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“Synthesis of Transition metal/SiO₂ Hybrid for Photocatalytic Degradation of Organic Pollutants”

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Abstract: A ZnO/SiO₂ photocatalyst was synthesized using a low-cost sol-gel wet chemical. The synthesized ZnO/SiO₂ hybrid exhibited superior performance in the photodegradation of methylene blue an organic dye under UV irradiation, with considerable degradation of methylene blue dye after 90 minutes of exposure to UV irradiation. The photocatalyst structure, microstructure, morphologies, and surface area were studied using X-ray diffraction, high-resolution transmission electron microscopy, field emission scanning electron microscopy, and Fourier transform infrared spectroscopy. The results demonstrate that the ZnO/SiO₂ photocatalyst has significant photocatalytic activity which is probably due to higher surface area and good photostability by the addition of silica in zinc oxide which effectively increases the number of active sites and hence improved the photocatalytic activity of the prepared material. The obtained results indicate that the photocatalytic data are in good agreement with the experimental characterization results for the prepared materials, including the XRD results, confirming a close association between the photocatalytic activity and the surface area of the fabricated photocatalyst.

Keywords: ZnO/SiO₂ photocatalyst, degradation of methylene blue dye, X-ray diffraction, high-resolution transmission electron microscopy, field emission scanning electron microscopy, and Fourier transform infrared spectroscopy, and XRD results

Introduction: Organic pollutants are discharged from industries including paper printing, pharmaceuticals, medicinal research, textiles, skincare, and food coloring. If leaked into the environment, these pollutants harm people, though advancements in nanotechnology have made modern life easier. TMO-based nanocatalysts are widely used due to their physical, chemical, and optical properties. Quantum dots are unique when it comes to fluorescence [1-4]. Photocatalytic degradation is an advanced oxidation process that degrades pollutants with

high concentration, complexity, and low biodegradability using light energy. Hybrid materials, such as composites with two molecular or nanoscale constituents, are referred to as hybrid materials [5-6]. There are about 100,000 types of dyes, with the textile industry consuming approximately 36,000 tons annually. Over 20% of dyes are lost during dyeing and mix directly with groundwater, posing health hazards [7]. Azo dyes account for more than 65% of the total organic dyes. Dye concentration as low as one part per million (ppm) can drastically alter aquatic ecosystems and freshwater color, impacting photosynthetic production [8]. Zinc oxide (ZnO) offers photo and chemical stability, non-toxicity, and free radical generation, making it a versatile catalyst. ZnO has a bandgap of around 3.3 eV and is well-suited for photocatalytic reactions due to its high photosensitivity, ease of synthesis, and two absorption/emission bands [9-11]. ZnO nanoparticles are synthesized using methods like sol-gel, co-precipitation, hydrothermal, self-assembly, and microwave processes [12-13]. Tin oxide, with a 3.6 eV bandgap, is a promising n-type semiconductor for catalysis due to its multiple oxidation states, high mobility, transparency, and thermal stability. Manganese oxide is favored as a catalyst for its polymorphism and availability. TMO nanoparticles are prepared through techniques such as microwave-assisted, sol-gel, co-precipitation, thermal decomposition, self-assembly, hydrothermal, and solvothermal methods [14]. The goal of this research was to lay out the fundamentals of nanoparticles, including the many kinds of nanoparticles and how they are made, To synthesize the ZnO/Silica hybrid nanoparticles with low cost, to overcome photo instability of ZnO nanoparticles by adding silica and to check photocatalytic degradation of the methylene blue dye by using ZnO/Silica hybrid as a photocatalyst.

1.1. Advantages of Photocatalytic method

Photocatalytic methods are among the most widely used due to their ability to destroy low-biodegradable organic molecules without the need for toxic chemicals. These processes are also very efficient and cost-effective [14-19]. Some believe that ZnO nanoparticles are a better photocatalyst for organic compounds than titanium dioxide. (TiO_2) nanoparticles. The use of many semiconductors is one strategy that has the potential to enhance the photocatalytic response to ultraviolet light irradiation and decrease electron-hole recombination. A popular material, silica (SiO_2) has many uses due to its environmental stability, compatibility with other substances, and relative ease of manufacture. This fact inspired us to develop a composite material consisting of ZnO and SiO_2 to enhance photocatalytic activity and stability [20-25]. It was demonstrated that rhodamine B degradation in aqueous solutions is facilitated by ZnO nanoparticles incorporated with SiO_2 , which improves stability and exhibits relatively greater photocatalytic activity [26]. Many studies conducted in this scenario indicate that the photocatalytic activity of ZnO nanostructures on silicon substrates can be enhanced when 4-chlorophenol and rhodamine B are photocatalyzed [27-30]. It is difficult to recycle the applied photocatalyst for future usage and UV light scattering occurs when photocatalysts are placed in suspension. The photocatalytic degradation of organic dyes in aqueous solutions was improved when a ZnO/ SiO_2 nanocomposite was used [31-33]. Zinc oxide/silica nanoparticles are more

