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Research paper

Improved photocatalytic degradation of methylene blue by novel hexagonal ZnO particles

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Recently, the use of nanoparticles as photocatalysts has gained great importance. However, nanoparticles exhibit some drawbacks for this application and there is a need for new particle technologies to mitigate these drawbacks. A novel particle technology called MicNo based on ZnO has been designed and manufactured, which exhibits the advantages and properties of both micron and nano size. Although performance of MicNo-ZnO has been tested in various applications, it has not been tested as a photocatalyst in any photocatalytic degradation process. In this study, novel designed ZnO was used as a catalyst for methylene blue (MB) degradation in the presence of UV irradiation. The MicNo-ZnO particles were characterized by structural and morphological properties by XRD, BET and SEM analyses. The effects of catalyst amount, pH, temperature and initial concentration on the degradation process were investigated. In addition, a reusability study was carried out with 4 cycles under optimum conditions. The MicNo-ZnO particles showed excellent photocatalytic activity with a degradation rate of 96% for methylene blue in 180 min. The pseudo-first-order rate constant for the photocatalytic degradation of MB by MicNo-ZnO was as high as 0.0236 min^{-1}, confirming that MicNo-ZnO particles can be effectively utilized as an alternative catalyst material.

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INTRODUCTION

Water is one of the most crucial substances for the sustainability of life. Expeditious development of economy and industry, the rapid rise in population and increasing living standards result in increased water demand. On the other hand, underground and surface water sources have been polluted rapidly as a result of irresponsible industrial and agricultural activities (Bagheri and Chaibakhsh, 2021; Gupta and Suhas, 2009; Hasanpour and Hatami, 2020; Sawyer et al., 2003). Water pollution is one of the biggest problems faced globally today. Pollution is increasing every year, and poses a significant threat to environmental and public health (Hasanpour and Hatami, 2020; Natarajan et al., 2018). Dyes are among the most important pollutants and cause comparatively greater environmental pollution than many other water pollutants. Dyes are widely utilized in many industries such as textile, rubber, paper, leather, plastic, cosmetics, pigment production, printing, food and beverage, photoelectrochemical cell, chemical, and petrochemical (Bensalah et al., 2009; Dawood et al., 2014; Forgacs et al., 2004; Gupta and Suhas, 2009; Hasanpour and Hatami, 2020; Natarajan et al., 2018; Sokolowska-Gajda et al., 1996; Welderfael et al., 2016; Wróbel et al. 2001; Wu, 2007; Ozudogru et al., 2022). More than 100 000 types of commercial dyes are consumed annually by these industries (Gupta and Suhas, 2009; Hasanpour and Hatami, 2020). It is estimated that 70 000 to 1 000 000 tons of commercial paints are produced annually and about 10–15% of the used dyes are released to the environment as wastes (Dizge et al., 2008; Dotto et al., 2012; Gupta et al., 2013; Gupta and Suhas, 2009; Hasanpour and Hatami, 2020; McMullan et al., 2001). Wastewater from industries that use dyes creates serious environmental problem, such as contamination with organic pollutants, when discharged directly to the receiving environment without any treatment. One of the most significant problems of dyes is their toxicity to humans, aquatic animals and plants. In addition, dyes are bioaccumulated in nature (Işık and Sponza, 2004; Rani et al., 2021; Wong and Yuen, 1996). Dyes are chemically and photolytically stable in natural environments, so they are resistant to biological degradation (Gupta et al., 2013; Işık and Sponza, 2004; Wong and Yuen, 1996). Dyes that cause turbidity in the receiving environment inhibit the penetration of sunlight. Subsequently, photosynthesis is diminished and the dissolved oxygen level declines in the water. Therefore, the ecological health of the water body is impaired. It is known that dye compounds are reduced in aquatic sediments and spread to the natural environment by producing carcinogenic aromatic substances (Cırık et al., 2013). Wastewater containing dyes can cause important problems affecting aquatic organisms (fish, algae, bacteria, etc.) and humans, as well as aesthetic problems, and hence it must be treated prior to discharge to the receiving environment (Cırık et al., 2013; Forgacs et al., 2004; Gupta et al., 2013; Hasanpour and Hatami, 2020; Wu, 2007).

Physical (membrane filtration, coagulation, adsorption, ion-exchange, irradiation), chemical (photocatalysis, electrochemical routes, ozonation, Fenton's Reagent), and biological (anaerobic degradation, aerobic degradation) treatment methods are used for the removal of organic matter from water/wastewater (Gupta and Suhas, 2009; Gusain et al., 2019; Song et al., 2015). Among these methods, adsorption and photocatalysis have been widely used as effective methods for dye removal. Although adsorption is one of the most widely used methods, this method has limitations due to long desorption times and potential of generating secondary organic pollutants (Guo et al., 2021).

On the other hand, photocatalytic degradation is one of the most effective methods used for the complete degradation of dyes in wastewater (Hasanpour and Hatami, 2020). In the photocatalytic process, various materials such as ZnO (Al-Zahrani et al., 2020; Becker et al., 2011; Lam et al., 2012; Mao et al., 2019; Yashni et al., 2021; Zheng et al., 2019); CdS (Li et al., 2017; Yang et al., 2019), Fe_2O_3 (Kusior et al., 2019), WO_3 (El-Yazeed and Ahmed, 2019; Singh et al., 2018), TiO_2 (Al-Mamun et al., 2019; Al-Zahrani et al., 2020; Tichapondwa et al., 2020; Torane et al., 2020; Wong and Yuen, 1996), SnO_2 (Manikandan et al., 2018), Ni-doped ZnO nanocatalysts (Ahmad et al., 2022), Fe-doped ZnS photocatalysts (Shakoor et al., 2024), and Sr-based nanomaterials (Bashir et al. 2023) are used as a photocatalyst in the degradation of organic environmental pollutants like dyes. The ideal catalyst to be used in water treatment should be photoactive under visible and/or UV light, biologically and chemically inert, stable, cost effective and non-toxic. Recently, utilization of nanoparticles as photocatalysts has gained enormous popularity. Furthermore, numerous studies have been conducted utilizing nanoparticles for the purpose of purifying and reclaiming a wide range of contaminants (Ansari Moghaddam et al., 2023; Bazrafshan et al., 2023; Bazrafshan et al., 2021; Ghamkhari et al., 2020; Mohammadi et al., 2021). Metal or metal oxide nanoparticles are one of the compounds that have been widely investigated in this regard. Although there has been a significant amount of research on the application of metal-based nanoparticles for wastewater treatment, a substantial component of these materials is produced from hazardous metals and can exhibit intrinsic toxicity. Therefore, it is crucial to meticulously select secure and dependable metal-based nanoparticles for efficiently eliminating pollutants in wastewater treatment procedures (Bashir et al., 2023).

At nano scale, the specific surface area of powders increases and both chemical and physical, as well as, impacting optical and biological behaviours change or are enhanced, with the possibility of the material gaining additional properties. On the other hand, there are disadvantages of powders at nanoscale due to the fact that they are very small particles. Nano particles have very high surface energy because of their very small particle size, and therefore tend to agglomerate. Due to this agglomeration, the structure becomes micron sized. Also, in agglomerating; nano-sized particles come together in a random arrangement; because of this randomness, the surface area of the structure decreases. These factors make nano-sized particles difficult to use in many applications including photocatalyic degradation. In addition, when becoming a micron-sized structure due to agglomeration, the properties that were present when the particles were nano sized, disappear. Another problem specific to the photocatalytic degradation process is related to the difficulty of filtration or recovery of the photocatalyst powders during and after the photocatalytic water treatment process due to their very small particle size. During the filtration of powders, efficient separation of the solution and the catalyst particles is critical to achieve effective purification or treatment of the water. Accordingly, there is a need for development of new particle technologies which will overcome uncontrolled agglomeration, as well as the filtration and recovery problems associated with nanoparticles, while still maintaining their advantages.

Recently, Suvaci and co-workers (2009) designed and manufactured a novel particle technology, called MicNo, based on ZnO. MicNo-ZnO particles are micron-sized platelets which are composed of fine primary particles. MicNo-ZnO particles exhibit the advantages and properties of both micron and nano size. In previous studies, it has been shown that MicNo-ZnO is much less phytotoxic (Nazikcan, 2015) and much more biocompatible (Genç et al., 2018) than simply ZnO nanoparticles. Although the performance of MicNo-ZnO has been tested in various applications, such as lithium battery cathode material (Dermenci et al., 2020), conductive fillers as antistatic/ESD additives (Sengun et al., 2020), and antimicrobial agents (Demirel et al., 2018), it has not been tested as a photocatalyst in any photocatalytic degradation process.

The intentionally manufactured, micron-sized, controlled agglomerated platelet morphology of MicNo-ZnO has the potential to eliminate the uncontrolled agglomeration problem and its micron size enables easier filtration and recovery of the MicNo-ZnO particles from the solution. Consequently, the research objective of this study was to investigate the water purification performance of the novel designed micron-sized ZnO platelets with nano infrastructure, in the presence of methylene blue under UV irradiation, and hence evaluate its usability for dye removal processes.

MATERIALS AND METHODS

Materials and reagents

In this study, methylene blue (MB), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were used. The sodium hydroxide (NaOH, 97%) and hydrochloric acid (HCl, 37%) were supplied by Merck; MB dye was provided by ChemBio Laboratory Research (Product code: CB2702, 100 g). MB is commercial grade and was used without further purification. 0.1 M HCl and 0.1 M NaOH were prepared for adjusting the pH. MB solutions were prepared from 100 mg/L stock solutions.

The chemical and structural properties of MB dye are detailed in Table 1.

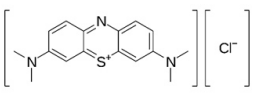
Instrumentation

All solutions were prepared with deionized water (Millipore Milli-Q Direct 8 Water Purification System). A pH meter (Thermo Orion Star A321 Portable pH Meter) was used for measuring the pH values of solutions. A precision balance (OHAUS Adventurer-Pro) was used for the preparation of the solutions. The samples were filtered using a 0.45 µm membrane filter. A UV-visible spectrophotometer (Hach Lange DR5000) with a 1 cm quartz cell was used for wavelength scanning of the MB solution and determining the absorbance values of the samples.

