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STUDY ON PHOTOCATALYTIC DEGRADATION VIOLET GL2B BY USING SYNTHESIZED $MgZnAl_2O_5$ NANOPARTICLES

Madhusudhana N.[1], Yogendra K.[*1], Mahadevan K. M.[2]

[1]Department of P. G. Studies and Research in Environmental Science, Kuvempu University, Jnana sahyadri, Shankaraghatta, Shivamogga, Karnataka, INDIA

[2] Department of P. G Studies and Research in Chemistry, P.G. Centre Kadur, Kuvempu University, Kadur (T), Chickmagalur (D), Karnataka, INDIA

** Corresponding Author: Yogendra K. Assistant Professor, Department of P. G. Studies and Research in Environmental Science Kuvempu University, Jnana Sahyadri, Shankaraghatta-577451, Shimoga, Karnataka, India*

ABSTRACT

This study investigated the photocatalytic degradation of Violet GL2B, textile azo dye in the incidence of semiconductor powder suspensions under natural sunlight using a $MgZnAl_2O_5$ nanocomposites. A $MgZnAl_2O_5$ powder with a crystalline size in the range of 20-30 nm was effectively prepared using fuel urea in concurrence with solution combustion method. The characterization of the synthesized sample was done through XRD, FE-SEM, TEM, EDXA, and UV-Vis absorption spectroscopy. The effect of operating factors containing dye concentration, photocatalyst dosage and pH on dye degradation efficiency was measured. The photocatalytic activity of the $MgZnAl_2O_5$ nanocomposite at pH 8 was evaluated by degradation of Violet GL2B under natural sunlight. The experimental results have showed that, the degradation efficiency is high for $MgZnAl_2O_5$ nano particle at pH 8. At this pH, the nanoparticle surface is negatively charged by adsorbed OH^- ions, favouring the formation of strong oxidant OH· radicals. Hence, the degradation efficiency is inversely related to the dye concentration.

Key words - *Decolourization, $MgZnAl_2O_5$, Nano-particles, Photocatalyst, Violet GL2B*

I. INTODUCTION

Synthetic organic dyes are one of the extensive groups of pollutants broadly used in the textile, paper, plastic, leather, food, and many other industries, whereas the hazardous effects of organic dyes in waste water have been a foremost concern and currently a crucial menace in the environment due to the significant pollution problems caused by them. About half of these dyes are azo compounds, such as Malachite Green (MG), Methyl Orange (MO), Congo red (CR), and Methylene blue (MB), which contain chromophore (–N=N–) in their molecular

structures [1]. Immense scientific and experimental awareness in the system under contemplation in the environmental facet is due to the opportunity to accomplish the oxidation of organic matter to a high degree of mineralization at moderately low temperatures, mainly in the presence of oxygen, ozone, and hydrogen peroxide with a significant reduction of energy utilization of the process when using sunlight [2].

Among semiconductor photocatalysis is one effective method that has great prospective to manage aqueous organic contaminants or air pollutants by solar light are those that are initiated by nanocomposites of transition metal (iron, copper, chromium, aluminium, etc.), for which photo reactivity is of essential environmental significance[3-5]. The coordination interaction of transition metal ions is particularly important in the photochemical processes of transformation of organic compounds in surface waters. Here in, there is generally extension to higher wavelengths of the spectral range of utilization of solar radiation reaching the Earth's surface [6]. Owing to the mounting complexity of wastewater, in meticulous through the intractable biological, toxic, and organic compounds and the majority promising techniques for water treatment are those based on the use of foremost photocatalytic oxidation processes.

The Advanced Oxidation Processes (AOP's) has been the latest trend in providing the solution to the environmental issues. Along with the Advanced Oxidation Processes, the semiconductor photocatalysis plays a vital role in the degradation of toxic chemicals using solar light [7, 8]. The heterogenic photocatalysis on semiconductor materials has been used on the constantly budding scale in the processes of water purification of pollutants and contaminants of natural and synthetic origin, artificial photosynthesis, mounting techniques of storing the energy of sunlight and photochemical water decomposition, and so onwards [9-11].