biocompatible than TiO_2 . exhibit antifungal, antibacterial, and anticancer properties, used in food supplements, cosmetics, plastics, rubber, cement, ceramics, ointments, lubricants, and adhesives. Most ZnO is synthesized rather than naturally occurring as zincite. Nanotechnology is now standard for biomedical applications due to its versatility [24-25,34]. ZnO nanoparticles are effective in sunscreens by absorbing UV light and remaining transparent to visible light. Zinc is essential but toxic at high concentrations; zinc acetate (E650) can prevent deficiency [35]. ZnO has advantages over other metal oxides, being safer, cheaper, and more biocompatible. ZnO nanoparticles show strong photocatalytic activity [36-38]. They do not spontaneously ignite, preventing dust explosions. ZnO aids in heat dissipation during tire use and accelerates rubber vulcanization. ZnO nanoparticles are widely used in the cosmetics industry, including as UV filters [39-40].

2.1. Methodology

Chemicals, solvents and reagents used in research were of better analytical quality and purchased from reputable vendors. Solvents were distilled for being used in research. These chemicals were obtained from Department of Chemistry Lahore Garrison University, Lahore.

2.1.1. Reagents and Chemicals: Tetraethyl orthosilicate, Zinc Nitrate, 6-hydrate, NaOH pellets, Acetic Acid and NH_4OH , with 35% ammonia in water. Distilled water and Ethanol are used as solvents.

2.1.2. Instruments: Analytical weighing balance, UV lamp, UV Visible Spectrophotometer (Ultra-3000), FTIR (Cary 630 FTIR), XRD and SEM

2.2. Experimental work

In the current study, experimental work ZnO, silica nanoparticles, and ZnO/Silica nanoparticles hybrid were synthesized by using sol-gel.

2.2.1. Step1: Synthesis of ZnO nanoparticles: In a given procedure 0.2M Zinc Nitrate, the 6-hydrate solution was prepared using 5.9 grams of Zinc Nitrate, 6-hydrate in 100 milliliters of distilled water with continual stirring on magnetic-stirrer or by shaking on shaker. After that 0.4M NaOH solution was prepared using 1.6-gram NaOH in 100 milliliters of distilled water with continual shaking. After 30minutes both solutions were mixed slowly with continuous stirring at 30 °C. White suspension appeared. The suspension was centrifuged for 20 minutes at a speed of 5000 rpm. Filtered the solution with filter paper. Precipitates were cleansed with distilled water 3 times and after that with ethanol. These obtained Zinc oxide nanoparticles precipitates/nanoparticles were dried in the oven and then calcinated for 4 hours at 500 °C. The schematic Figure 1 given below explains it briefly.