Catalyst particles and their characterization

MicNo-ZnO particles, used in this study, were provided by Entekno Materials, Inc. The particles were characterized by an x-ray diffractometer (XRD) and a scanning electron microscope (SEM) to determine crystal phase, and size and morphology of the particles, respectively. In addition, specific surface area

Table 1. Chemical and structural properties of methylene blue dye

Dye	Molecular formula	Molecular weight	CAS registry number	Structure
Methylene blue	$C_{16}H_{18}ClN_3S$	319.85 g/mol	122965-43-9	

of the particles was measured by a BET analyser. Prior to the BET analyses, the powder samples were degassed at 120°C for 18 h. Furthermore, particle size distribution of the particles was determined by the laser light scattering method. Aqueous suspensions of the particles were treated by an ultrasonic tip for 3 min before the analyses.

Photocatalytic degradation of methylene blue

The photocatalytic experiments (Fig. 1) were performed on a WTW TR-1 Heidolph UNIMAX 2010 shaker. 15 W UV-C lamp was used as the light source. The shaker and UV-C lamp were placed in an aluminium foil–covered cabinet to eliminate the influence of external light. There is also a unit to adjust the temperature in the cabinet, which was kept constant. A UV-C lamp does not affect the temperature of the reactor.

Photocatalytic degradation (Fig. 2) is used to purify water by breaking down organic pollutants into inorganic acids such as CO_2, H_2O, and HCl. This method is based on the use of a combination of ultraviolet light and semiconductors to break down organic pollutants in water. A photocatalytic system consists of semiconductor particles suspended in the liquid phase and a light source that is used to illuminate this suspension. A semiconductor has a valence band (VB) filled with electrons and a conductivity band (CB) containing empty energy levels. A spherical semiconductor particle is shown in Fig. 2. When the *hv* energy of the light used is greater than the energy difference (E_g) between the valence band and the conductivity band of the semiconductor, the semiconductor particle interacts with the photon (*hv*) to excite an electron in the valence band to the conductivity band, leaving a positive gap (h^+_{VB}) inside the particle. The electron/space enables the formation of e^-_{CB}(electron)/h^+_{VB} (hole) pairs (Eq. 1) These formed electron/space pairs cause redox reactions to start on the semiconductor surface. The pairs of spaces form hydroxyl radicals (OH*) by absorbing OH^- or H_2O molecules, and electrons react with oxygen to form anionic superoxide radicals (O_2^{-*}) (Eqs 2–3). These radicals oxidize the adsorbed organic molecules. Organic intermediate products are re-oxidized by molecular oxygen and/or OH* radicals, producing carbon dioxide and water (Eq. 4). These radicals then form molecular oxygen and hydrogen peroxide. Thus, photo-stimulated semiconductor photocatalyst enables both oxidation and reduction to occur at the surface (Al-Mamun et al., 2019; Lam et al., 2012; Natarajan et al., 2018; Shakoor et al., 2024).

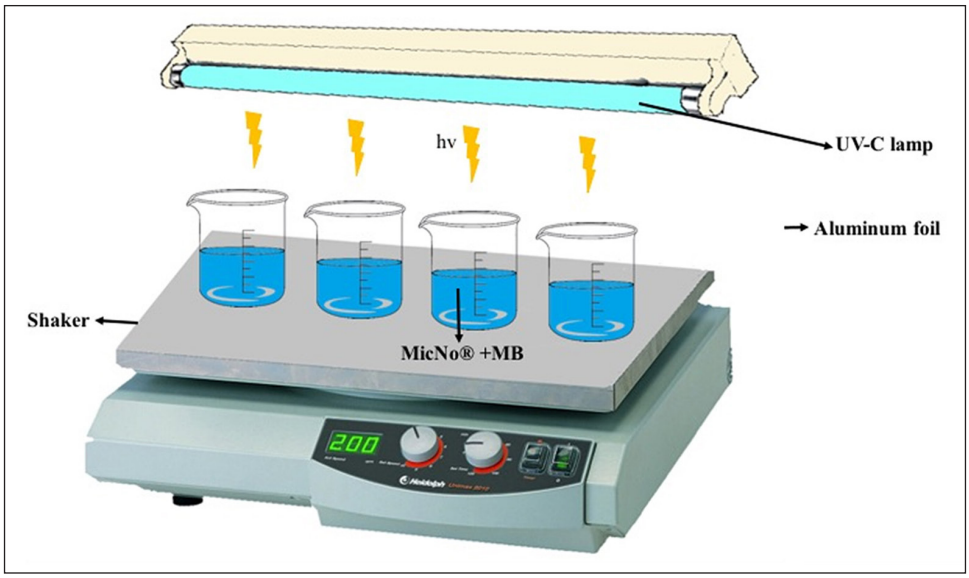


Figure 1. Photocatalytic experimental design

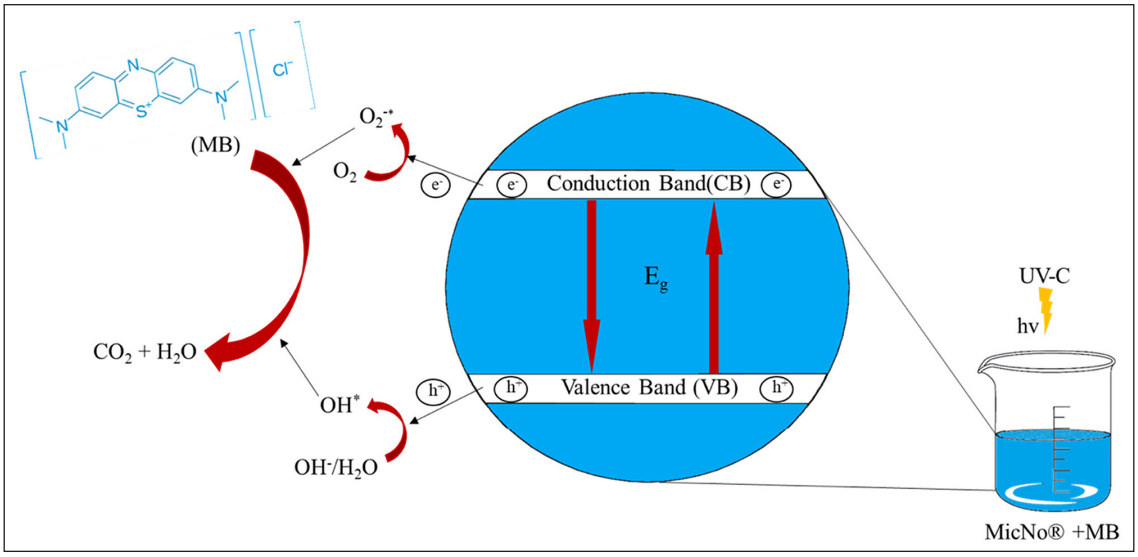


Figure 2. Schematic mechanism of photocatalytic degradation of MB

$$\text{MicNo-ZnO} + h\nu \rightarrow e^-_{CB} + h^+_{VB} \quad (1)$$

$$e^-_{CB} + O_2 \rightarrow O_2^{-*} \quad (2)$$

$$h^+_{VB} + OH^-/H_2O \rightarrow OH^* \quad (3)$$

$$O_2^{-*} + OH^* + \text{MB(dye)} \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \quad (4)$$

$$\text{Dye} + h^+_{VB} \rightarrow \text{oxidation products}$$

$$\text{Dye} + e^-_{CB} \rightarrow \text{reduction products}$$

In this study, photocatalytic MB degradation experiments were conducted under 270 min of UV light irradiation at 200 r/min stirring speed, different catalyst dosages, pH, temperatures and initial MB concentrations. The photocatalytic MB degradation rate was calculated using Eq. 5. C_0 is the initial concentration of MB, and C_t is the concentration after irradiation time t; A_o represents the initial absorbance. A_t describes the change in absorbance of the MB at the characteristic absorption wavelength 664 nm (Bel Hadjltaief et al., 2018; Bhatia et al., 2016; El-Yazeed and Ahmed, 2019; Güy et al., 2016; Natarajan et al., 2018).

$$\text{Degradation rate \%} = \frac{(C_0 - C_t)}{C_0} \times 100 = \frac{(A_0 - A_t)}{A_0} \times 100 \quad (5)$$

MicNo-ZnO was collected under optimum conditions to examine the post-reaction reusability of the catalyst. Two methods were used for reusability experiments. First, after the catalyst was air-dried, it was kept under UV light for 3 h. In the second method, the catalyst was washed with distilled water a few times and dried at 110°C for 12 h (Bel Hadjltaief et al., 2018). Photocatalytic experiments were carried out with MicNo-ZnO collected by these two methods, and the removal efficiencies were investigated.

Kinetic study

The photodegradation reactions of many organic compounds using various nanoparticles follows the Langmuir Hinshelwood (L-H) kinetics model (Hasanpour and Hatami, 2020; Li et al., 2018; Li et al., 2016). The kinetic study for MicNo-ZnO nanoparticles (photocatalyst) for photodegradation of MB was thus done using the Langmuir-Hinshelwood kinetic model. Since the organic pollutant concentration C_0 is very low, the Langmuir Hinshelwood (L-H) kinetics model can be simplified to an obvious pseudo-first-order kinetic equation (Eq. 6) (Chowdhury et al., 2018; Hasanpour and Hatami, 2020; Konstantinou and Albanis, 2004; Trandafilović et al., 2017). Methylene blue photocatalytic degradation kinetics were investigated using the pseudo-first-order rate law equation which can be expressed as:

$$\ln (C_t/C_0) = -kt \quad (6)$$

where: k is the rate constant, C_0 is the initial concentration at time $t = 0$, and C_t is the concentration at any time t during the reaction. According to pseudo-first-order kinetics, the reaction constant (k) is calculated by plotting $\ln (C_t/C_0)$ versus the reaction time (t). In general, the pseudo-first-order kinetics model is convenient for the overall concentration range for low concentrations. Various studies have shown that the rate of photocatalytic activity was well assessed by fitting the experimental data to this kinetic model (Hasanpour and Hatami, 2020; Kim et al., 2013; Lu et al., 2018; Najafidoust et al., 2019; Vaiano et al., 2014; Wang, 2007; Xiao et al., 2007). The resulting linear relationship demonstrates that the photodegradation of organic pollutants is well described by the Langmuir-Hinshelwood (L-H) kinetic model.