Hence, in continuation of our quest in photocatalytic degradation of organic azo dyes by different methods with the use of nanocomposites, we demonstrate a new strategy to introduce $MgZnAl_2O_5$ nanoparticles employing novel precursor using fuel urea in concurrence with solution combustion method. In support to their without using high dilution conditions an easy and rapid photocatalytic application of $MgZnAl_2O_5$ nanoparticles for degradation of Violet GL2B azo dye was screened via, the incidence of semiconductor powder suspensions under natural sunlight.

II.MATERIAL AND METHODS

1. MATERIALS

Chemicals used for the synthesis of $MgZnAl_2O_5$ are Magnesium nitrate ($Mg(NO_3)_2.4H_2O$), Zinc nitrate ($Zn(NO_3)_2.6H_2O$), Aluminium Nitrate ($Al_2(NO_3)_3).9H_2O$) and Urea (NH_2CONH_2), are obtained from Hi media chemicals Mumbai, and used without further purification. The Violet GL2B (λ_{max}=545nm) dye used for the photocatalytic study was purchased from Colourtex Limited, Surat, Gujarat. The structure of the azo dye is given in Figure 1.

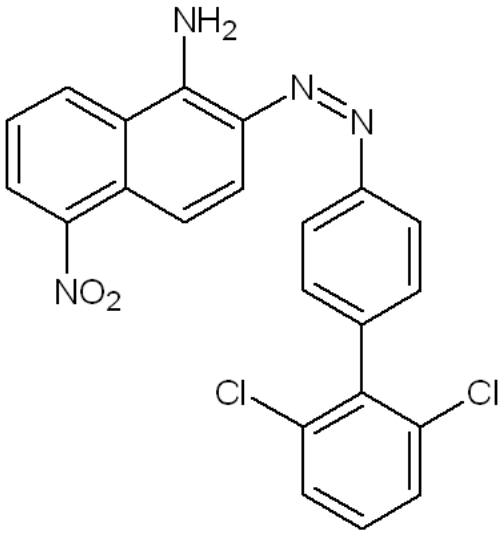

Figure 1: Chemical Structure of Violet GL2B azo dye

2. PHOTOCATALYST PREPARATION

The $MgZnAl_2O_5$ nanoparticle was prepared by solution combustion method by commercially available Magnesium nitrate, zinc nitrate, aluminium nitrate, and Urea as fuel. Stoichiometric compositions of Magnesium nitrate (7.69g), zinc nitrate (8.92g), Aluminium nitrate (22.50g) and urea (1.51g) was taken in a 100 cm^3 silica crucible by using double distilled water. After a while the Crucible was placed in the muffle furnace for calcination, which was preheated to 600°C. According to propellant chemistry the reaction is as follows.

$$3\ Mg(NO_3)_2 + 3\ Zn(NO_3)_2 + 6\ Al(NO_3)_3 + 25\ NH_2CONH_2 \rightarrow 3\ MgZnAl_2O_5 + 50\ H_2O + 25\ CO_2 + 40\ N_2$$

3. PHOTOCATALYST CHARACTERIZATION

UV–visible spectra analysis was performed, the absorption maxima were analyzed at a wavelength of 200–800 nm using UV–visible spectrophotometer (Ocean Optics DH-2000, Department of Nanotechnology, Kuvempu University). Powder X-ray diffraction (XRD) measurements were made using a Bruker D-8 system with Cu radiation ($\lambda = 0.15418$ nm) at 40 kV and 100 mA. To determine the crystal structure, the experimental data were collected in the 2θ range of 10°–80° with a step of 0.02°/0.3 s. The morphology and elemental dispersion on the surface adsorbents were analyzed using scanning electron microscope with energy-dispersive X-ray (SEM-

EDX) FEI-QUANTA FEG 650. The studies on size and shape of $MgZnAl_2O_5$ nanoparticles were performed by transmission electron microscopy (JEOL JEM-2100 TEM).