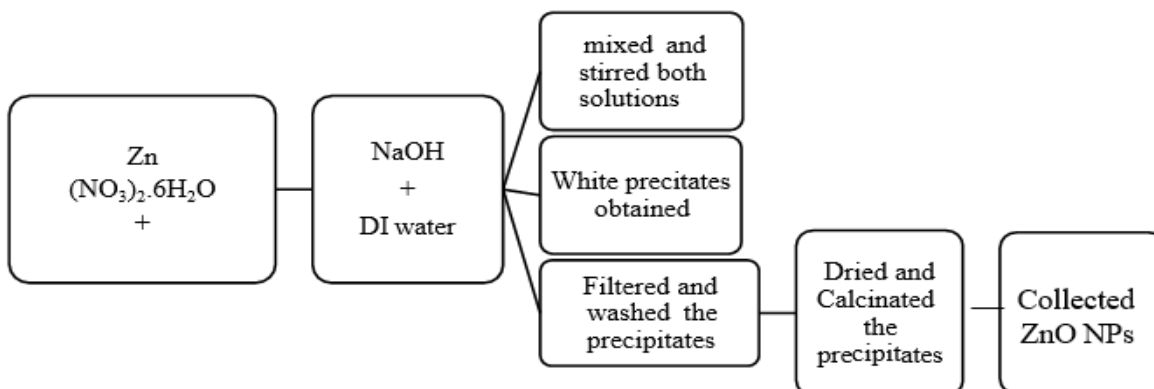


Figure 1: Flow sheet diagram for synthesis of ZnO NPs

2.2.2. Step 2: Synthesis of SiO₂ nanoparticle: Silica nanoparticles were synthesized by using the sol-gel method. There was no need for additional purification because every reagent utilized was analytical grade. In this work, tetraethyl orthosilicate (Aldrich 99%), ethanol (EtOH 99.5%, System), acetic acid (S.D. Fine), and ammonium hydroxide were used. 10 milliliters of distilled water were added to 75 milliliters of ethanol in a flask, and the mixture was stirred for 15 minutes. Tetraethyl orthosilicates 6 milliliters were added to the solution above and agitated for two hours. After that, 15 milliliters of acetic acid were added, and for the following four hours, the temperature was maintained at 80°C and 1000 rpm. Following the completion of the mixing procedure, the flask is filled with 15 milliliters of ammonium hydroxide. A thick, viscous fluid began to form in the flask's solution. This suggested that the response had begun and was proceeding smoothly. The mixing procedure was carried out for an hour. After that, adjust the stirrer's temperature to 200°C and speed to 1100 rpm. Mixed the mixture for another 8 to 9 hours, or until a thick gel-like fluid forms. The thick gel's formation signified that the reaction was finished. The gel was dried for two hours at 100°C to remove any remaining water and organic materials to produce nanoparticles. The dry gel was calcinated for up to three hours at 500°C to create a powder, which was then ground to create nanoparticles. The schematic Figure 2 given below explains it briefly.

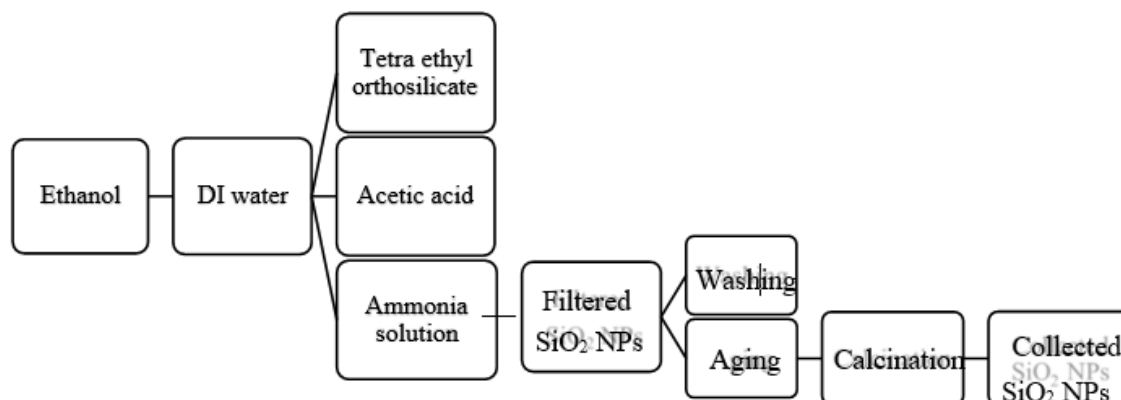


Figure 2: Flow sheet diagram of SiO₂ NPs

2.2.3. Step 3: Synthesis of ZnO/SiO₂ hybrid: Equal quantities of the produced zinc oxide and silica NPs were thoroughly disseminated in 25 milliliters of distilled water individually. When these nanoparticles were disseminated in distilled water; the following two solutions were assorted and agitated vigorously at 80°C for 4 hours till white precipitates were produced. Then obtained precipitates were filtered and rinsed with distilled water. So, rinsed precipitates were dried overnight in an oven at 80°C and calcinated for up to 4 hours at 500°C. The schematic Figure 3 given below explains it briefly.