RESULTS AND DISCUSSION

Preliminary experimental studies

Wavelength scanning for MB was performed, and a standard calibration curve was prepared. According to the wavelength scanning results (Fig. 3), readings were made at 664 nm peak wavelength.

The mixture of MB and catalyst (MicNo-ZnO) was stirred in the dark for 15 min to ensure adsorption-desorption equilibrium before UV light irradiation. Subsequently, samples were collected at intervals of 10 min for the first 30 min, then at 30 min intervals, and filtered through a 0.45 µm membrane filter. Readings were done on a UV-visible spectrophotometer. Also, control experiments were carried out, as shown in Fig. 4. The MB concentration appears to be stable under a UV lamp without the catalyst. Addition of MicNo-ZnO achieves the removal of 10.27% of the MB in the dark environment, and is almost constant. Under visible light, 32.61% removal was achieved in the 120th minute and the removal efficiency curve follows a wave pattern.

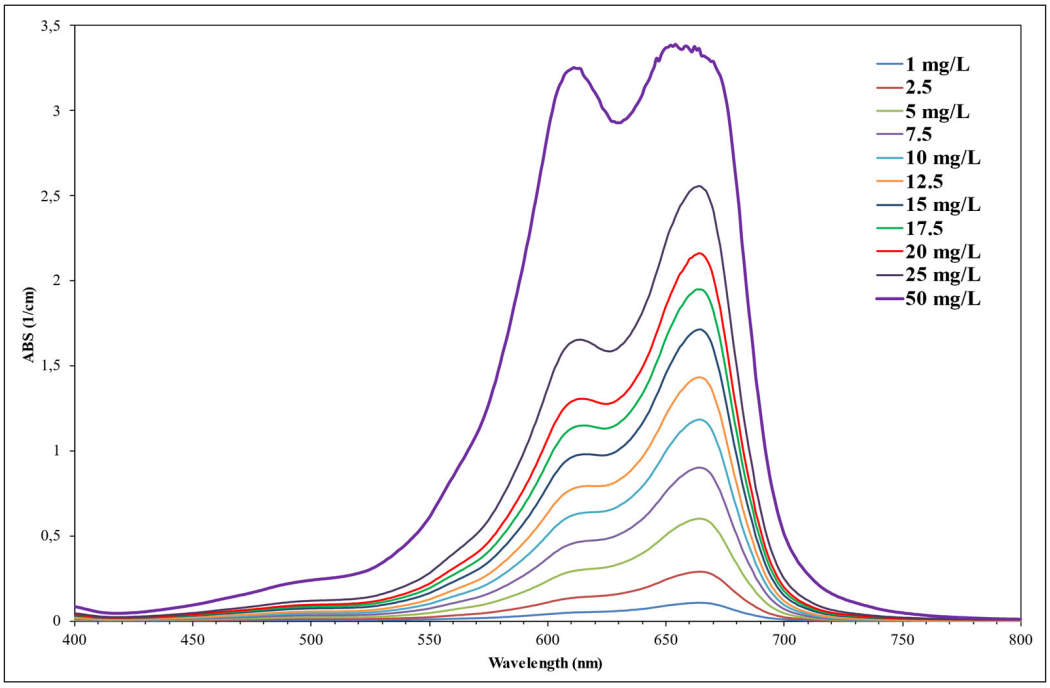


Figure 3. UV-vis absorption spectra of 1–50 mg/L methylene blue

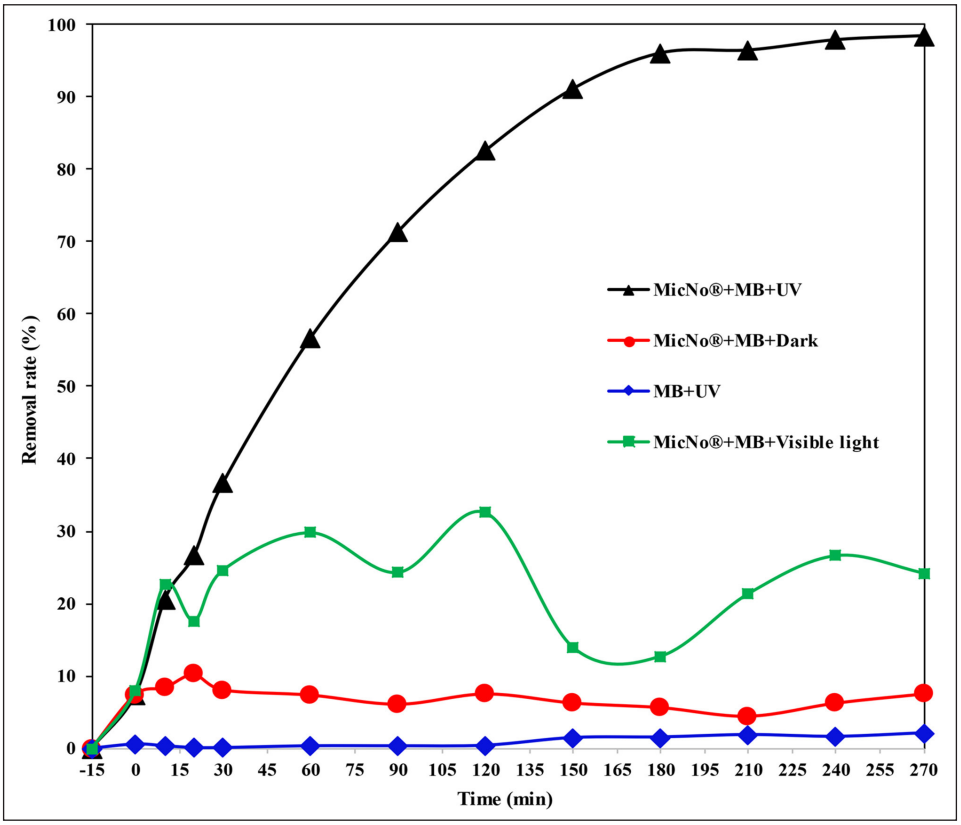


Figure 4. Comparison of MicNo-ZnO+MB+UV / MicNo-ZnO+MB+Dark / MB+UV

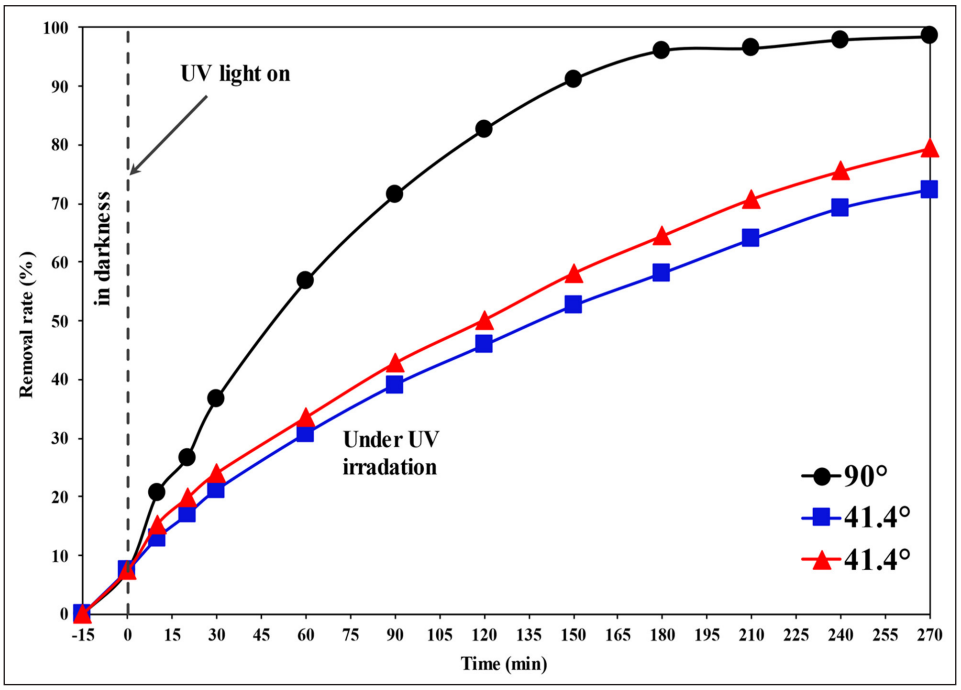


Figure 5. Effect of UV lamp location on the photocatalytic degradation of MicNo-ZnO (C_0 = 10 mg/L, pH = 6, T = room temperature (25°C), catalyst dose = 0.25 g/L)

This can be attributed to the fact that the adsorption-desorption of MB on MicNo-ZnO occurs at certain intervals. Under the UV lamp with catalyst, MB removal reached 91.13% in the 150th minute and 96.04% in the 180th minute.

Studies were carried out at three different positions on the shaker to determine whether the UV lamp, located 10.5 cm above the mixing device, would give the same effect at every point of the shaker. The study was carried out by placing beakers in the middle (90°), right (41.4°) and left (41.4°) rows of the shaker according to the angle of the UV lamp. It is concluded that the UV effect perpendicular to the beakers is higher than the effect for the other two rows (Fig. 5). Although 96.04% removal for MB was achieved in the 180th minute in the vertical position, in the other two rows a removal of 72.29–79.33% was achieved in the 270th minute. It was thus decided to perform the studies under a UV lamp at a vertical distance of 10.5 cm. In the 180th minute 96.04%

removal was achieved and the removal efficiency in the 270th minute approached almost 100%. Therefore, the photocatalytic degradation studies were conducted for 270 min.