3. RESULTS AND DISCUSSION

3.1 SCANNING ELECTRON MICROSCOPE WITH ENERGY-DISPERSIVE X-ray (SEM-EDX)

The SEM was recorded for surface morphology of $MgZnAl_2O_5$ nanoparticles. The shapes of the $MgZnAl_2O_5$ photocatalytic particles were determined from the obtained images (Figure 2(A)). The SEM photographs revealed synthesized $MgZnAl_2O_5$ owing a hexagonally edged hydrotalcite-like particles representative of a layered structure [12]. EDX pattern of $MgZnAl_2O_5$ illustrates patterns of 1% carrageenan at pH 4 as shown in Figure 2(B). The percentage weight of $MgZnAl_2O_5$ was found to be of O = 34.28%, Mg = 12.02%, Zn = 28.33% and Al = 25.37%. The results verify the high purity of the nanoparticles produced.

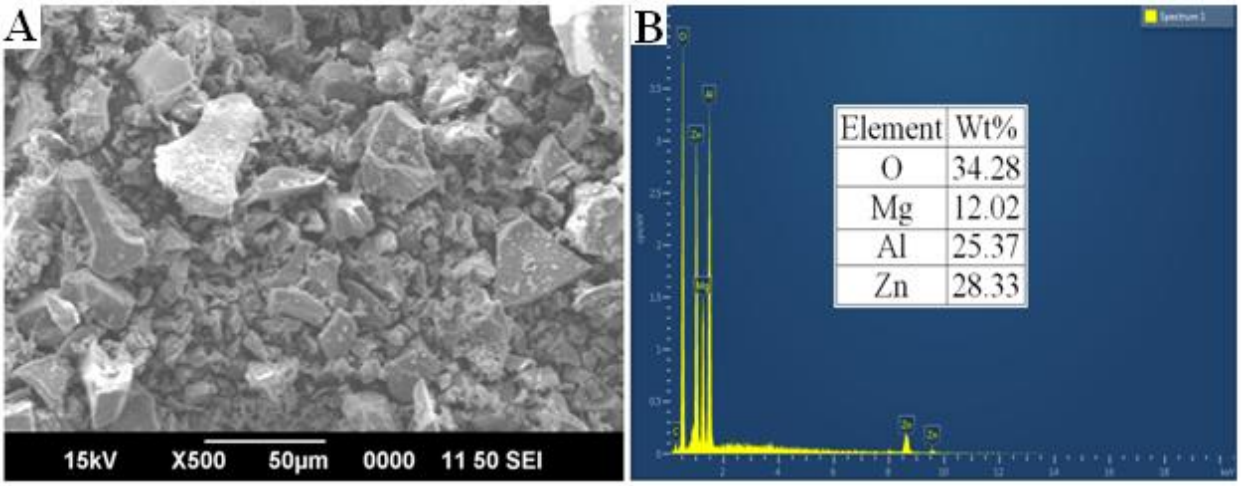

Figure 2: (A) SEM image with magnification of 500; (B) EDX result of $MgZnAl_2O_5$

3.2 X-RAY DIFFRACTION (XRD)

Figure 3 shows the X-ray diffraction pattern of synthesized $MgZnAl_2O_5$ nanoparticles. Numerous dominant 2θ peaks were observed. The X-ray diffraction pattern crystalline nature of resulting materials has apparently shown for the individual diffraction pattern analogous to the (003), (006), (009), (110) and (113) planes of $MgZnAl_2O_5$, showing the form of a hydrotalcite-like structure with crystalline phase matching with the XRD library JCPDS 22-0700 data. The strong and sharp diffraction peaks inferred that the as prepared $MgZnAl_2O_5$ nanoparticles possess good crystalline nature. The size of the nanoparticles was calculated through the Scherer's formula, $D=0.94\lambda/\beta \cos\theta$, Where D is the average crystal size, β is the half-height width of the diffraction peak, θ is the diffraction angle, and λ is the X-ray wavelength (0.1541 nm). The average particle size of the photocatalyst was 25 nm.