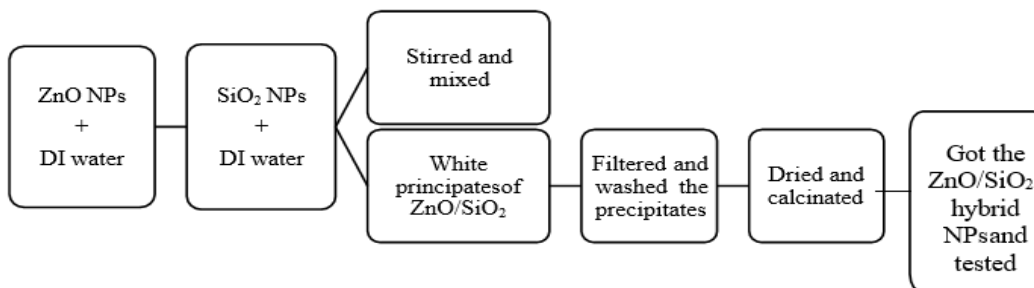


Figure 3: Flow sheet diagram for ZnO-SiO₂ hybrid nano-particle

2.2.4. Photocatalytic degradation of dyes

The photodegradation of an aqueous solution containing 10 ppm of methylene blue was carried out to assess the photocatalytic activity of ZnO/SiO₂ hybrid.

3.1. RESULTS AND DISCUSSION

As a result of their exceptional adaptability, nanocomposites have garnered a significant amount of attention. In the current study, it is reported that some of the recent advancements in nanocomposites have the potential to contribute to the protection of the environment using photocatalytic degradation of organic substances. Intercalation, precipitation, and evaporation are the three processes that are utilized in the production of nanocomposites. Several constraints are inherent to composite materials, including possible toxicity, photo instability, the need for uniform nanoparticle dispersion within the composite, and the fact that these constraints influence both the size and structure of the nanoparticles. The main goal of this work was to synthesize composites with zinc oxide and silica nanoparticles taking into account the unique properties of composite materials. Sol-gel method was the main technique used to create iron ZnO/SiO₂ nanocomposites in this investigation. ZnO nanoparticles used as photocatalysts in photocatalytic systems have their photocatalytic activity significantly reduced due to photo instability caused by photo corrosion when exposed to UV light. SiO₂ nanopowders to ZnO nanoparticles increased their photocatalytic activity for decolorizing dye [42].

Several different characterization techniques have been utilized to investigate the nanocomposite in terms of its dimensional characteristics, morphology, and chemical functioning. This inquiry has made use of many different techniques, including FTIR, XRD, and SEM. A full investigation of the structural, chemical, and morphological features of the nanocomposite can be effectively accomplished by the use of these approaches combined.

3.1.1. Zinc oxide nanoparticles FTIR spectrum

The Fourier-transform infrared spectra of the nanoparticles that were manufactured were recorded in the range of 400–4000 cm⁻¹, and the result is depicted in Figure 4. This is Fourier transform infrared spectra of the ZnO nanoparticles, which were obtained in the region of 4000 to 400 cm⁻¹. In ZnO spectra peak appears at a wavelength of 2913 cm⁻¹ is for the stretching vibration of vibrations of C-H. It is determined that the stretching vibration of C-O stretching is responsible for the absorption peaks that occur about 1024 cm⁻¹. For Zn-OH₂, the peak is located at 616 cm⁻¹. For Zn-O, the peaks that occur at 514 to 442 cm⁻¹ are located.

3.1.2. Zinc oxide/Silica nanoparticles FTIR spectrum

This is the Fourier transform infrared spectra of the ZnO/Silica hybrid depicted in Figure 5, which was obtained in the region of 4000 to 400 cm⁻¹. In the case of ZnO/SiO₂ nanocomposite peaks are found at 1004 cm⁻¹ for Si-OH stretching, 1097 cm⁻¹ for Si-O-Si asymmetric stretching, 804 cm⁻¹ for Si-O-Si symmetric stretching, and 484 cm⁻¹ for Si-O-Si bending. The appearance of the absorption band at 939 cm⁻¹ in this spectra is associated with the Si-O-Zn absorption band which confirms that SiO₂ indeed binds with ZnO.