Catalyst characterization

Figure 6 shows the XRD pattern of the catalyst particles. The peaks in the XRD pattern confirm that the catalyst particles are single-phase ZnO with a hexagonal wurtzite-type crystal structure. It should be also noted that the peaks demonstrate a broadening effect which suggests that the primary particles of the catalyst are nano-sized.

Figures 7 and 8 show the SEM image and EDX result, respectively, for the catalyst particles. The particles exhibit a polygonic (mostly hexagonal) morphology with a 2–10 µm particle size. The laser scattering analyses also showed that the catalyst particle size distribution lies in the 2–10 µm range with a mean value of approx. 5 µm. It can be observed in the SEM micrographs that the particles are thin enough to be transparent, such that the particles beneath them are also visible. All these results indicate that the catalyst particles are micron-sized platelets, composed of chemically bonded nano-sized particles. The BET analyses showed that the catalyst particles exhibit a specific surface area of 20–30 m^2/g.

Figure 9 shows the uncontrolled aggregated particles and MicNo-ZnO particles, formed via controlled aggregation of the same number of particles as in the uncontrolled case. MicNo-ZnO's novel morphology enables one to achieve improved surface coverage and greater surface reactivity which is desired for effective photocatalytic degradation processes.

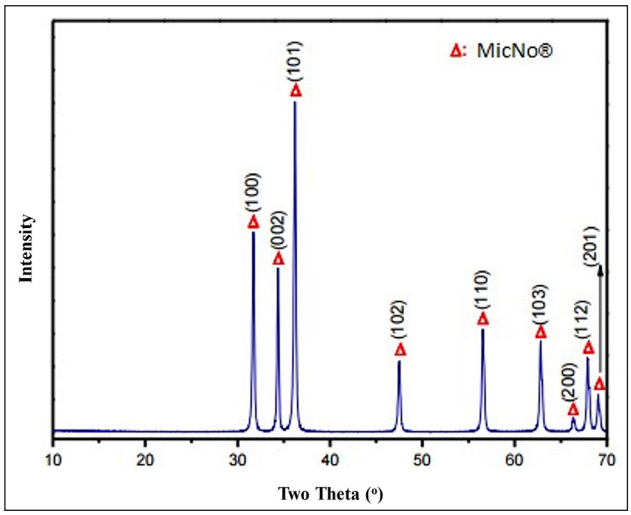


Figure 6. XRD pattern of MicNo-ZnO

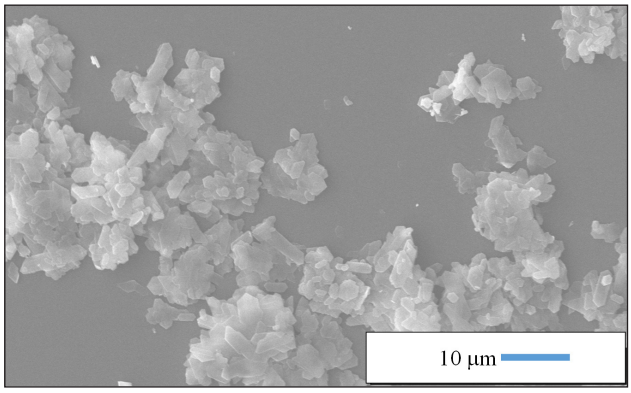


Figure 7. SEM image of MicNo-ZnO

Effect of various processing parameters on the photocatalytic degradation of MB

Catalyst dosage, pH, temperature and initial concentration parameters were evaluated for photocatalytic degradation of MB.

Effect of catalyst dosage

The amount of catalyst is one of the main parameters determining the dye degradation rate. Figure 10 shows that when the amount of catalyst in the reactor increases from 0.1 g/L to 0.25 g/L, removal efficiency also increases. Generally, the increase in the active site on the catalyst surface with increasing dosage increases the dye degradation rate (Bel Hadjltaief et al., 2018). It is seen that the removal efficiencies are almost the same when using 0.5 g/L and 1 g/L catalyst. Since the increased amount of catalyst increases the turbidity of the suspension and thereby decreases UV light penetration with the increased scattering effect, the removal efficiency decreases (Bel Hadjltaief et al., 2018). The photocatalytic degradation rate with the active region formed when 0.25 g/L was added approached the removal efficiency (~97–98%) when 0.5 g/L and 1 g/L were added.

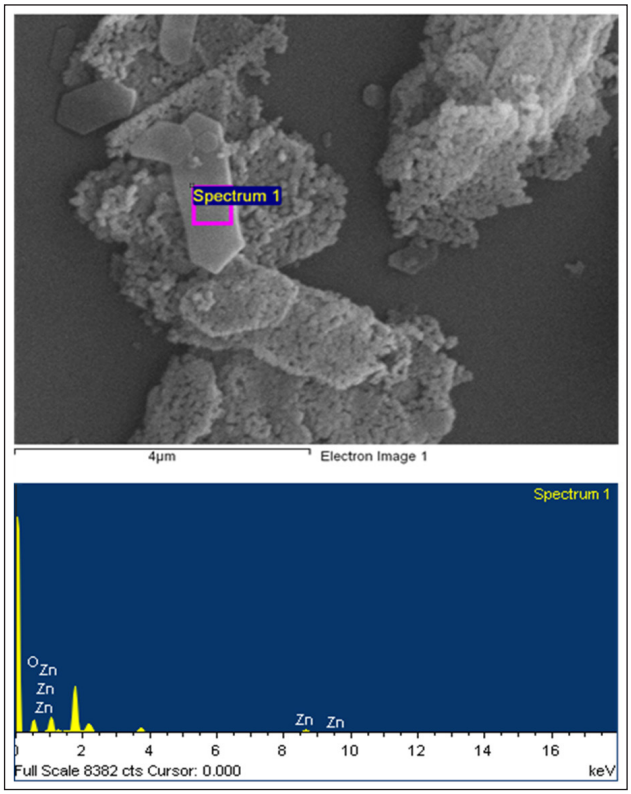


Figure 8. EDX result for MicNo-ZnO

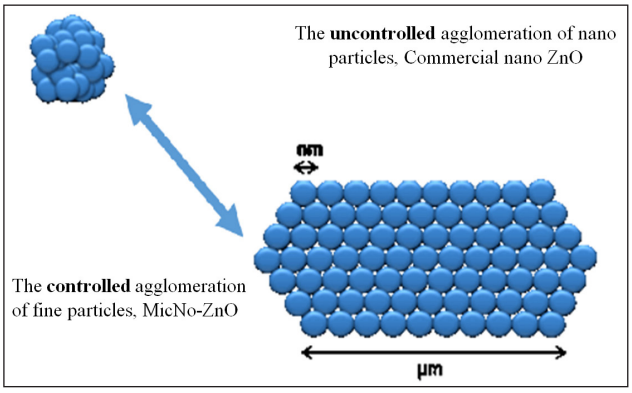


Figure 9. Schematic view of commercial ZnO and MicNo-ZnO particles

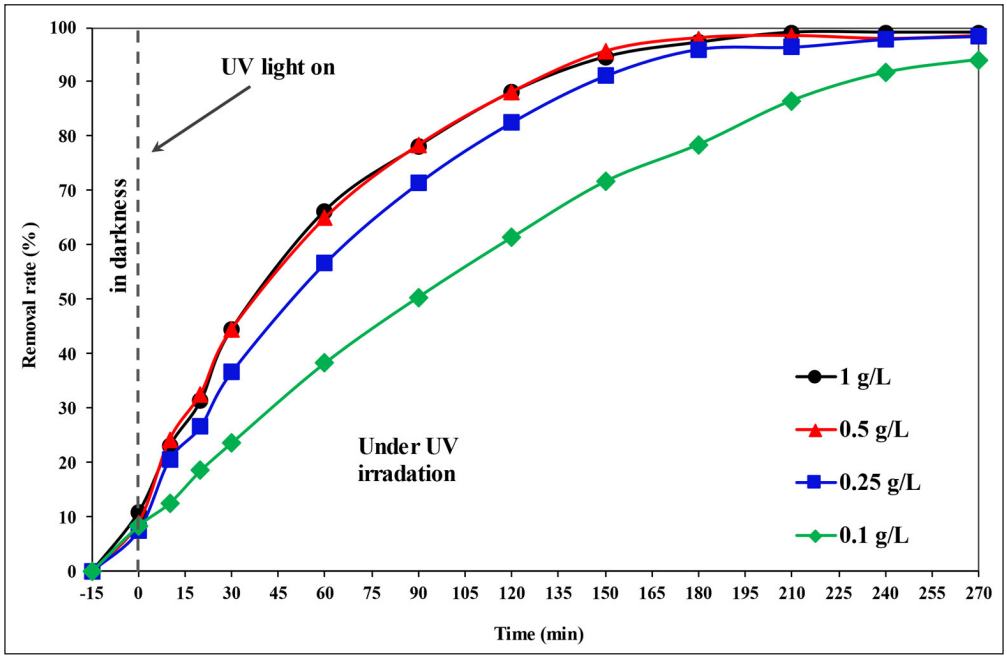


Figure 10. Effect of catalyst dosage on the photocatalytic degradation of MicNo-ZnO (C_0 = 10 mg/L, pH = 6, T = room temperature (25°C))