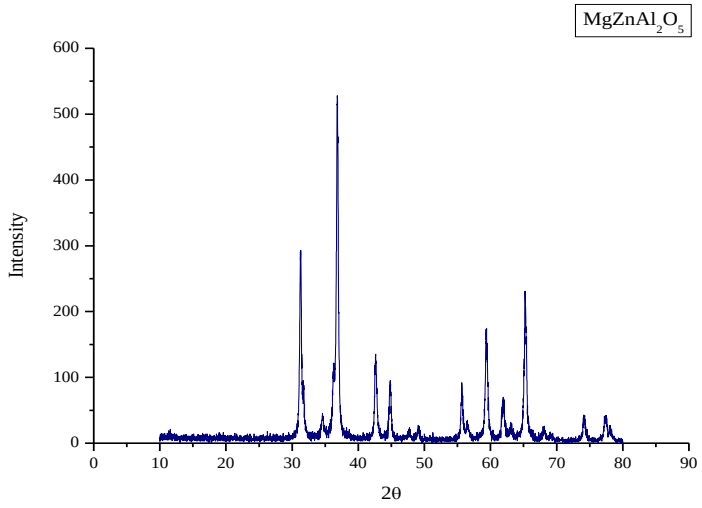

Figure 3: XRD patterns for the prepared $MgZnAl_2O_5$

3.3 UV-Vis ABSORPTION SPECTROSCOPY

The optical property of the synthesized $MgZnAl_2O_5$ was investigated via UV–Vis diffuse reflectance spectroscopy, which is shown in Figure 4. It clearly shows that, their absorption edges are located at 397.57 nm, suggesting that the photocatalysts can be excited by visible light irradiation. The color of the photocatalyst is pale yellow, which accord with its absorption spectrum. The strong absorption spectrum reveals that the visible light absorption is not due to the transition from the impurity but due to band-gap transition.

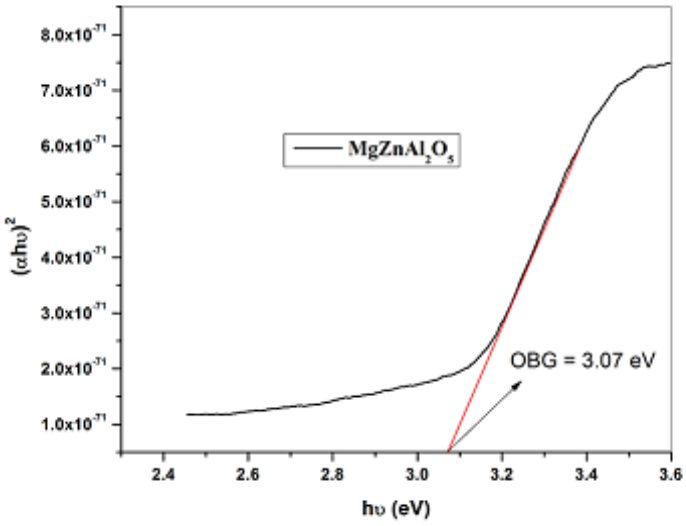

Figure 4: UV- DRS spectrum of synthesized $MgZnAl_2O_5$

The band gap energy of the photo catalyst was determined from the following formula, Eg = 1240/ λ eV, Where, Eg is the band gap energy (eV), his Planck's constant (6.626 x 10^{-34}Js), C is the light velocity (3 x 10^{8} m/s) and λ is the wavelength (nm) [13]. According to this formula, the band gap energy of synthesized $MgZnAl_2O_5$ was estimated to be 3.1 eV respectively, similar values were reported in literatures [12].

The absorbance for the dye solution was determined by using the instrument UV-Vis spectrophotometer. λ_{max} of VGL2B was found to be 545nm. All the experiments were conducted under direct sunlight. A known concentration of dye solution was prepared by dissolving 0.03g of VGL2B azo dye in 1000ml double distilled water and investigated for its decolourization in the presence of $MgZnAl_2O_5$ nano-particle at different catalyst dosages and pH levels. After the experiments, the extent of decolourization was estimated by recording absorbance of the dye solution using UV-VIS spectrophotometer 169 in order to get the optimum catalyst dose. The experiments were repeated at different pH levels (from 2 to 11) for the 100ml of same standard dye solutions with the optimum catalyst dose. The percentage of decolourization was calculated by using the equation, Decolourization = $(A_0 - A_t)/ A_0 \times 100$. Where, A_0 is the initial absorbance of the dye solution, A_t is absorbance at time interval 't' i.e., after 120 minutes.

3.4 TRANSMISSION ELECTRON MICROSCOPY (TEM)

The TEM photograph of the synthesized $MgZnAl_2O_5$ nano-composites is given in Figure 5. The photograph shows that the semiconductor powder suspensions are of an equable distribution except for a few aggregated particulates. The average grain size calculated by proportion of the photograph is about 20-30 nm, which is uniform with the result of the XRD patterns.