3.1.3. X-ray diffraction study of Zinc oxide nanoparticles

X-ray diffraction was used to investigate the phase purity and composition of the particles that were created by a sol-gel technique. In this work, ZnO nanoparticles were produced, and Figure

6 depicts a typical XRD pattern of these sample particles. At a scanning step of 0.01, a series of Bragg reflections with 2θ values of 31.74° , 34.88° , 36.83° , 47.62° , 57.73° , 62.91° and 68.27° are seen. These reflections correspond to the (100), (002), (101), (102), (110), (103), and (201) planes, and they exhibit a characteristic XRD pattern of ZnO nanoparticles in the range of 5° - 70° . None of the distinctive peaks of impurity phases, except ZnO, were discovered, which demonstrated that the sample was of an excellent crystalline form.

3.1.4. X-ray diffraction study of ZnO/Silica nanoparticles

ZnO/SiO₂ nanoparticles were produced, and Figure 7 depicts a typical XRD pattern of these sample particles. The purpose of the XRD test was to determine the crystal structure of ZnO/SiO₂ nanocomposite. At a scanning step of 0.01, a series of Bragg reflections with 2θ values of 31.74° , 34.88° , 36.83° , 47.62° , 57.73° , 62.91° and 68.27° are seen. These reflections correspond to the (100), (002), (101), (102), (110), (103), and (201) planes, and they exhibit a characteristic XRD pattern of ZnO nanoparticles. The existence of SiO₂ in the nanocomposite caused loss of crystallinity because the SiO₂ has an amorphous phase, but there are two other definite peaks in the ZnO/SiO₂ nanocomposite which confirm the presence of silica with ZnO in the samples. These two peaks are at 25.13° and 42.90° with planes (111) and (222). These two peaks may appear due to temperature fluctuation.

4.4 Photocatalytic degradation

The degradation of methylene blue in an aqueous solution was monitored and recorded to determine the photocatalytic activity of the nanocomposite. We know the fact that dye in visible light and the absence of a photocatalyst does not or negligibly degrade as it depends on the electron-hole pair of the photocatalyst/semiconductor and this electron-hole pair production is related to band gap energies of the photocatalyst/semiconductor used. The photocatalytic degradation also depends on the amount of catalyst used, pH, photostability of photocatalyst, and surface area. The optimal active sites and amount of photocatalyst give birth to optimal $\cdot\text{OH}$ radicals which serve as oxidants and generate electron-hole pairs during the dye degradation process. These factors enhance the number of active sites on the photocatalyst, and oxidation and reduction reactions of dyes with photo catalyst and ultimately boost the photocatalytic activity.

4.5 UV analysis for photoactivity of Zinc oxide/Silica nanocomposite

ZnO/Silica hybrid nanoparticles were used as a photocatalyst against methylene blue dye in this evaluation. Photo catalyst was suspended in a reactor containing a solution of methylene blue dye to experiment and less than 400 nm wavelength was emitted from UV filter. At 30 C, the reaction was conducted isothermally. Using a UV-Vis spectrophotometer, the absorbance intensity of solution samples at their maximum absorbance wavelength of 664 nm was recorded on a Shimadzu UV-2450 with a 1 cm path length spectrometric quartz cuvette at room temperature. This allowed for the determination of the concentration of residual methylene blue in the solution following irradiation. The following equation was used to determine the photodegradation efficiency of methylene blue:

$$\% \text{ Photodegradation efficiency} = \frac{C_0 - C}{C_0} \times 100$$

C_0 is the initial concentration of methylene blue dye that is 2.15 M. Where C is the remaining concentration of methylene blue dye in solution which changes with time. Table 1 presents the photodegradation efficiency of methylene blue using ZnO/SiO₂ hybrid nanoparticles as the catalyst.

Sr. no	Time (minutes)	C (M)	$C_0 - C$ (M)	$C_0 - C / C_0$ (M)	$C_0 - C / C_0 \times 100$
1	0	2.15	2.15-2.15	2.15-2.15/2.15	0 %
2	10	2.05	2.15-2.05	2.15-2.05/2.15	4.61 %
3	20	1.96	2.15-1.96	2.15-1.96/2.15	8.83 %
4	30	1.89	2.15-1.89	2.15-1.89/2.15	12.09 %
5	40	1.69	2.15-1.69	2.15-1.69/2.15	21.39 %
6	50	1.52	2.15-1.52	2.15-1.52/2.15	29.30 %
7	60	1.36	2.15-1.36	2.15-1.36/2.15	36.74 %
8	70	1.16	2.15-1.16	2.15-1.16/2.15	46.04 %
9	80	0.95	2.15-0.95	2.15-0.95/2.15	55.81 %
10	90	0.69	2.15-0.69	2.15-0.69/2.15	67.20 %

Table 1: Photodegradation efficiency of methylene blue using ZnO/SiO₂ hybrid nano-particles

It was observed that with the passage of time degradation of dyes was greater than in short intervals. An ultraviolet-visible spectra of methyl blue in the presence of nanoparticles is presented in figure 8.

