Photocatalytic Degradation of Methylene Blue Dye from Aqueous Solutions in the Presence of Synthesized ZnO Nanoparticles

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Abstract

The photo catalytic degradation of an aqueous solution of methylene blue dye has studied under different conditions of preparation Zinc oxide nanoparticles and study effect of various mass of zinc oxide on the removal of methylene blue dye and initial concentration of MB dye. Several techniques were used to determine the surface properties of the prepared nano-zinc oxide such as XRD, TEM. Results showed that, the phot catalytic degradation process was high at the beginning and then decreased with time. and the phot catalytic degradation efficiency, increased by increasing weight of zinc oxide nanoparticle from 0.05 g to 0.3 g. and decrease with increase weight of zinc oxide nanoparticle from 0.5 g to 0.7g. also showed that the best weight to removal MB dye 0.3 gm.

Key Words: Phot Catalytic, Methylene Blue Dye, Zinc Oxide Nanoparticles.

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Introduction

Water contamination is one of the world's most vexing environmental issues, and it needs to be addressed. Textile mills generate a large amount of effluent, which contains a variety of impurities such as acidic or caustic dissolved solids, hazardous chemicals, and various colours. Many organic dyes are toxic to aquatic life and can cause a variety of diseases and disorders . Synthetic dyes are widely utilized in a variety of sectors, including textiles, paper printing, color photography, pharmaceuticals, leather, cosmetics, plastics, and many more. Because of its extreme toxicity, industrial wastewater containing dyes causes serious environmental hazards Synthetic dyes are a group of most dangerous pollutants in water. Even relatively modest concentrations of dyes in water impede light penetration through the water surface, preventing aquatic flora photosynthesis (Aljeboree, et. al. 2019; Kareem; et. al. 2016).

Advanced oxidation processes (AOPs) have been used to remove refractory organic contaminants and xenobiotics employing UV or near-UV light as potent oxidizing agents (catalytic initiators). Photo catalytic oxidation, particularly ZnO-mediated photo catalysis, has been shown to be a potential water treatment approach for destructing a variety of organic and inorganic pollutants. ZnO is a viable, beneficial, important, strategic, and versatile organic material that has a wide range of applications. individually, ZnO is referred to as a the sixth through tenth group of transition metals. In addition to being capable of chemical sensing, it has optical, conductive, and semiconducting properties.

In the near ultraviolet range, ZnO has a band gap of 3.3 eV and a natural n-type electrical conductivity. At room temperature, ZnO has a 60 me V excitonic binding energy.

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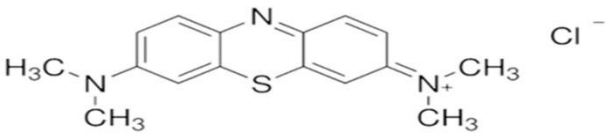
ZnO 's unique properties allow it to be used in a wide variety of fields. (Amna Sirelkhatim 2015). Despite the fact that ZnO exhibits a light covalent character, ZnO exhibits extremely strong ionic bonding between Zn and O. zinc oxide have 2 U V B and U V A regions that vary greatly in spectroscopic absorption, photochemical activity, and spectral catalytic activity (Z. Song 2011).

Experimental Part

Materials and Methods

The adsorbate methylene blue dye (MB, $C_{16}H_{18}ClN_3S$), purchased from Kermel Chemical Reagent Co., Ltd (Tianjin, China), were used without any further purification. Accurately weighted quantities of methylene blue were dissolved (1 g) in distilled water to prepare stock solution (1000 mg/L). The Physicochemical properties of MB are presented in Table 1.

Table 1. The Physicochemical properties of MB dye

Dye	**Methylene blue (MB)**
Generic name	proveblue
Molecular weight	319.85 gm/mol
Chemical Formula	$C_{16}H_{18}ClN_3S$
λmax	663 nm
Chemical structure	

Create of ZnO Nanopartecles by Hydruthermal Methode

The Hydrothermal technique was utilized to create ZnO nanoparticles using 3 step:

Step 1: 10 g of Zinc Acetate Dehydrate utilized as a basis of zinc was added bit by bit to 50 ml of deionize water and was stir for 15 min.

Step 2: 8 g of Oxalic Acid was dissolved in 100 ml of deionize water and was stir for 15 min.