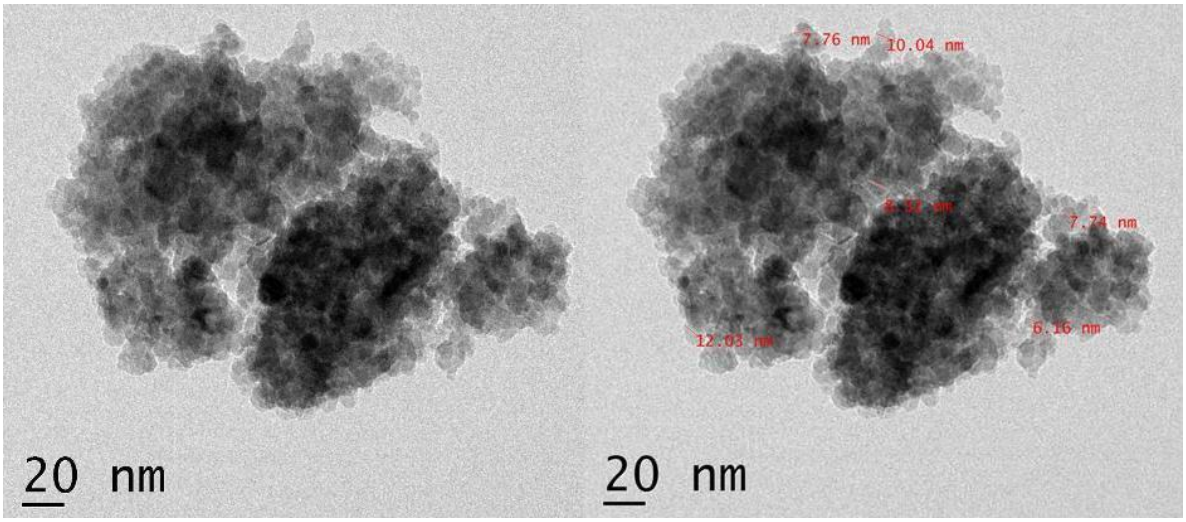

Figure 5: The SEM images of synthesized $MgZnAl_2O_5$

3.5 MECHANISM OF THE PHOTOCATALYTIC DEGRADATION

$MgZnAl_2O_5 + h\nu \rightarrow (e^{-CB} + h^{+VB})$……..(Eq. 1)

Step 1: Nanoparticle molecules get excited and transfer electrons to the conduction band.

$e^{-CB} + O_2 \rightarrow O_2^{\bullet-}$ ……(Eq. 2)

Step 2: An electron in the conduction band of the nanoparticles can reduce molecular oxygen and produce the super oxide radical.

$H_2O + O_2^{\bullet-} \rightarrow OOH^{\bullet} + OH^{-}$ ……..(Eq. 3)

$2OOH^{\bullet} \rightarrow O_2 + H_2O_2$ ……(Eq. 4)

$O_2^{\bullet-}$ + Violet GL2B → Violet GL2B $OO^{\bullet-}$ ……(Eq. 5)

Step 3: Molecular oxygen, adsorbed on the surface of the photocatalysts prevents the hole-electron pair recombination process [14]. Recombination of hole-electron pair decreases the rate of photocatalytic degradation. This radical may form hydrogen peroxide or organic peroxide in the presence of oxygen and organic molecule.

$OOH^{\bullet} + H_2O + e^{-CB} \rightarrow H_2O_2 + OH^{-}$ ……(Eq. 6)

Step 4: Hydrogen peroxide can be generated in another path.

$H_2O_2 + e^{-CB} \rightarrow OH^{\bullet} + OH^{-}$ ……(Eq. 7)

$H_2O_2 + O_2^{\bullet-} \rightarrow OH^{\bullet} + OH^{-} + O_2$ ……(Eq. 8)

Step 5: Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents.

$OH^{\bullet}$ / $O_2^{\bullet-}$/ $MgZnAl_2O_5^{\bullet+}$ + Violet GL2B → Violet GL2B degradation ……(Eq. 9)

Step 6: The radicals produced are capable of attacking dye molecules and degrade them.