4.7 SEM study of Zinc oxide nanoparticles

SEM pictures of synthesized zinc oxide nanoparticles using sol gel method usually show the structure and morphology of the synthesized particles. Some typical features of scanning electron micrographs (SEMs) of zinc oxide nanoparticles manufactured by the sol gel process. Occasionally, scanning electron microscopy (SEM) pictures may reveal groups of densely packed particles called agglomerates of nanoparticles. As seen in Figure 9, the zinc oxide nanoparticles exhibited aggregated particles arranged in huge, sphere-like shapes. SEM study helps researchers to optimize synthesis parameters and customize the material's characteristics for specific uses in areas like photocatalytic degradation, environmental engineering, and materials science.

4.8 SEM study of ZnO/Silica nanoparticles

To create ZnO/Silica nanoparticles, a sol-gel method was used. SEM image of sol-gel formed ZnO/Silica nanoparticles revealed its structure shape and morphology. Figure 10 shows what scanning electron microscopy (SEM) pictures of ZnO/Silica nanoparticles made using this method would look like.

Scanning electron microscopy (SEM) image shows that the prepared ZnO/Silica nanoparticles hybrid material has less agglomeration and more homogeneity, So, it is confirming that the addition of silica in zinc oxide nanoparticles decreases the agglomeration.

5.1. Conclusion

The primary aim of the present research endeavor was to successfully synthesize a ZnO/SiO₂ hybrid and subsequently conduct a comprehensive characterization of the resultant material. To accomplish this objective, the Sol-gel method was judiciously selected for the fabrication of the desired nanocomposite, primarily due to its cost-effectiveness and environmentally benign nature. The synthesis process was meticulously tailored to create nanoparticles of ZnO/Silica, ensuring their optimal compatibility against organic pollutants i.e. methylene blue dye. ZnO loaded on SiO₂ is considered to be a promising for the removal of methylene blue dyes, which act as organic pollutant model. The photocatalytic procedure is typically conducted by exposing the photocatalyst surface to UV irradiation, which generates reactive radicals. However, agglomeration of ZnO was the main challenge that reduces the photo-reactivity during the removal of organic pollutants . Herein, a promising route to augment the photocatalytic reactivity of ZnO via its homogenous distribution over a supporting material silica to increase the photo reactivity is reported. This kind of support plays a decisive role in the photocatalytic degradation of the organic dye. The photocatalytic removal results show that methylene blue dye is degraded considerably after approximately 90 minutes of irradiation treatment over the ZnO/SiO₂ photocatalyst.

Future Perspectives

Zinc oxide/Silica hybrid NPs have significant potential applications and versatile properties in many fields and ongoing research and development to enhance the applications that are expected of the future. Zinc oxide/Silica hybrid NPs have many applications so in the future we can anticipate advancement in many research areas, especially in the removal of organic pollutants and treatment of wastewater. ZnO/Silica hybrids have a lot of attention as photocatalysts because of their better photocatalytic properties which are due to the high surface area, a greater number of active sites, increased stability, and less agglomeration. They are also simple to manufacture.