Step 3: The mixture from step two was progressively applied to the mixture from step one and stirred continuously on magnetic stirrers for 10 minutes until it became a white solution. The final mixture was moved to a stainless steel autoclave lined with teflon and held at 170 oC for 24 hours (P. M. Aneesh 2007; G. Amin 2011). After that, cooled to 25C. The result white outcome was treated with deionize water and then dry overnight at a temperature of 50-60 degrees Celsius in an oven. Following this step, the product powder is annealed at 500°C for 2 hours in a digital furnace.

Photo Catalytic Experiments

The degradation of MB dye wastewater was used to determine the photocatalytic activity of the ZnO photo catalyst. All tests were conducted in a 250 ml photo-reaction vessel. It emitted a maximum of 125 W of light with a light source which was using mercury pressure of 365 nm. UVA meters were used to maintain the beakers in a defined distance from the light source when exposed to ultraviolet light, so as to prevent unwanted reactions (e.m. thermal) from occurring between the solution and the beakers. in order to be sure the output was stable prior to each test, the lamp was turned on for ten minutes and allowed to warm up. The expansion process is carried out as follows: After which, the dye solution was allowed to darken for ten minutes, 0.3 g of zinc oxide was added to 200 mL of dye solution and the mixture was stirred to enable the catalyst to interact with the two substances for a better, the resulting mixture had the desired color to achieve equilibrium with the catalyst particles.

Following that, the mixture was put into the photo-catalytic reactor where the experiments were started, where the degradation processes began. an air diffuser was located at the bottom of the reactor and was working at a flow rate of 0.1 ml/min to provide an evenly spread mist of air to the solution

every two hours, samples were taken and then centrifuged for inspection at a defined intervals to remove particles. Using a UV spectrophotometer with a chromate cell that has a 3 cm of path length and a procedure with a Cal Spots, the MB concentration was measured to be maximum absorbance at 663 nm, and the measured absorbance multiplied by a curve was used to calculate the total amount of MB present.

The effect of various operational parameters on

photo degradation efficiency was investigated. These included the amount of catalyst (0.05–0.7 g L-1) and the dye concentration (5–40 mgL-1. The percentage of MB dye degraded through photocatalysis and the apparent first order rate constant were determined at this relationships.

$$PDE\ (\%) = (C_0 - C_t)/C_0 \times 100 \qquad (1)$$

Where Numerator denote the foremost and photolysis concentrations, respectively (mg L^{-1}), PDE denotes the photocatalytic degradation efficiency, t denotes the irradiation time (min.), and k denotes the apparent first order rate constant (min-1). Where C0 and Ct denote the initial and photolysis concentrations, respectively (mg/L), PDE denotes the photocatalytic degradation efficiency, t denotes the irradiation time (min.), and k denotes the apparent first order rate constant (min-1).

Results and Discussion

XRD Analysis

In **Fig. 1** These diffraction patterns at 2 θ = 31.7°, 34.4°, 36.2°, 47.5°, and 56.5° correspond to (100,002,101,102,110) plane of hexa-gonal construction of wurtzit zinc oxide, as mentioned on the J.C.P.D.S nameplate (Published Card Deck of Standards of Photographic Publications) (no. 36-1451). (M. Zhou 2013; X. Wang 2014) To ensure the purity of Zn, the patterns produced showed no diffraction patterns corresponding to Zn or other contaminants. It was found that for all investigated annealing temperatures, the plane (the 101) exhibited the strongest line.

By Scherer's eq.2

$$D = 0.9\lambda.(\beta \cos \theta)^{-1} \qquad (2)$$

D: medium crystal volume, λ: wave length of Cupper-Kα ray (λ=.15406 nm), βis total framework on partial max. deviation peak, & θ is Brag's angularity, medium crystal volume for Zn O is fateful to be about (20.2 nm).

