Photocatalytic degradation of Congo red by using graphene oxide/Zinc oxide composite materials

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Abstract

Graphene oxide (GO) was prepared by modified Hummer's method, Graphene oxide/Zinc oxide composite was made by adding GO at three distinct weight percentages (3%, 7%, and 10%) to ZnO. The samples were calcined at three different calcination temperatures (300, 350 and 400oC). Congo red dye was used to investigate the degradation percentage by using UV/visible light photocatalytic degradation. According to the results, the composite has a high capacity for photocatalytic degradation of Congo red dye. The reaction follows first order kinetics, according to the process kinetics study.

Introduction

The use of semiconductor materials in heterogeneous photocatalysis for water and air purification has gained significant attention in the past few decades. [1]. Zinc oxide's superior photocatalytic rate and physicochemical stability have attracted a lot of interest. [2-5]. Among many semiconductors zinc oxide is a semiconductor with a wide band-gap [6, 7]. Zinc oxide is widely used, but structural defects such its large band gap of 3.37 eV, which requires UV light for photocatalytic activation, and its propensity to agglomerate during manufacture pose problems despite this extensive utilization. Reducing the band gap of ZnO particles and improving absorption in the visible area are necessary to get beyond this disadvantage [8].

ZnO photocatalysis occur in the presence of sunlight, water, and oxygen, the result is the formation of holes (h+) and electrons (e−) when the semiconductor exited by UV light with energy above the band gap energy (e.g., 3.37 e.V). The creation of an electron-hole pair, which subsequently reacts with water, oxygen, and hydroxyl ions to produce hydroxyl (•OH) radicals. By undergoing a series of chemical reactions, the hydroxyl (•OH) radicals interact with the organic molecules that are attached to the photocatalyst, resulting in the conversion of the dye into carbon dioxide (CO_2) and H_2O [9-12].

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Graphene oxide has made a breakthrough in the field of photocatalysts by lowering zinc oxide's band gap and absorbing electrons [13]. It is now clear that morphological control and GO structure are crucial for a variety of applications [14]. Due to its distinctive features, including a large surface area, pliable sheets, exceptional electrical and thermal conductivity, and high mobility of charge carriers. (GO) has received a great deal of focus in recent times for photocatalysis use cases [15]. GO is the perfect substance for applications involving catalysis, energy conversion, and optoelectronics. The high concentration of reactive functional groups of oxygen on the GO sheet surface makes this material an innovative catalytic promoter or carrier [16]. According to reports, adding zinc oxide to the graphene oxide framework results in special photocatalytic activity [17].

Since carbon atoms are so near together, holes behave similarly to electrons as bulk-free charge transporters, which causes electronic overlap. Reduced charge recombination can be achieved by adding ZnO to nanostructured carbon materials as carbon nanotubes, fullerenes, and GO sheets [18]. High surface area and well-acid characteristics of the support material allow the transfer of charge across surfaces from the photocatalyst surface to the substrate because they adsorb organic pollutants close to the active sites. Additionally, the photocatalytic efficiency is increased by reducing recombination of electron with hole, which further increases the rate at which organic pollutants are degraded by photocatalysis [19].

The most recent research focused on synthesizing graphene oxide and used it as a base for loading zinc oxide. The activity of the generated compounds was evaluated by assessing the degradation of Congo red (CR) dye through photocatalysis.

2. Experimental

2.1. Synthesis of graphene oxide

Graphene oxide (GO) was synthesized using a modified version of the Hummer's process starting with graphite with a purity of 99.9995% [20-23]. 1 gram of graphite was stirred with 1 gram of $NaNO_3$ and 25 milliliters of concentrated H_2SO_4. The mixture was agitated rapidly for about one hour in an ice bath at 0°C. Subsequently, 4g of $KMnO_4$ was added gradually over approximately 1 hour while maintaining the temperature below 20°C. The cooling process completed in 2 hours, resulting in the mixture turning green. The next step was removing the ice bath and vigorously stirring the liquid, allowing it to stand at room temperature for 24 hours. Throughout the reaction, the mixture thickened gradually over time. 100 milliliters of distilled water was added slowly to the paste, leading to violent effervescence due to the oxidation of $KMnO_4$ accompanied with rising the temperature. The temperature was maintained below 98°C until the suspension's color changed to brown at the cessation of the effervescence. After 15 minutes, 200 mL of boiled distilled water was added to the mixture. When the temperature cooled down to 60°C, 30 ml of H_2O_2 (30 wt. %) was added to reduce the residual $KMnO_4$, resulting in the suspension turning bright yellow with bubbling. The solution was rinsed three times with hydrochloric acid (10%) and then with water. After being dried at 100°C overnight, graphene oxide sheets are obtained.