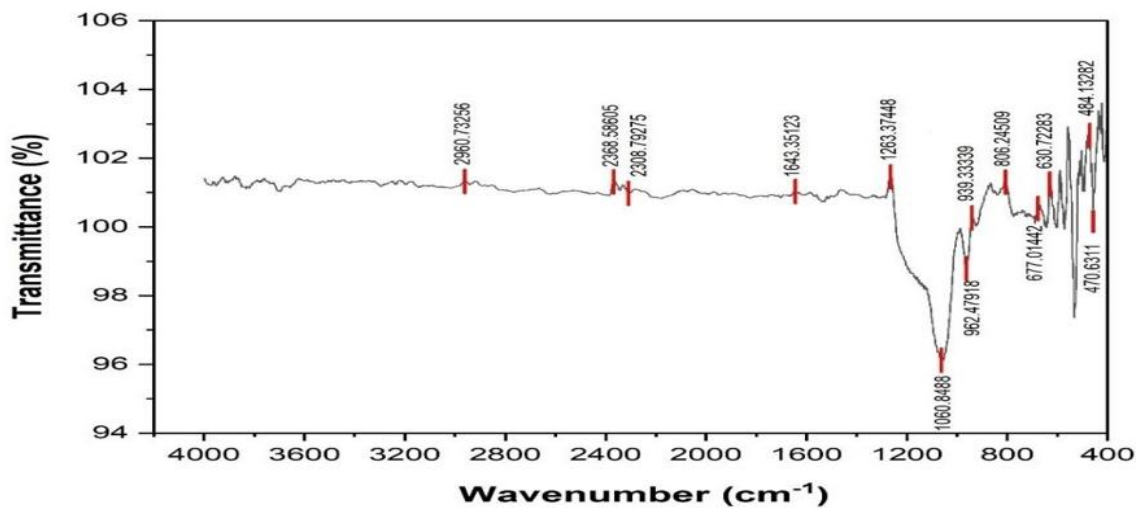


Figure 4: FTIR spectrum of ZnO NPs

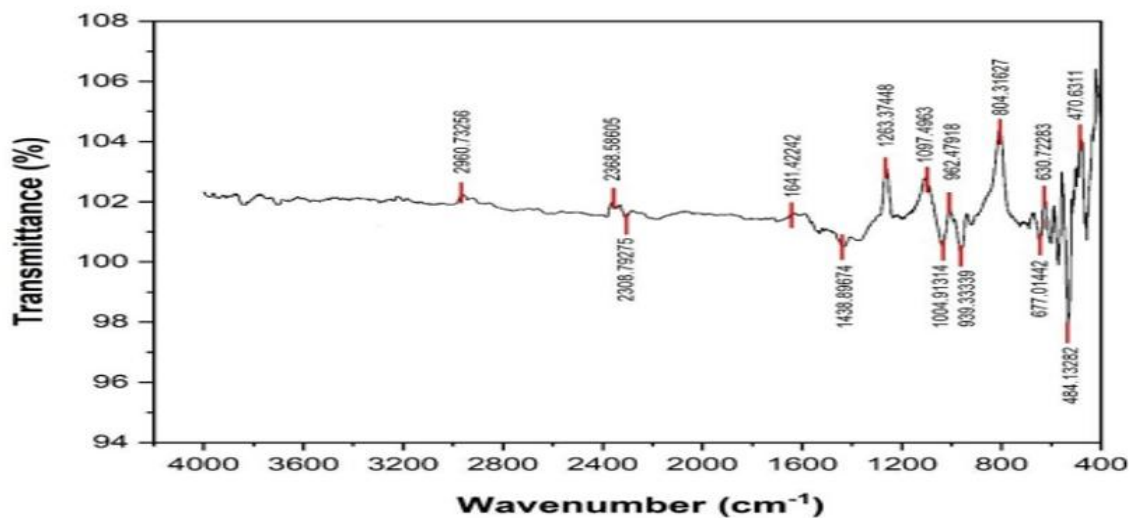


Figure 5: FTIR spectrum of ZnO/SiO₂ hybrid NPs

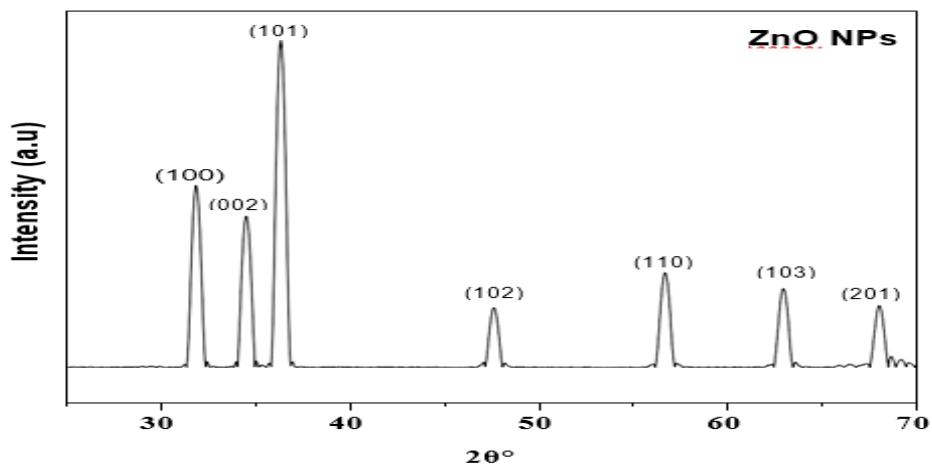


Figure 6: XRD pattern of ZnO nanoparticles

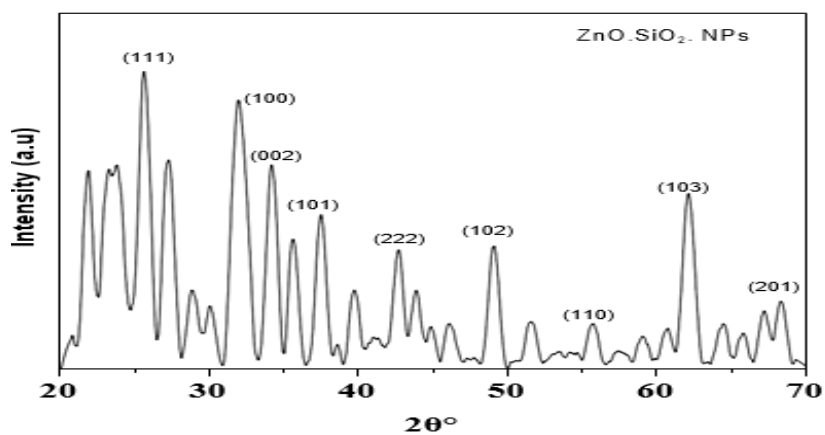


Figure 7: XRD pattern of ZnO/SiO₂ hybrid nano-particles