3.6 EFFECT OF CATALYST CONCENTRATION ON VIOLET GL2B

The effect of catalyst concentration on the photocatalytic degradation was studied over a range of the catalyst amount from 0.1 to 1g/100ml for Violet GL2B. The synthesized nanoparticles have shown appreciable results. The $MgZnAl_2O_5$ (urea) with the nanoparticle of size 25 nm has shown 96.36% degradation. Since, the photodegradation was most effective at 0.7g/100ml in 120 minutes for $MgZnAl_2O_5$ nanoparticle dosages showed in (Figure. 6) (Photo 1), further experiments were continued with same dosages.

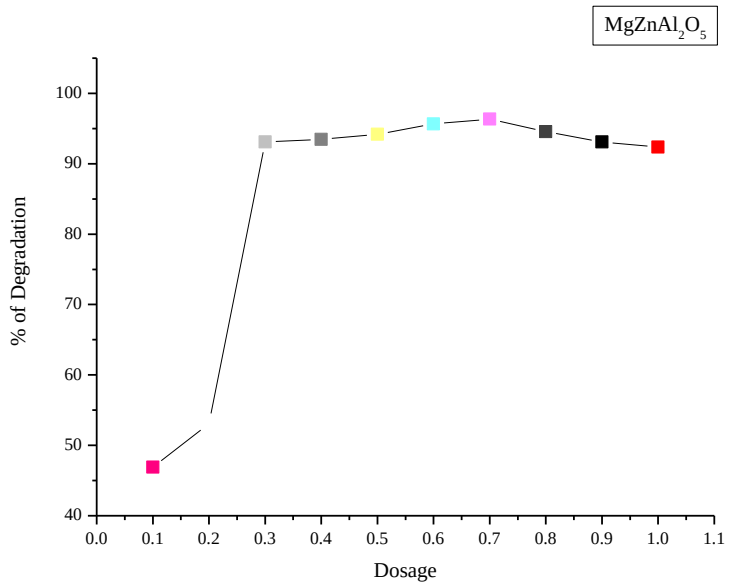

Figure 6: Effect of catalyst concentration on Violet GL2B at 120 minutes [Violet GL2B =30 ppm, pH=7, $MgZnAl_2O_5$]

Photo 1: Effect of catalyst concentration on Violet GL2B at 120 minutes [Violet GL2B =30 ppm, pH=7, $MgZnAl_2O_5$]

The photocatalytic activity results in creating more number of H^+ ions and e^{-CB} by generating $OH^{\bullet}$ radicals which act as the main oxidizing species. In this result, maximum degradation is mainly due to the availability of number active sites on the nano-particle surface and sunlight irradiation into the suspension, which is because of the increased scattering of light and screening effect. The more increase in the catalyst amount i.e., above 0.8g/100ml photocatalytic degradation is decreased by small extent. This is mainly because coincide of adsorption sites and also because of overcrowding owing to collision with ground state catalysts [15].

3.7 EFFECT OF pH ON VIOLET GL2B

According to many literatures, pH value will be the major criteria for the rate of photocatalytic process. Hence, experiments were conducted to find the optimal pH for

decolourization of VGL2B. The results showed that pH significantly affected the degradation efficiency (Figure 7) (Photo 2).

