proved that ZnO-700 has the highest removal efficiency of Malachite Green dye compared to the other ZnO photocatalysts. This might be due to the increase of oxygen vacancies and electron transfer rate in ZnO-NPs calcined in higher temperatures.

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