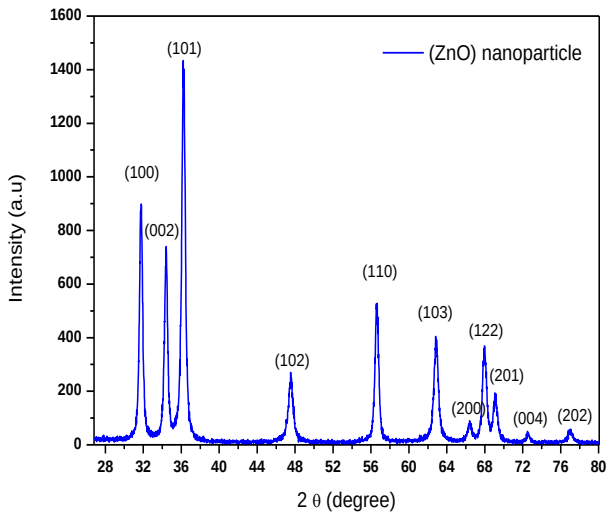


Fig. 1. XRD diffraction patterns of ZnO nanoparticles

TEM Transmittance Electron Microscopy

The morphology of the surface of ZnO nanoparticle were investigated by using TEM morphology surface analysis; was clear from figure (2). TEM data help clarify the geometrical composition of as-prepared ZnO nanoparticle that appear as clustered clusters interconnected with each other in the form of regular circular rings, evidence of the formation of zinc oxide nanoparticles.

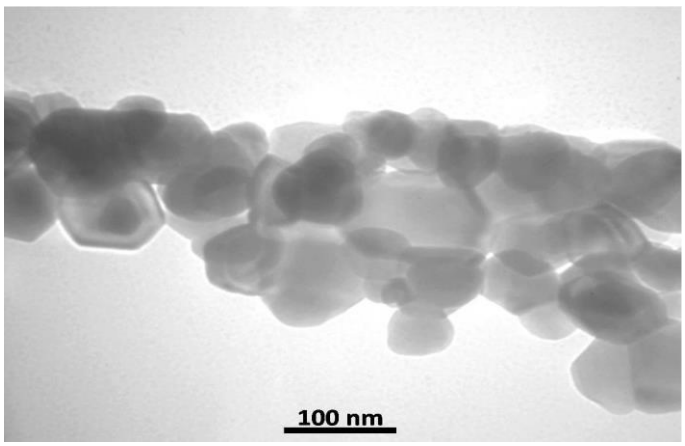


Fig. 2. The TEM of ZnO nanoparticle

Effect of Mass Dosage

To investigate the impact of catalyst loading to an final-decolonization-efficiency, variety to experiments was run in which the catalyst concentration ranged from 0.05 to 0.7 $g.L^{-1}$ on solute with 25 $mg.L^{-1}$ dye-concentration, reaction temperature was set at 25 °C, and time was allotted for two hours. This is a diagrammatic representation of photocatalytic degradation, shown in Figure 3.

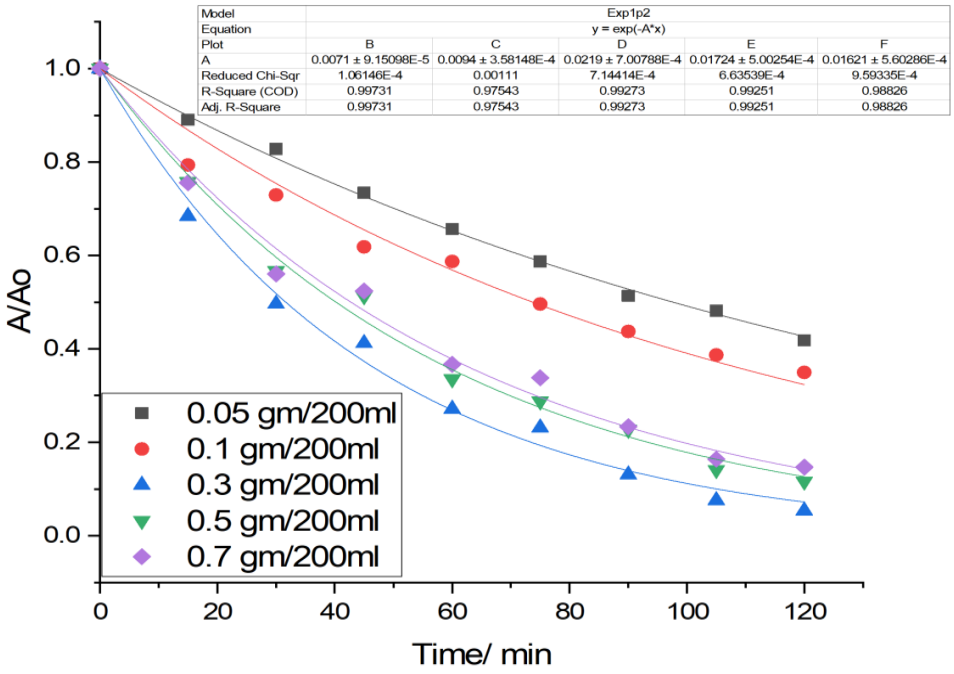


Fig. 3. Photo catalytic degradation for MB at dissimilar mas dosage : Initial conc 25 mg /L, temp 25 °C