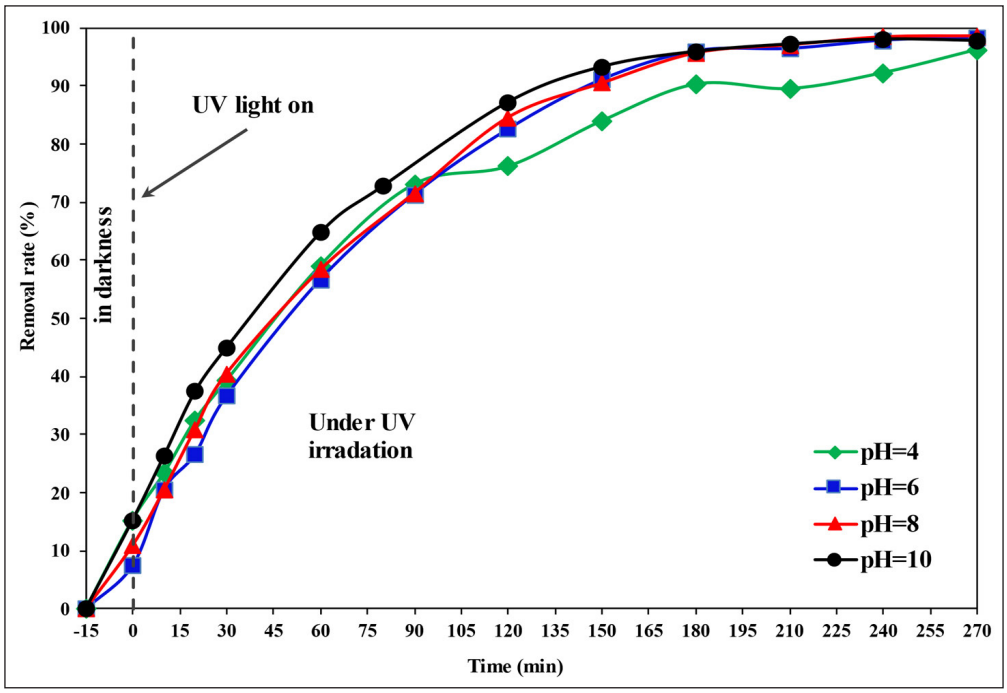


Figure 11. Effect of pH on the photocatalytic degradation of MicNo-ZnO (C_0 = 10 mg/L, T = room temperature (25°C), catalyst dose = 0.25 g/L)

Effect of pH

Since the pH range of wastewater differs, pH is one of the other main parameters to be considered for dye degradation in the presence of a catalyst. In photocatalytic dye degradation, the initial pH may result in a different activity for each dye and catalyst (Hasanpour and Hatami, 2020). In Fig. 11, the effect of initial pH on photocatalytic degradation of 10 mg/L MB using 0.25 g/L MicNo-ZnO is shown. The MB solution has an initial pH of about 6. In this study, pH values of 4, 6, 8, and 10 were studied. There is no sharp change in MB degradation over time at pH values of 6, 8 and 10 (Fig. 11). There is a minimal increase in removal at pH 10 compared to pH 6 and 8. This may be related to the pH zero-charge point (pH_{pzc}) value of MicNo-ZnO being 8.5. Above the pH_{pzc} value, the net surface charge of MicNo-ZnO becomes negative, indicating that better results can be obtained for MB with a cationic character. At pH 4, the removal efficiencies until the 90th minute are approximately the same as for other pH values, while a decrease is observed after the 120th minute.

Effect of temperature

The effect of photocatalytic degradation of MB solution with catalyst on temperature was investigated and the results shown in Fig. 12 were obtained. Very close removal efficiencies were obtained at 20°C and room temperature (25°C). Increasing the reactor temperature to 40°C will reduce the removal efficiency a little and cause additional energy consumption in the system. Therefore, it was concluded that the room temperature was optimum for the studies.

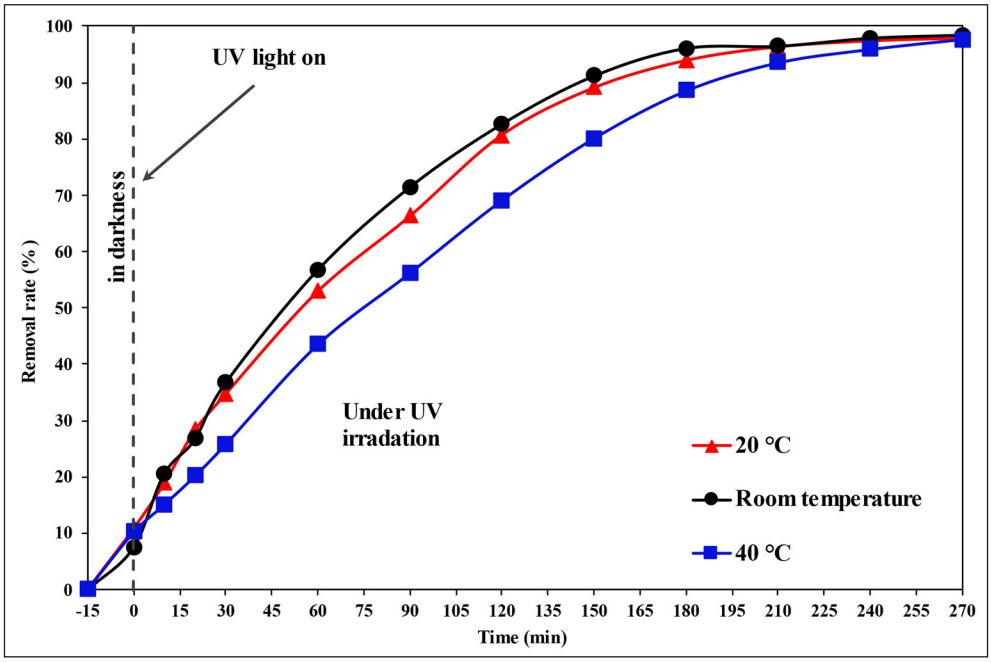


Figure 12. Effect of temperature on the photocatalytic degradation of MicNo-ZnO (C_0 = 10 mg/L, pH = 6, catalyst dose = 0.25 g/L)

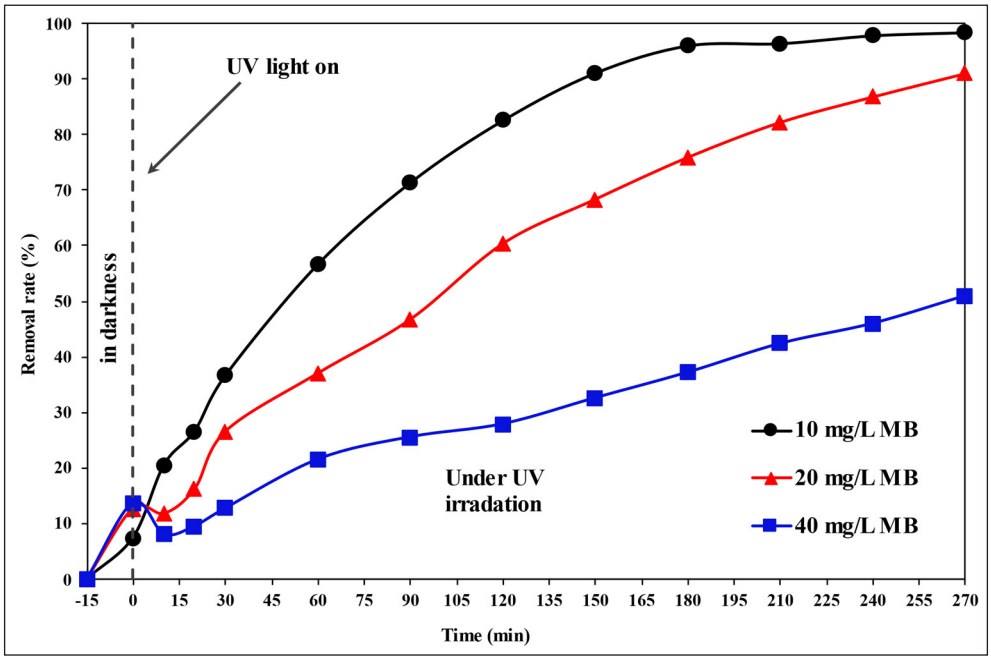


Figure 13. Effect of initial MB concentration on the photocatalytic degradation of MicNo-ZnO (pH = 6, *T* = room temperature (25°C), catalyst dose = 0.25 g/L)

Effect of initial MB concentration

The photocatalytic activity of MicNo-ZnO was determined at different initial concentrations of MB with 0.25 g/L catalyst. The lowest concentration tested, at 10 mg/L MB, degraded the fastest (Fig. 13: 91.13% at 150 min, 96.04% at 180 min, 96.44% at 210 min, 97.86% at 240 min, 98.42% at 270 min). An increase in initial MB concentration resulted in lower degradation and lower removal/efficiency.

The photocatalytic degradation achieved is inversely proportional to the initial concentration. The likely cause is that more and more dye molecules are adsorbed to the catalyst surface when the initial concentration increases. Therefore, since there are only a few active sites for the adsorption of hydroxyl ions and hydroxyl radicals, the formation of hydroxyl radicals will be reduced. Furthermore, as the concentration of a dye solution increases, photons are captured before they reach the catalyst surface; hence the absorption of photons by the catalyst decreases and, as a result, the percentage degradation decreases (Bel Hadjltaief et al., 2018; Tichapondwa et al., 2020).

Reusability of catalyst

Reusability of catalyst materials is an important and decisive factor for sustainable and practical applications (Bel Hadjltaief et al., 2018; El-Yazeed and Ahmed, 2019; Najafidoust et al., 2019). In this study, reusability was investigated under optimum conditions in consecutive periods with two methods specified in the title "Photocatalytic degradation of methylene blue" (Bel Hadjltaief et al., 2018) MicNo-ZnO efficiency was investigated for up to 4

cycles (Fig. 14). The methods were performed again after each cycle. It was concluded that Method 1 (air-dried, kept under UV light for 3 h) is better for this catalyst to recondition the surface activity. With this method, a decrease in degradation of 26% occurred in the second cycle, which indicates that the catalyst's efficiency tends to decrease slowly from the second cycle onward.

Kinetic study

Kinetic models for photocatalytic degradation of MB with MicNo-ZnO catalyst were investigated using the optimum parameters (pH = 6, C_0 = 10 mg/L, $[catalyst]_0$ = 0.25 g/L, T = room temperature). As shown in Fig. 15, the curve is linear and reveals that the kinetic data for photocatalytic degradation of MB fit the pseudo-first-order reaction kinetic model. Rate constants for dye degradation (k) and regression coefficients (R^2) were calculated from a pseudo-first-order linear fit to be 0.0177 min^{-1} and 0.9718, respectively. Table 2 shows the pseudo-first-order kinetic coefficients obtained with photocatalytic dye removal with different catalysts in this and previous studies.