2.2. Synthesis of Graphene oxide/zinc oxide composite materials

Graphene oxide suspension was prepared in ethanol by sonication for 2 hours. 50 mL of pure ethanol were added to ZnO and sonicated for two hours to form an ethanol suspension of ZnO. This suspension was then combined with the ZnO

dispersion and agitated for twenty-four hours at an elevated temperature. The final product was washed with absolute ethanol. The product was subsequently re-dispersed in 10 mL of absolute ethanol and dried to generate ZnO-GO nanoparticles at different concentrations (ZnO-GO 3%, ZnO-GO 7%, ZnO-GO 10%) [23].

2.3. Studying the ready-made specimens

The GO/ZnO photocatalyst's activity was studied by observing the deterioration of Congo red (CR) under UV/visible light. Research on dye degradation involved adding 50 mg of activated photocatalyst to 50 ml solutions of CR. All samples were raised for one hour in the dark to reach adsorption equilibrium. After 40 min. of stirring in UV/visible light, the produced materials attained the degradation equilibrium of CR. The suspension was filtered by centrifugation and the quantities of Congo red were measured using a spectrophotometer at λ_{max} =490 nm.

3. Characterization

The chemical molecular structure of the prepared samples was examined by Fourier transform infrared (FTIR) analysis. FTIR is utilized to analyze the stretching vibrations in GO, while a UV-Vis spectrophotometer is employed to measure the absorbance of the dye solution. Utilizing a scanning electron microscope (SEM), the morphology of the photocatalyst (GO and GO-ZnO) is examined. The crystalline structures GO and GO-ZnO samples were examined using a transmission electron microscope (TEM).

3.1. FT-IR Characterization

FTIR spectra have been used to investigate the IR stretching frequency of the GO, as illustrated in Figure 1. The IR stretching (asymmetric) of O–H takes place around 3337 cm^{-1}. The C=O stretching vibration occurs at 1711 cm^{-1}, the C=C band stretching is at 1620 cm^{-1}, and the C–O bond is related to the band stretching at 1155 cm^{-1}, [24, 25].
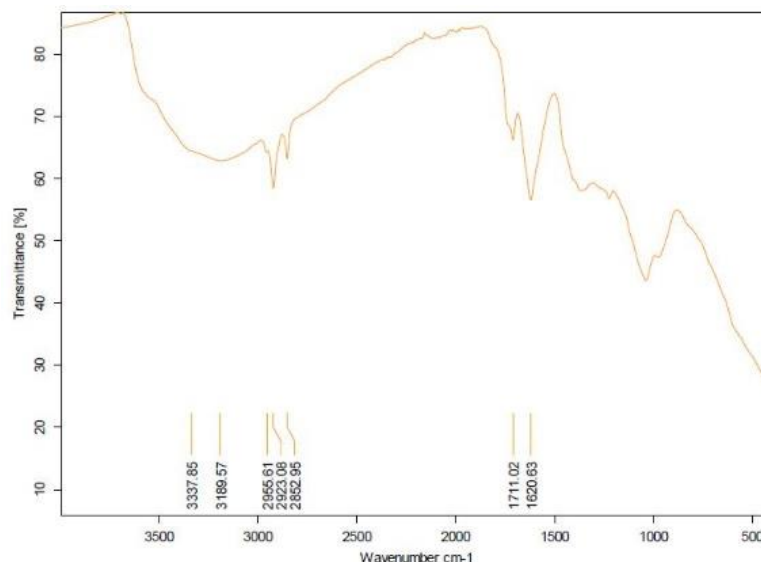