The graph in figure 4 demonstrates the link between the catalyst loading and the deterioration rate. From Fig. 4, it is obvious that when the amount of the catalyst grows, the degradation rate increases first and remains constant at a given scale. However, when the amount of the catalyst exceeds 0.3 g/L, the degradation rate does not change. This may be due to the additional free catalyst particles that form in the aggregation process, and also due to the phenomenon known as "screening" (T. Sauer 2002).

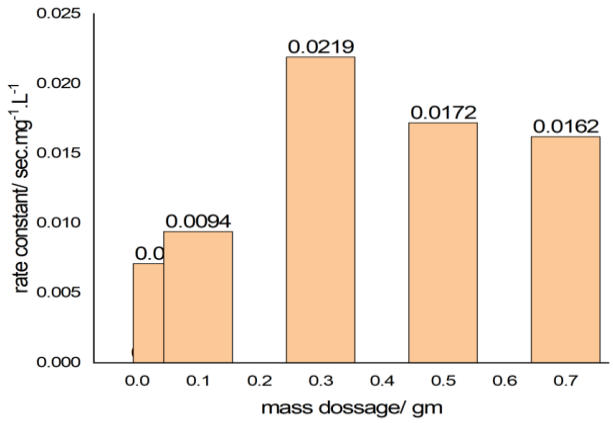


Fig. 4. MB, degradation rate constant on dissimilar catalyst loading.: Initial conc 25 mg/L, temp 25 °C

Results are in agreement with a number of other studies which conclude that there is an optimal quantity of catalyst loading(A. Akyol 2004). When the catalyst concentration is less than the ideal value, the effective-surface-area for catalyst, amount of light absorbed by the catalyst are an primary factors determining the photocatalytic 56 degradation rate. (A. Akyol 2004; H. Wang 2007).

The initial increase in dye degradation rate with increasing catalyst concentration are due to increase on the amount of active sits for the photo-catalyst-surface. As a result, the number of photo generated electron hole pars increases, increasing a quantity for hydroxyl radicals responsible for dye degradation. (H. Wang 2007; M. S. Mashkour 2011; J. Kaur 2014). Shows in **Fig. 5.**

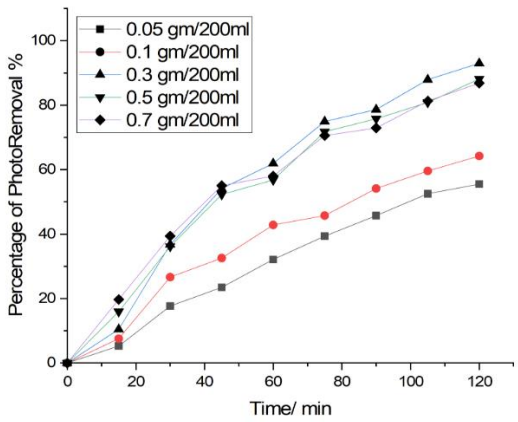


Fig. 5. MB, photo catalytic degradation efficiency.: Initial conc 25 mg/L, temp 25 °C

Effect of Concentration of Dye

To assess an suitability for solution-grown ZnO nanocomposite as a photocatalyst for the Photodegradation of the textile contaminant methylene blue dye, The initial dye solution concentration is critical in determining the rate of dye breakdown. (B. Pare 2008; L. Yang 2010). We investigated the photocatalytic breakdown kinetics of these compounds at room temperature in the presence of UVA light at a wavelength of 365 nm (3.39 eV).