When 0.25 g/L of MicNo-ZnO was used in the experiment, the k value was obtained as 0.0177 min^{-1}. If the amount of MicNo-ZnO is increased to 1 g/L, the k value becomes 0.0236 min^{-1} (R^2 = 0.9541). Although the surface area of the catalyst in our study is quite low compared to the photocatalysts used in other studies (Ahmed et al., 2013; Bel Hadjltaief et al., 2018; Dassanayake et al., 2018), it has a similar k value when approximately the same amount of catalyst (0.8–1 g/L) is used. The reason for deciding not to increase the amount of MicNo-ZnO used as photocatalyst in this study was the difficulty of recovery processes in the slurry system.

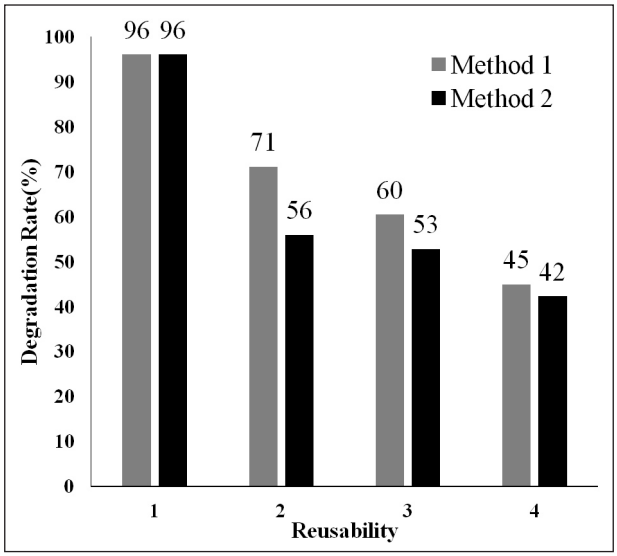


Figure 14. Reusability of MicNo-ZnO photocatalytic degradation of methylene blue

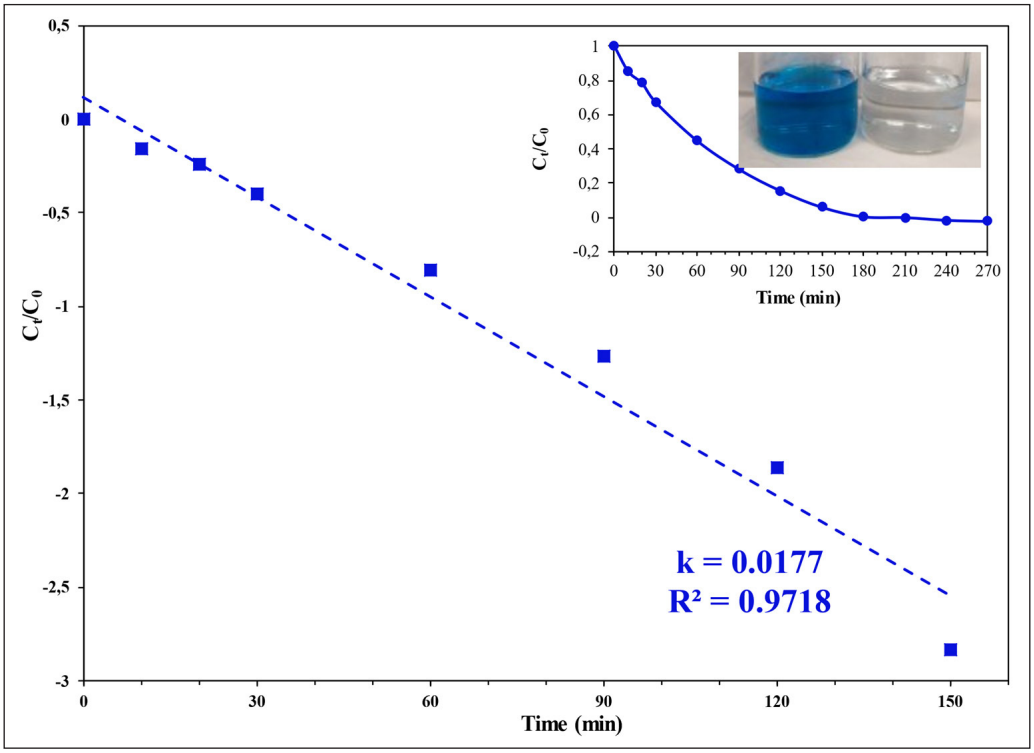


Figure 15. Pseudo-first-order kinetics for the photocatalytic degradation of methylene blue using MicNo-ZnO (C_0 = 10 mg/L, pH = 6, T = room temperature (25°C), catalyst dose = 0.25 g/L)

Table 2. Comparison of pseudo-first-order kinetic parameters for the present study versus previous studies on photocatalytic dye removal

Dye	Material/catalyst	Light source	Surface area (m^2/g)	Catalyst dose (g/L)	K (min^{-1})	Reference
Reactive green 19	WO_3 nanorods	Sunlight irradiation	-	-	0.036	Singh et al. (2018)
Methylene blue	Fe_2O_3/ TiO_2	UV irradiation	68–182	1	0.0064–0.042	Ahmed et al. (2013)
Malachite Green	ZnO/Clay	UV irradiation	132.1	1	0.033	Bel Hadjltaief et al. (2018)
Red Congo			132.1	0.8	0.0238	
Direct red -31	Er-doped ZnO nanoparticles	UV irradiation	-	-	0.07010	Bhatia et al. (2016)
Methylene blue	GO/F-TiO_2	UV light irradiation	5–204	1	0.0242–0.0493	Dai et al. (2014)
Methylene blue	Aerochitin–TiO_2 composite	UV light irradiation	119.5	1	0.0182	Dassanayake et al. (2018)
Methylene blue	Nb_2O_5/tannin-formaldehyde xerogel	UVC	-	2	0.011–0.025	De Moraes et al. (2019)
Methylene blue	TiO_2/carbonaceous aerogel	UV irradiation	10.101–113.33	-	0.00567–0.775	Shi et al. (2016)
Methylene blue	Co-doped ZnO	UV	-	1	0.0102	Xiao et al. (2007)
Methylene blue	MicNo-ZnO	UV	39.395	0.25	0.0177	This study
Methylene blue	MicNo-ZnO	UV	39.395	1	0.0236	This study

CONCLUSIONS

Wastewater containing dyes creates a severe environmental problem when directly discharged to the receiving environment without any treatment. The objective of this study was to test novel designed MicNo-ZnO particles for the first time as photocatalysts to remove methylene blue from water.

Results of the photocatalytic experiments showed that the optimum dose for 10 mg/L MB was 0.25 g/L MicNo-ZnO, achieving a removal efficiency of 96% at the 180th minute. The pseudo-first-order rate constants for the photocatalytic degradation of MB by MicNo-ZnO were found to be as high as 0.0236 min^{-1} and the kinetic study confirmed that the photocatalytic degradation of MB follows the kinetics of the pseudo-first-order model. These results show that MicNo-ZnO is a suitable candidate for effective photocatalytic dye degradation of methylene blue and possibly other dyes.

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DISCLOSURE STATEMENT

No potential conflict of interest was reported by the author(s).

AUTHOR CONTRIBUTIONS

ZYA: writing – original draft, writing – review and editing, conceptualization, methodology, supervision, resources. ID: conceptualization, methodology, writing – review and editing, visualization. ES: writing – review & editing, conceptualization, methodology, supervision, resources.

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REFERENCES

AHMAD I, ASLAM M, JABEEN U, ZAFAR MN, MALGHANI MNK, ALWADAI N, ALSHAMMARI FH, ALMUSLEM AS and ULLAH Z (2022) ZnO and Ni-doped ZnO photocatalysts: Synthesis, characterization and improved visible light driven photocatalytic degradation of methylene blue. *Inorg. Chim. Acta* **543** 121167. https://doi.org/10.1016/j.ica.2022.121167

AHMED MA, EL-KATORI EE and GHARNI ZH (2013) Photocatalytic degradation of methylene blue dye using Fe2O3/TiO2 nanoparticles prepared by sol–gel method. *J. Alloys Compounds* **553** 19–29. https://doi.org/10.1016/j.jallcom.2012.10.038

AL-MAMUN MR, KADER S, ISLAM MS and KHAN MZH (2019) Photocatalytic activity improvement and application of UV-TiO_2 photocatalysis in textile wastewater treatment: A review. *J. Environ. Chem. Eng.* **7** (5) 103248. https://doi.org/10.1016/j.jece.2019.103248

AL-ZAHRANI FAM, EL-SHISHTAWY RM, AHMED NSE, AWWAD NS, HAMDY MS and ASIRI AM (2020) Photocatalytic decolourization of a new water-insoluble organic dye based on phenothiazine by ZnO and TiO_2 nanoparticles. *Arab. J. Chem.* **13** (2) 3633–3638. https://doi.org/10.1016/j.arabjc.2019.12.007

ANSARI MOGHADDAM A, MOHAMMADI L, BAZRAFSHAN E, BATOOL M, BEHNAMPOUR M, BANIASADI M, MOHAMMADI L and NADEEM ZAFAR M (2023) Antibiotics sequestration using metal nanoparticles: An updated systematic review and meta-analysis. *Inorgan. Chim. Acta* **550** 121448. https://doi.org/10.1016/j.ica.2023.121448

BAGHERI F and CHAIBAKHSH N (2021) Efficient visible-light photocatalytic ozonation for dye degradation using Fe_2O_3/MoS_2 nanocomposite. *Sep. Sci. Technol.* **56** (17) 3022–3032. https://doi.org/10.1080/01496395.2020.1861018

BASHIR M, BATOOL M, ARIF N, TAYYAB M, ZENG Y-J and NADEEM ZAFAR M (2023) Strontium-based nanomaterials for the removal of organic/inorganic contaminants from water: A review. *Coordination Chem. Rev.* **492** 215286. https://doi.org/10.1016/j.ccr.2023.215286