Figure 1: Graphene oxide IR analysis

3.2. The prepared samples' surface morphology

SEM was used to investigate the surface morphology of the GO, as shown in Figure 2. The micrograph provides a two-dimensional view of the catalyst's surface morphology. The prevalent structures are two-dimensional and smooth, like flat corn. GO is gathered into flat, overlapping structures that resemble corn kernels.
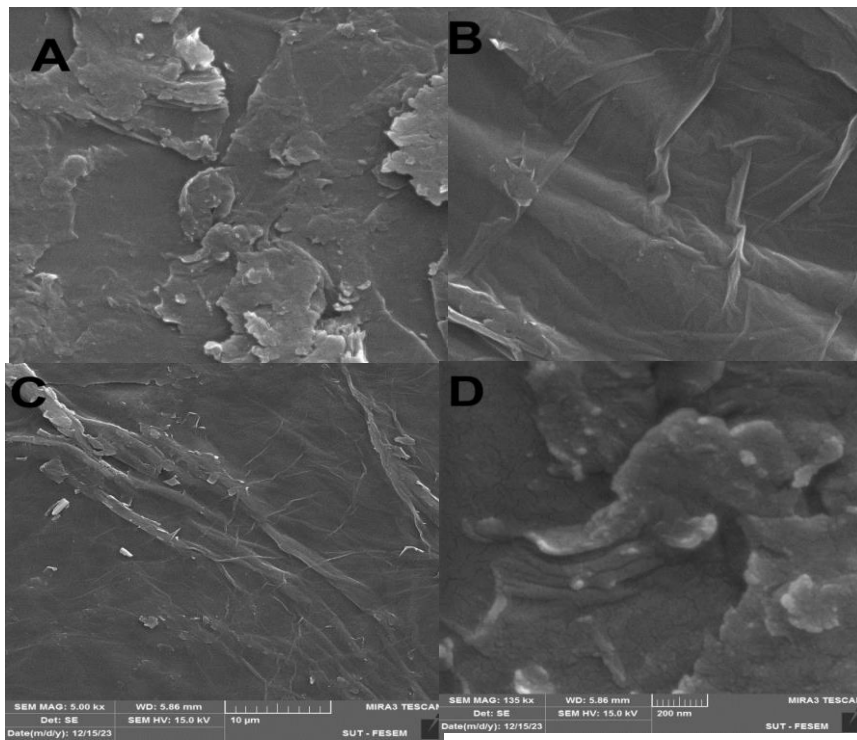
Figure 2: (A, B, C and D) Graphene oxide SEM image

The shape of GO-ZnO composite is shown in the Figure 3 as a high coverage area, spongy structure resembling a coral reef. The GO/ZnO broad free surfaces or grain boundaries may offer the ideal surface for the quick photo-catalytic response.
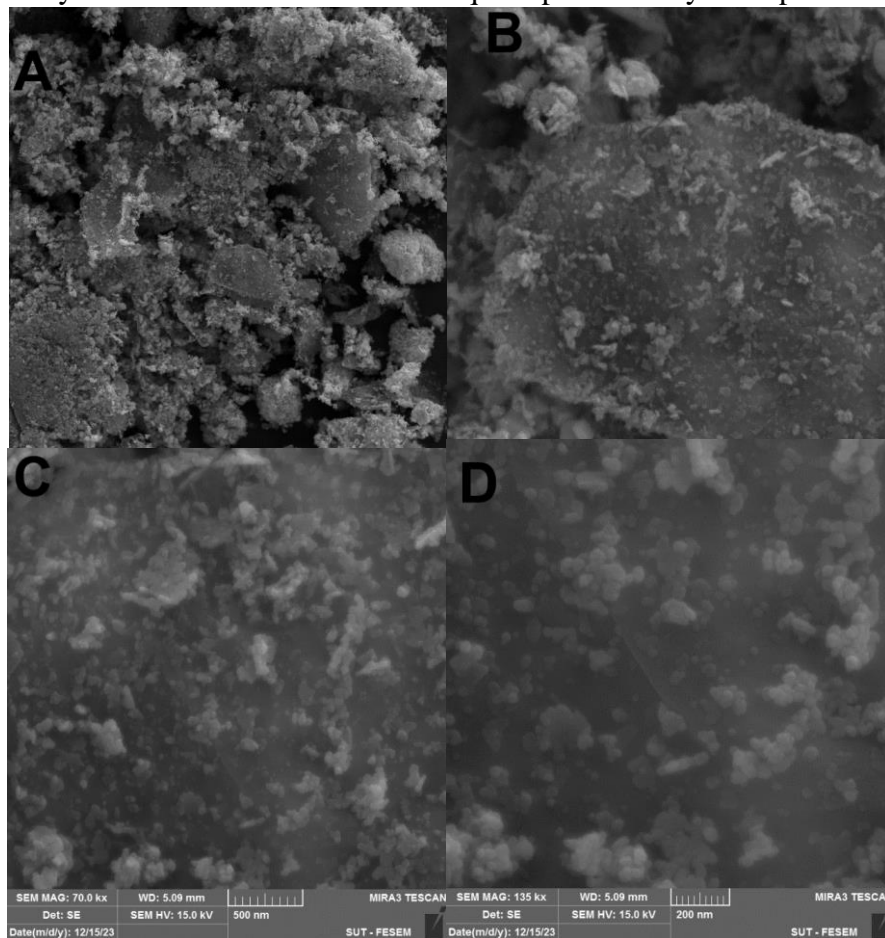