The influence of initial MB dye concentration on degradation efficiency was investigated by altering the dye concentration from (5, 10, 15, 20, 25, 30, 40) ppm while maintaining the catalyst concentration at 0.3 gm. The degradation efficiency of MB dye under UVA light decreased with increasing dye concentration, which may be a result of competition for adsorption on the catalyst surface between dye molecules and dissolved O2. Oxygen molecules serve as an electron acceptor on photo catalytic reaction, less oxygen adsorb on catalyst-surface compared to an dye, the lower the degradation efficiency and rate constant (Saikia, Bhuyan et al.). Alternatively, the number of photo generated electron–hole pairs and, consequently, hydroxyl radicals is equal. The quantity of dye molecules, on the other hand, is increasing. As a result, the effective amount of hydroxyl radicals available for dye degradation decreases, resulting in a drop in dye degradation rate. **Fig. 6** illustrates the time course of photocatalytic degradation of MB dye at various doses.

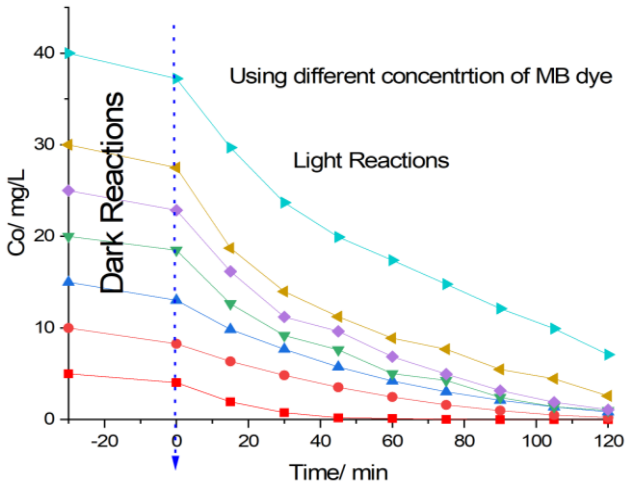


Fig. 6. Photo catalytic degradation for MB at dissimilar original concentration.: amount of mass 0.3 g /L, temp 25 °C

Fig. 7 show photo catalytic degradation rate of MB, **Fig. 7** revealed as the initial concentration of MB dye was increased, the photocatalytic degradation rate dropped. result indicate an initial-dye-concentration has a significant effect on the degradation efficiency. The degradation efficiency reduces significantly as the original dye concentration increases, especially once an initial-dye-concentration is between 25 and 40 mg L^{-1}. detrimental effects for initial-dye-concentration are attributed for competence of dyi and hydroxide adsorption to an catalyst-surface. dye adsorption inhibits OH ion adsorption, resulting in a decrease in the production of hydroxyl radicals. Simultaneously, the pathway lingth of fotons entering the solute decreases as initial-dye-concentration increases. Thus, in a solut with a constant-catalyst-concentration, generation of hydroxyl radicals capable of attacking contaminants is reduced, resulting in a decreased decolonization efficiency.(M.A. Behnajady 2006; L. Yang 2010).

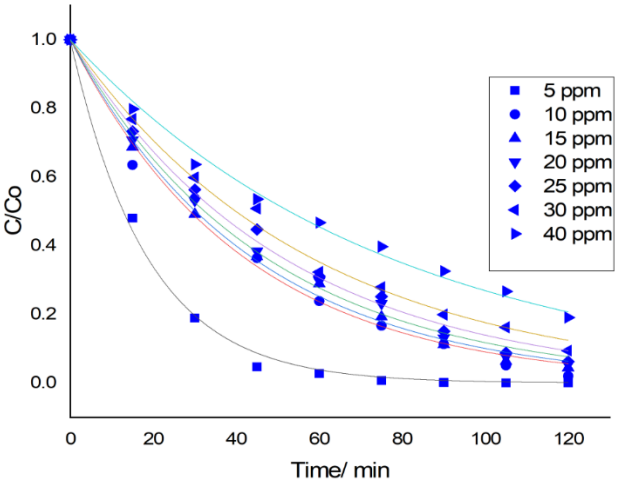


Fig. 7. Initial-dye-concentration effect to rat. Experimental Conditions: mass amount 0.3 g.L-1, Temp. 25 °C

Conclusions

ZnO shows highly active photocatalyst for degradable methylene blue dye; our results show good agreement first order kinetic under different parameters such as mass catalyst and initial due concentration.

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