BAZRAFSHAN E, DAHMARDEH Z, MOHAMMADI L, NADEEMZAFAR M, DARGAHI A and PIRDADEH F (2023) Synthesis of magnesium oxide nanoparticles and its application for photocatalytic removal of furfural from aqueous media: Optimization using response surface methodology. *Arab. J. Chem.* **16** (8) 104998. https://doi.org/10.1016/j.arabjc.2023.104998

BAZRAFSHAN E, ZAREI AA, MOHAMMADI L, ZAFAR MN, FOROUGHI M, AMAN S, SABRI F, MAHVI AH, BARAHUIE F and ZAFAR M (2021) Efficient tetracycline removal from aqueous solutions using ionic liquid modified magnetic activated carbon (IL@mAC). *J. Environ. Chem. Eng.* **9** (6) 106570. https://doi.org/10.1016/j.jece.2021.106570

BECKER J, RAGHUPATHI KR, ST. PIERRE J, ZHAO D and KOODALI RT (2011) Tuning of the crystallite and particle sizes of ZnO nanocrystalline materials in solvothermal synthesis and their photocatalytic activity for dye degradation. *J. Phys. Chem. C* **115** (28) 13844–13850. https://doi.org/10.1021/jp2038653

BEL HADJLTAIEF H, BEN AMEUR S, DA COSTA P, BEN ZINA M and ELENA GALVEZ M (2018) Photocatalytic decolorization of cationic and anionic dyes over ZnO nanoparticle immobilized on natural Tunisian clay. *Appl. Clay Sci.* **152** 148–157. https://doi.org/10.1016/j.clay.2017.11.008

BENSALAH N, ALFARO MAQ and MARTÍNEZ-HUITLE CA (2009) Electrochemical treatment of synthetic wastewaters containing alphazurine A dye. *Chem. Eng. J.* **149** (1) 348–352. https://doi.org/10.1016/j.cej.2008.11.031

BHATIA S, VERMA N and BEDI RK (2016) Optical application of Er-doped ZnO nanoparticles for photodegradation of direct red - 31 dye. *Optic. Mater.* **62** 392–398. https://doi.org/10.1016/j.optmat.2016.10.013

CHOWDHURY S, JIANG Y, MUTHUKARUPPAN S and BALASUBRAMANIAN R (2018) Effect of boron doping level on the photocatalytic activity of graphene aerogels. *Carbon* **128** 237–248. https://doi.org/10.1016/j.carbon.2017.11.089

CIRIK K, ÇINAR Ö, ŞAHINKAYA E, UYSAL Y, BAŞAK S, AYDOĞMUŞ D, ÖZDEMIR Ş, YIĞIT N, KITIŞ M and CIVELEKOĞLU G (2013) Boyar madde içeren atıksu arıtma tesislerinin işletilmesine yönelik el kitabı. Republic of Turkey Ministry of Environment and Urbanisation, Ankara.

DAI K, LU L, LIU Q, ZHU G, LIU Q and LIU Z (2014) Graphene oxide capturing surface-fluorinated TiO_2 nanosheets for advanced photocatalysis and the reveal of synergism reinforce mechanism. *Dalton Transact.* **43** (5) 2202–2210. https://doi.org/10.1039/C3DT52542B

DASSANAYAKE RS, RAJAKARUNA E and ABIDI N (2018) Preparation of aerochitin-TiO_2 composite for efficient photocatalytic degradation of methylene blue. *J. Appl. Polymer Sci.* **135** (8) 45908. https://doi.org/10.1002/app.45908

DAWOOD S, SEN TK and PHAN C (2014) Synthesis and characterisation of novel-activated carbon from waste biomass pine cone and its application in the removal of congo red dye from aqueous solution by adsorption. *Water Air Soil Pollut.* **225** (1) 1818. https://doi.org/10.1007/s11270-013-1818-4

DE MORAES NP, BACETTO LA, PAIVA LK, DOS SANTOS GS, DA SILVA MLCP and RODRIGUES LA (2019) Novel and inexpensive Nb2O5/tannin-formaldehyde xerogel composites as substitutes for titanium dioxide in photocatalytic processes. *J. Sol-Gel Sci. Technol.* **89** (2) 571–585. https://doi.org/10.1007/s10971-018-4905-6

DEMIREL R, SUVACI E, ŞAHIN İ, DAĞ S and KILIÇ V (2018) Antimicrobial activity of designed undoped and doped MicNo-ZnO particles. *J. Drug Delivery Sci. Technol.* **47** 309–321. https://doi.org/10.1016/j.jddst.2018.07.024

DERMENCI KB, YANIK T, DAĞ S, SUVACI E, KESIM MT, SAVACI U and TURAN S (2020) Electrochemical properties of ZnO anode materials with MicNo® morphology. *Int. J. Appl. Ceramic Technol.* **17** (4) 1882–1890. https://doi.org/10.1111/ijac.13486

DIZGE N, AYDINER C, DEMIRBAS E, KOBYA M and KARA S (2008) Adsorption of reactive dyes from aqueous solutions by fly ash: Kinetic and equilibrium studies. *J. Hazardous Mater.* **150** (3) 737–746. https://doi.org/10.1016/j.jhazmat.2007.05.027

DOTTO GL, VIEIRA ML and PINTO LA (2012) Kinetics and mechanism of tartrazine adsorption onto chitin and chitosan. *Ind. Eng. Chem. Res.* **51** (19) 6862–6868. https://doi.org/10.1021/ie2030757

EL-YAZEED WSA and AHMED AI (2019) Photocatalytic activity of mesoporous WO3/TiO_2 nanocomposites for the photodegradation of methylene blue. *Inorg. Chem. Commun.* **105** 102–111. https://doi.org/10.1016/j.inoche.2019.04.034

FORGACS E, CSERHÁTI T and OROS G (2004) Removal of synthetic dyes from wastewaters: a review. *Environ. Int.* **30** (7) 953–971. https://doi.org/10.1016/j.envint.2004.02.001

GENÇ H, BARUTCA B, KOPARAL AT, ÖZÖĞÜT U, ŞAHIN Y and SUVACI E (2018) Biocompatibility of designed MicNo-ZnO particles: Cytotoxicity, genotoxicity and phototoxicity in human skin keratinocyte cells. *Toxicol. Vitro* **47** 238–248. https://doi.org/10.1016/j.tiv.2017.12.004

GHAMKHARI A, MOHAMADI L, KAZEMZADEH S, ZAFAR MN, RAHDAR A and KHAKSEFIDI R (2020) Synthesis and characterization of poly(styrene-block-acrylic acid) diblock copolymer modified magnetite nanocomposite for efficient removal of penicillin G. *Composites B: Eng.* **182** 107643. https://doi.org/10.1016/j.compositesb.2019.107643

GUO R-F, LIANG P, LI X-Y and LIU Z-H (2021) Fabrication of a dual Z-scheme GACN/NiO/Ni3(BO3)2 composite with excellent photocatalytic activity for methylene blue and tetracycline removal. *Sep. Purif. Technol.* **264** 118414. https://doi.org/10.1016/j.seppur.2021.118414

GUPTA VK, KUMAR R, NAYAK A, SALEH TA and BARAKAT MA (2013) Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: A review. *Adv. Colloid Interf. Sci.* **193–194** 24–34. https://doi.org/10.1016/j.cis.2013.03.003

GUPTA VK and SUHAS (2009) Application of low-cost adsorbents for dye removal – A review. *J. Environ. Manage.* **90** (8) 2313-2342. https://doi.org/10.1016/j.jenvman.2008.11.017

GUSAIN R, GUPTA K, JOSHI P and KHATRI OP (2019) Adsorptive removal and photocatalytic degradation of organic pollutants using metal oxides and their composites: A comprehensive review. *Adv. Colloid Interf. Sci.* **272** 102009. https://doi.org/10.1016/j.cis.2019.102009

GÜY N, ÇAKAR S and ÖZACAR M (2016) Comparison of palladium/zinc oxide photocatalysts prepared by different palladium doping methods for congo red degradation. *J. Colloid Interf. Sci.* **466** 128–137. https://doi.org/10.1016/j.jcis.2015.12.009

HASANPOUR M and HATAMI M (2020) Photocatalytic performance of aerogels for organic dyes removal from wastewaters: Review study. *J. Molec. Liq.* **309** 113094. https://doi.org/10.1016/j.molliq.2020.113094

IŞIK M and SPONZA DT (2004) Decolorization of azo dyes under batch anaerobic and sequential anaerobic/aerobic conditions. *J. Environ. Sci. Health A* **39** (4) 1107–1127. https://doi.org/10.1081/ESE-120028417

KIM YN, SHAO GN, JEON SJ, IMRAN S, SARAWADE PB and KIM HT (2013) Sol–gel synthesis of sodium silicate and titanium oxychloride based TiO_2–SiO_2 aerogels and their photocatalytic property under UV irradiation. *Chem. Eng. J.* **231** 502–511. https://doi.org/10.1016/j.cej.2013.07.072

KONSTANTINOU IK and ALBANIS TA (2004) TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review. *Appl. Catal. B: Environ.* **49** (1) 1–14. https://doi.org/10.1016/j.apcatb.2003.11.010

KUSIOR A, MICHALEC K, JELEN P and RADECKA M (2019) Shaped Fe_2O_3 nanoparticles – Synthesis and enhanced photocatalytic degradation towards RhB. *Appl. Surf. Sci.* **476** 342–352. https://doi.org/10.1016/j.apsusc.2018.12.113

LAM S-M, SIN J-C, ABDULLAH AZ and MOHAMED AR (2012) Degradation of wastewaters containing organic dyes photocatalysed by zinc oxide: a review. *Desalin. Water Treat.* **41** (1–3) 131–169. https://doi.org/10.1080/19443994.2012.664698

LI X, WANG Y, XIE Y, YIN S, LAU R and XU R (2017) CdS nanoparticles loaded on porous poly-melamine–formaldehyde polymer for photocatalytic dye degradation. *Res. Chem. Intermed.* **43** (9) 5083–5090. https://doi.org/10.1007/s11164-017-3048-7