Figure 3: (A, B, C and D) GO/ZnO composite SEM image

The TEM pictures of the as-synthesised GO is shown in Figure 4. The TEM micrograph displays the appearance of a thin, irregularly shaped sheet of GO. It is clear

that GO displayed a sheet-like structure with a smooth surface, wrinkled edge, and a significant thickness and surface area.
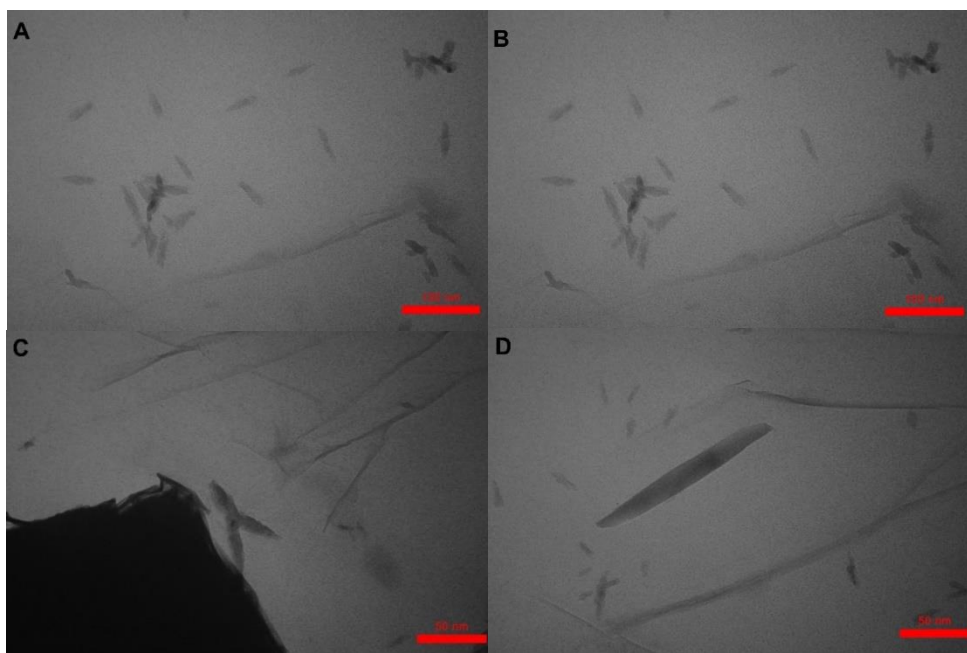

Figure 4: (A, B, C and D) Graphene oxide TEM image

The TEM picture of GO/ZnO composite is shown in Figure 5; the GO layer encapsulates the ZnO nanoparticles. It confirm the formation of spherical and hexagonal particles that were self-assembled. The agglomeration of ZnO nanoparticles is clear in some parts which were useful for enhancing the activity of the catalyst in the degradation of the Congo red dye.
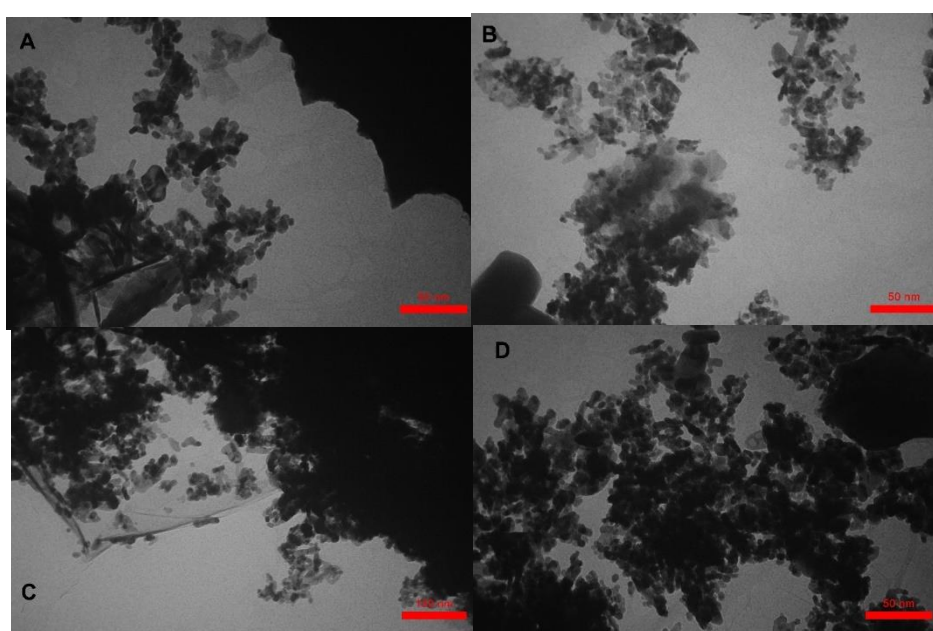