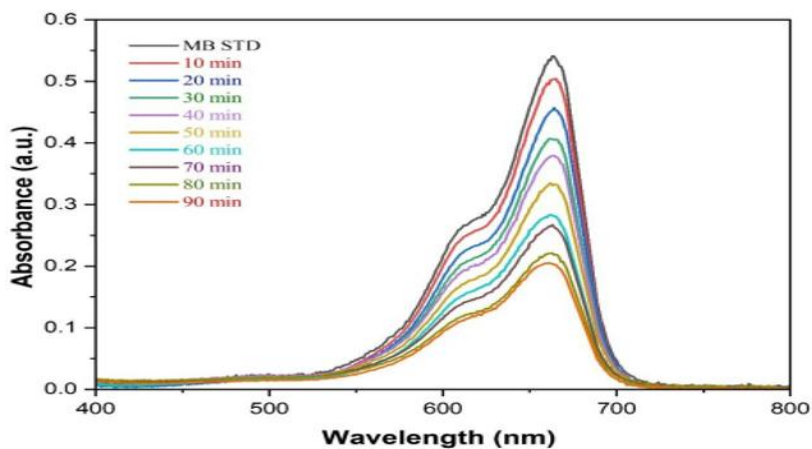


Figure 8: Photocatalytic activity of methylene blue dye using ZnO/SiO₂ hybrid nano-particles

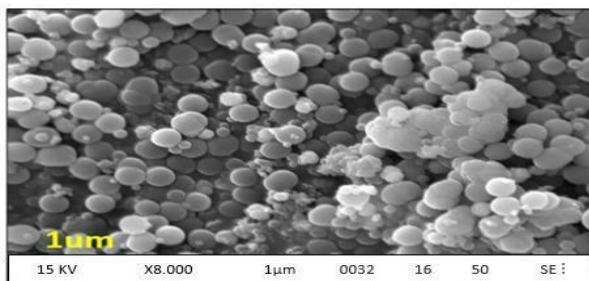
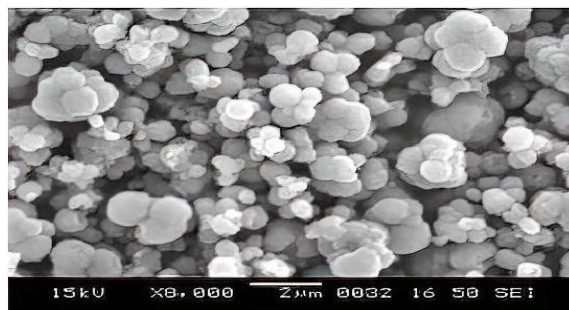


Figure 9: SEM image of zinc oxide nanoparticles

Figure: 10 SEM image of ZnO/Silica nanoparticles

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