LI X, XIE J, JIANG C, YU J and ZHANG P (2018) Review on design and evaluation of environmental photocatalysts. *Front. Environ. Sci. Eng.* **12** (5) 1–32. https://doi.org/10.1007/s11783-018-1076-1

LI Z-D, WANG H-L, WEI X-N, LIU X-Y, YANG Y-F and JIANG W-F (2016) Preparation and photocatalytic performance of magnetic Fe_3O_4@ TiO_2 core–shell microspheres supported by silica aerogels from industrial fly ash. *J. Alloys Compounds* **659** 240–247. https://doi.org/10.1016/j.jallcom.2015.10.297

LU J, HU H, YANG S, SHANMUGAM P, WEI W, SELVARAJ M and XIE J (2018) ZnS@ carbonaceous aerogel composites fabricated in production of hydrogen and for removal of organic pollutants. *J. Mater. Sci.: Mater. Electron.* **29** (10) 8523–8534. https://doi.org/10.1007/s10854-018-8866-x

MANIKANDAN A, RENUKADEVI K, RAVICHANDRAN K and SINDHUJA E (2018) Ag activated SnO_2 films for enhanced photocatalytic dye degradation against toxic organic dyes. *J. Mater. Sci.: Mater. Electron.* **29** (10) 8547–8554. https://doi.org/10.1007/s10854-018-8868-8

MAO Y, LI Y, ZOU Y, SHEN X, ZHU L and LIAO G (2019) Solvothermal synthesis and photocatalytic properties of ZnO micro/nanostructures. *Ceramics Int.* **45** (2, Part A) 1724–1729. https://doi.org/10.1016/j.ceramint.2018.10.054

MCMULLAN G, MEEHAN C, CONNEELY A, KIRBY N, ROBINSON T, NIGAM P, BANAT I, MARCHANT R and SMYTH W (2001) Microbial decolourisation and degradation of textile dyes. *Appl. Microbiol. Biotechnol.* **56** (1–2) 81–87. https://doi.org/10.1007/s002530000587

MOHAMMADI L, ZAFAR MN, BASHIR M, SUMRRA SH, SHAFQAT SS, ZAREI AA, DAHMARDEH H, AHMAD I and HALAWA MI (2021) Modeling of phenol removal from water by $NiFe_2O_4$ nanocomposite using response surface methodology and artificial neural network techniques. *J. Environ. Chem. Eng.* **9** (4) 105576. https://doi.org/10.1016/j.jece.2021.105576

NAJAFIDOUST A, HAGHIGHI M, ASL EA and BANANIFARD H (2019) Sono-solvothermal design of nanostructured flowerlike BiOI photocatalyst over silica-aerogel with enhanced solar-light-driven property for degradation of organic dyes. *Sep. Purif. Technol.* **221** 101–113. https://doi.org/10.1016/j.seppur.2019.03.075

NATARAJAN S, BAJAJ HC and TAYADE RJ (2018) Recent advances based on the synergetic effect of adsorption for removal of dyes from waste water using photocatalytic process. *J. Environ. Sci.* **65** 201–222. https://doi.org/10.1016/j.jes.2017.03.011

NAZIKCAN Ö (2015) Investigation of effects of nanomaterıals whıch have produced by different methods on plant development. Masters thesis, Anadolu University, Eskişehir.

OZUDOGRU I, YIGIT AVDAN Z, BALBAY S (2022) A novel carbon-based material recycled from end-of-life tires (ELTs) for separation of organic dyes to understand kinetic and isotherm behavior. *Sep. Sci. Technol.* **57** (13) 2024–2040. https://doi.org/10.1080/01496395.2022.2029489

RANI UA, NG LY, NG CY, MAHMOUDI E, NG Y-S and MOHAMMAD AW (2021) Sustainable production of nitrogen-doped carbon quantum dots for photocatalytic degradation of methylene blue and malachite green. *J. Water Process Eng.* **40** 101816. https://doi.org/10.1016/j.jwpe.2020.101816

SAWYER CN, McCARTY PL and PARKIN GF (2003) *Chemistry for Environmental Engineering and Science.* (5th edn). McGraw Hill, Boston

SENGUN P, KESIM MT, CAGLAR M, SAVACI U, TURAN S, SAHIN İ and SUVACI E (2020) Characterization of designed, transparent and conductive Al doped ZnO particles and their utilization in conductive polymer composites. *Powder Technol.* **374** 214–222. https://doi.org/10.1016/j.powtec.2020.07.025

SHAKOOR I, JABEEN U, AHMAD I, RIAZ S, TAYYAB M, SYED A, BAHKALI AH, RIAZ M, ZAIROV RR and ZAFAR MN (2024) ZnS and Fe-doped ZnS photocatalysts for improved visible light driven photocatalytic degradation of methylene blue. *Inorg. Chim. Acta* **560** 121837. https://doi.org/10.1016/j.ica.2023.121837

SHI M, WEI W, JIANG Z, HAN H, GAO J and XIE J (2016) Biomass-derived multifunctional TiO_2/carbonaceous aerogel composite as a highly efficient photocatalyst. *RSC Adv.* **6** (30) 25255–25266. https://doi.org/10.1039/C5RA28116D

SINGH J, KAUR H and RAWAT M (2018) A novel green approach for the synthesis of tungsten oxide nanorods and its efficient potential towards photocatalytic degradation of reactive green 19 dye. *J. Mater. Sci. Mater. Electron.* **29** (16) 13715–13722. https://doi.org/10.1007/s10854-018-9501-6

SOKOLOWSKA-GAJDA J, FREEMAN HS and REIFE A (1996) Synthetic dyes based on environmental considerations. Part 2: Iron complexes formazan dyes. *Dyes Pigments* **30** (1) 1–20. https://doi.org/10.1016/0143-7208(95)00048-8

SONG J, WANG X, CHEN O-P, CHEN C-K and CHANG C-T (2015) Photocatalytic degradation of reactive black-5 dye with novel graphene-titanium nanotube composite. *Sep. Sci. Technol.* **50** (9) 1394–1402. https://doi.org/10.1080/01496395.2014.969377

TICHAPONDWA SM, NEWMAN JP and KUBHEKA O (2020) Effect of TiO_2 phase on the photocatalytic degradation of methylene blue dye. *Phys. Chem. Earth A/B/C* **118–119** 102900. https://doi.org/10.1016/j.pce.2020.102900

TORANE AP, UBALE AB, KANADE KG and PAGARE PK (2020) Photocatalytic dye degradation study of TiO_2 material. *Mater. Today: Proc.* https://doi.org/10.1016/j.matpr.2020.06.476

TRANDAFILOVIĆ LV, JOVANOVIĆ DJ, ZHANG X, PTASIŃSKA S and DRAMIĆANIN MD (2017) Enhanced photocatalytic degradation of methylene blue and methyl orange by ZnO:Eu nanoparticles. *Appl. Catal. B Environ.* **203** 740–752. https://doi.org/10.1016/j.apcatb.2016.10.063

VAIANO V, SACCO O, SANNINO D, CIAMBELLI P, LONGO S, VENDITTO V and GUERRA G (2014) N-doped TiO_2/s-PS aerogels for photocatalytic degradation of organic dyes in wastewater under visible light irradiation. *J. Chem. Technol. Biotechnol.* **89** (8) 1175–1181. https://doi.org/10.1002/jctb.4372

WANG C-T (2007) Photocatalytic activity of nanoparticle gold/iron oxide aerogels for azo dye degradation. *J. Non-Crystalline Solids* **353** (11–12) 1126–1133. https://doi.org/10.1016/j.jnoncrysol.2006.12.028

WELDERFAEL T, PATTABI M, PATTABI RM and G AKT (2016) Photocatalytic activity of Ag-N co-doped ZnO nanorods under visible and solar light irradiations for MB degradation. *J. Water Process Eng.* **14** 117–123. https://doi.org/10.1016/j.jwpe.2016.11.001

WONG PK and YUEN PY (1996) Decolorization and biodegradation of methyl red by *Klebsiella pneumoniae* RS-13. *Water Res.* **30** (7) 1736–1744. https://doi.org/10.1016/0043-1354(96)00067-X

WRÓBEL D, BOGUTA A and ION RM (2001) Mixtures of synthetic organic dyes in a photoelectrochemical cell. *J. Photochem. Photobiol. A Chem.* **138** (1) 7–22. https://doi.org/10.1016/S1010-6030(00)00377-4

WU C-H (2007) Adsorption of reactive dye onto carbon nanotubes: Equilibrium, kinetics and thermodynamics. *J. Hazardous Mater.* **144** (1) 93–100. https://doi.org/10.1016/j.jhazmat.2006.09.083

XIAO Q, ZHANG J, XIAO C and TAN X (2007) Photocatalytic decolorization of methylene blue over Zn1–xCoxO under visible light irradiation. *Mater. Sci. Eng. B* **142** (2) 121–125. https://doi.org/10.1016/j.mseb.2007.06.021

YANG X, YANG Y, WANG B, WANG T, WANG Y and MENG D (2019) Synthesis and photocatalytic property of cubic phase CdS. *Solid State Sci.* **92** 31–35. https://doi.org/10.1016/j.solidstatesciences.2019.04.004

YASHNI G, AL-GHEETHI A, MOHAMED R, HOSSAIN MS, KAMIL AF and ABIRAMA SHANMUGAN V (2021) Photocatalysis of xenobiotic organic compounds in greywater using zinc oxide nanoparticles: a critical review. *Water Environ. J.* **35** (1) 190–217. https://doi.org/10.1111/wej.12619

ZHENG K, LIU H, NIE C, ZHANG X, HU H, MA G, WANG H and HUO J (2019) Controllable synthesis of honeycomb-structured ZnO nanomaterials for photocatalytic degradation of methylene blue. *Mater. Lett.* **253** 30–33. https://doi.org/10.1016/j.matlet.2019.06.017