Figure 5: (A, B, C and D) GO/ZnO composite TEM image

4. Results and Discussion

4.1. Photocatalytic Degradation of Congo red

4.1.1. Effect of GO content

The catalytic activity rises as the concentration of GO grows up to 7wt%, but then decreases at 10wt%. Figure 6 shows the duration of irradiation of CR (10 mg/L) by various substances. After 30 minutes, all samples reached equilibrium. The sample containing 7wt% GO/ZnO showed the highest degradation, consuming 96% of the congo red within 40 minutes.
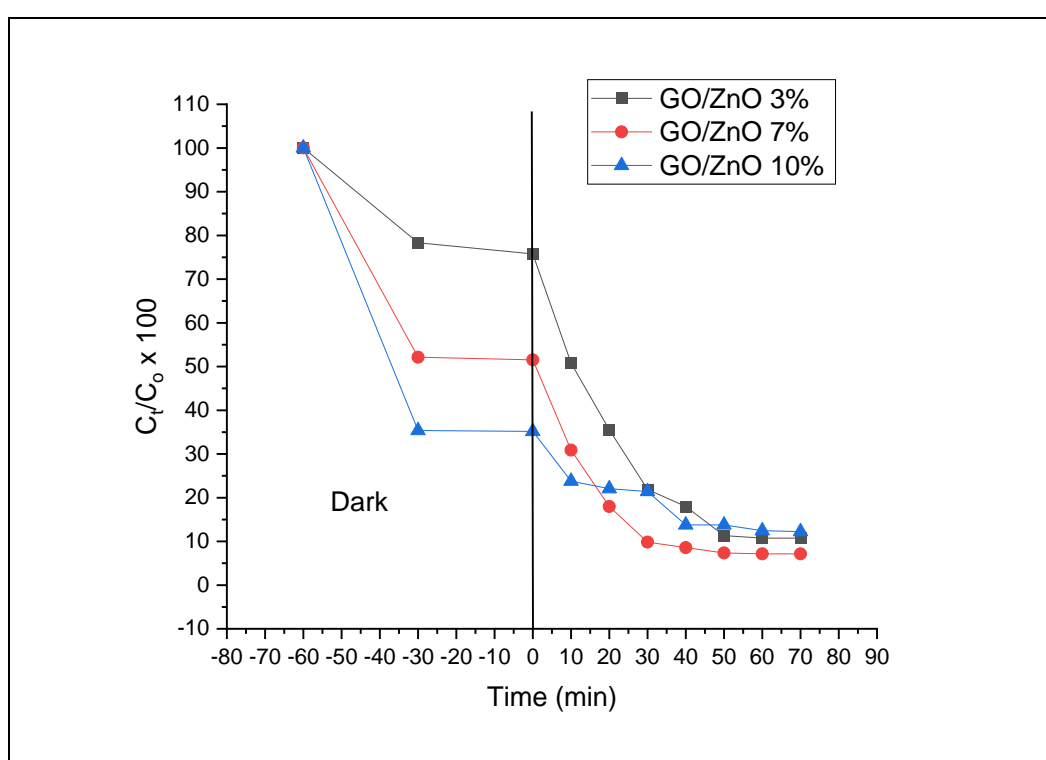

Figure 6: Effect of GO content

4.1.2. Calcination Temperature Impact

The samples underwent calcination at three distinct temperatures: 300°C, 350°C, and 400°C. Results demonstrate that calcination at 350°C yielded the best results for all GO content on ZnO, as depicted in Figure 7.
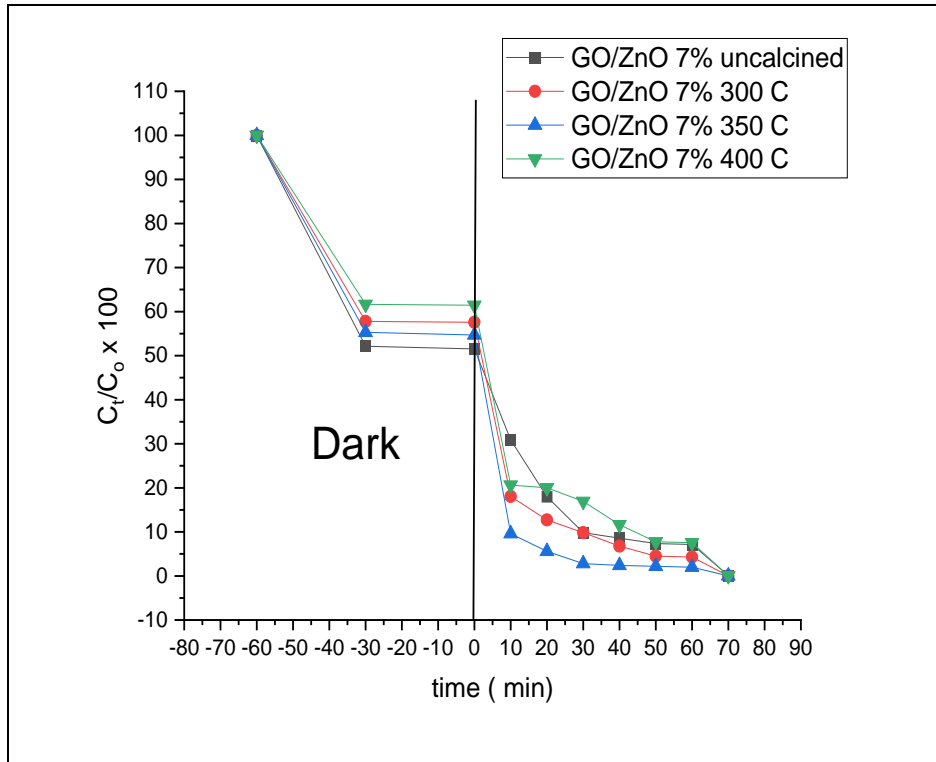
Figure 7: Effect of Calcination temperature on GO/ZnO 7%

4.1.3. Weight of the catalyst's effect

Different amounts of catalyst were utilized, and Figure 8 clearly shows that greater amount of catalyst led to increased photocatalytic degradation activity. To avoid an ineffective surplus of catalyst and to achieve the ideal weight for photocatalytic degradation, one gram per liter of catalyst was used [26, 27].
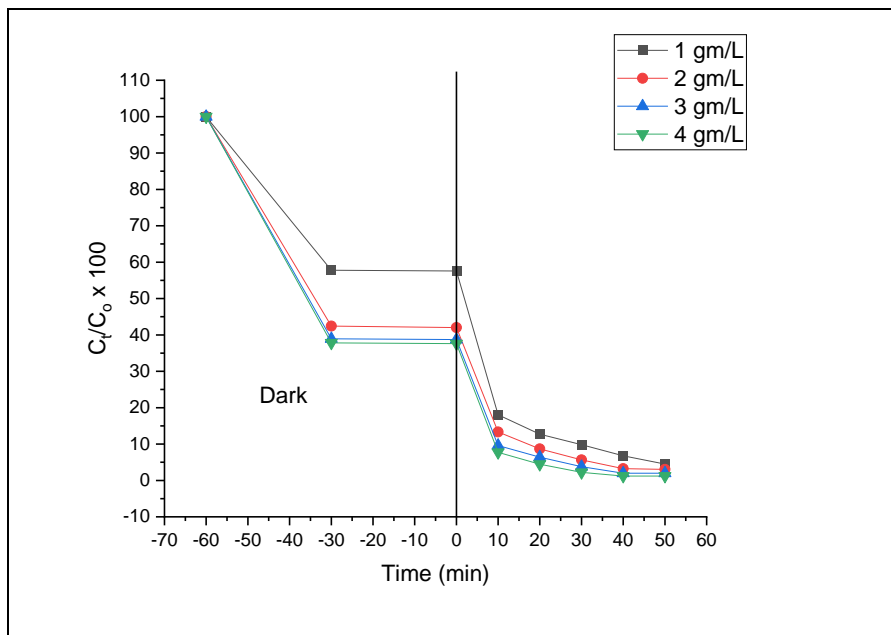

Figure 8: Effect of Catalyst concentration GO/ZnO 7% 350ºC

4.1.4. Impact of CR's initial concentration

The initial concentration of a dye has a notable effect on the photodegradation of organic pollutants [28] Hydroxyl radicals have a short lifespan of a few nanoseconds, limiting their ability to react far from where they are produced. This results in a drop in the rate of photocatalytic degradation as the original concentration increases [29]. Figure 8 shows the change in initial CR concentration from 10 mg/L to 30 mg/L with 1 gm/L of 7% GO/ZnO at 350°C.
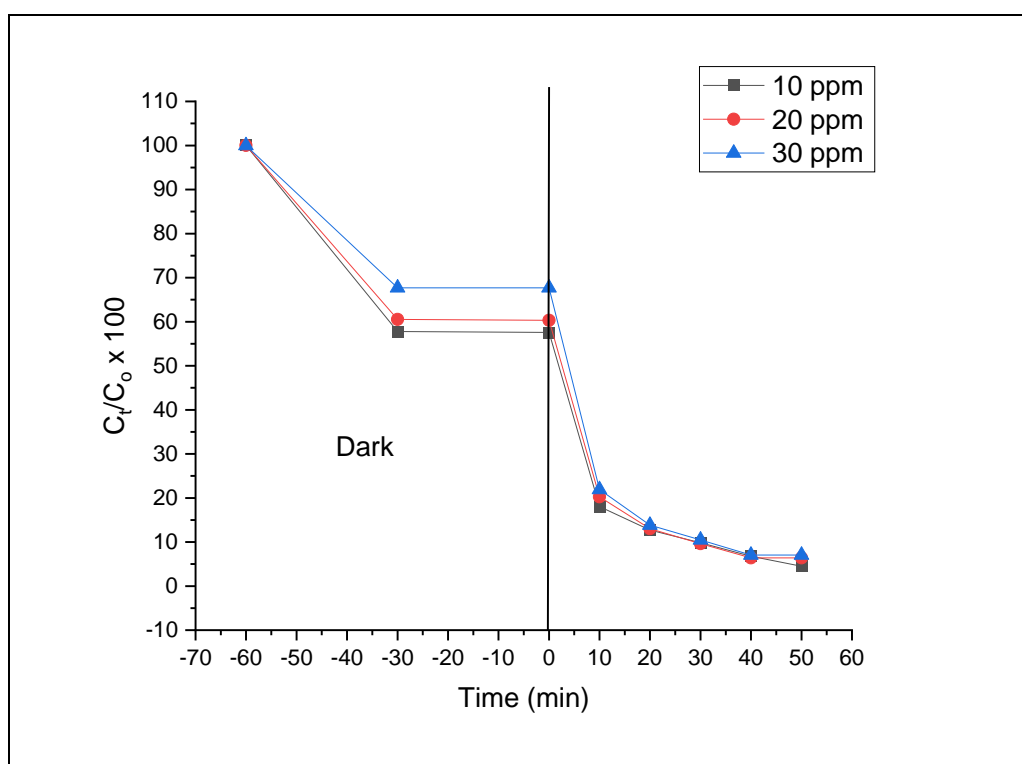

Figure 9: Effect of initial concentration GO/ZnO 7% 350ºC

5. Conclusion

GO was created using a modified version of the Hummer's approach. Zinc oxide nanoparticles were enhanced for photocatalytic degradation by loading them with different quantities of graphene oxide. The sample containing 7% weight of graphene oxide (GO) and zinc oxide (ZnO) was the most effective in degrading CR dye. The samples were calcined at temperatures of 300, 350, and 400 degrees Celsius, with 350 degrees Celsius being the optimal temperature. Various studies have examined the

photocatalyst dosage, calcination temperature, catalyst amount, and initial dye concentration. Photocatalytic degradation efficiency decreased with higher dye concentrations, but increased with greater photocatalyst weight.

6. Conflicts of interest

The authors declare no conflicts of interest.

7. References

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