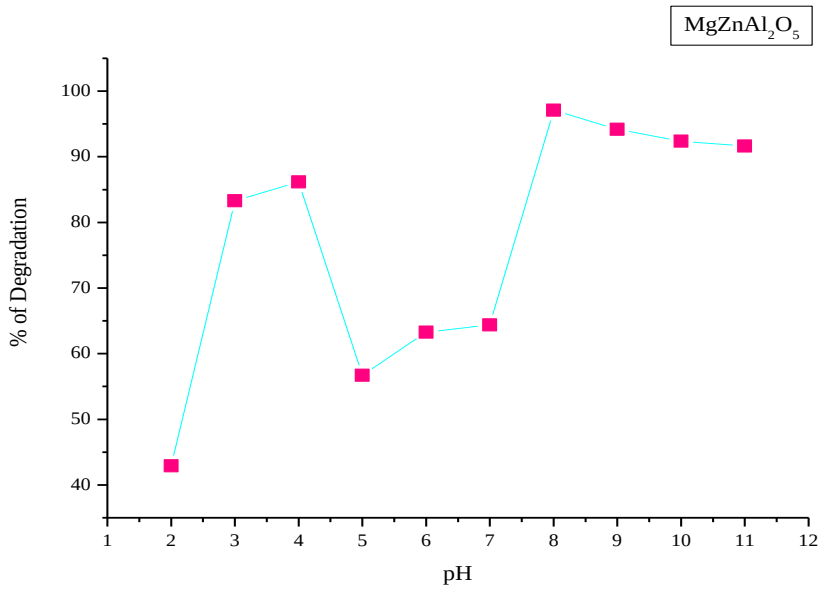

Figure 7: Effect of pH on Violet GL2B at 120 minutes [Violet GL2B =30 ppm, $MgZnAl_2O_5$]

The degradation rate of Violet GL2B for $MgZnAl_2O_5$ the degradation of the Violet GL2B increased from 42.90% to 97.09% from pH 2 to 8 and decreased 91.63% at pH 11 in 120 minutes for 0.7g/100ml. The maximum degradation rate for the nanoparticle was achieved 97.09% at pH 8 [16].

Photo 2: Effect of pH on Violet GL2B at 120 minutes [Violet GL2B = 30 ppm, $MgZnAl_2O_5$]

The maximum degradation rate for $MgZnAl_2O_5$ nanoparticle was achieved at pH 8. More efficient formation of hydroxyl radicals was found to occur in alkaline medium. Excess of hydroxyl anions increases the formation of $OH^{\bullet}$ radicals. These $OH^{\bullet}$ radicals are the main oxidizing species responsible for photocatalytic degradation [17,

18]. At pH greater than 8, the decrease in degradation efficiency can be explained on the basis of amphoteric nature of $MgZnAl_2O_5$ photocatalyst. Here catalyst surface becomes negatively charged for higher pH values causes the electrostatic repulsion between the catalyst and negatively charged dyes [16].

3.8 EFFECT OF INITIAL DYE CONCENTRATION

The experiments were conducted to study the effect of initial dye concentration by varying the Violet GL2B concentration from 30, 50 and 70 ppm respectively (Photo 3). The results obtained for $MgZnAl_2O_5$ is 97.09% for 30 ppm, 79.87% for 50 ppm and 75.57% for 70 ppm respectively (Figure 8).

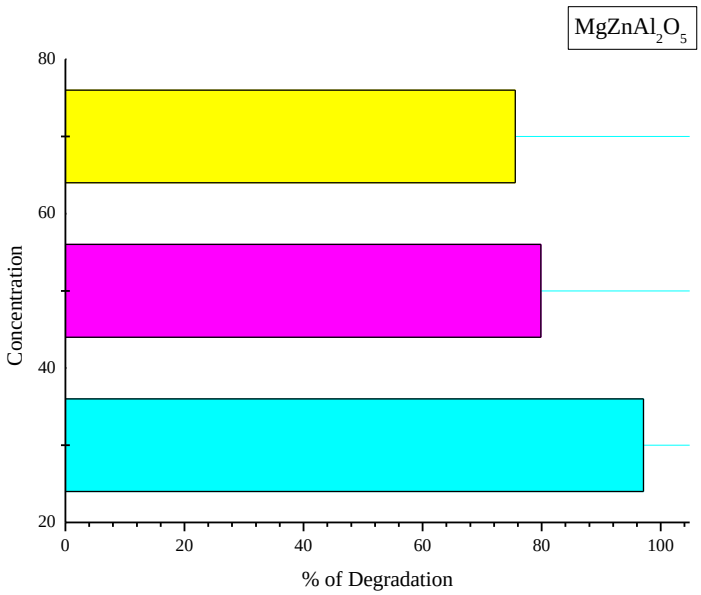

Figure 8: Effect of initial dye concentration on the photocatalytic degradation of Violet GL2B [$MgZnAl_2O_5$ g/pH=0.7/8 and Violet GL2B = (30, 50 and 70) ppm]

Photo 3: Effect of initial dye concentration on the photocatalytic degradation of Violet GL2B [$MgZnAl_2O_5$ g/pH=0.7/8 and Violet GL2B = (30, 50 and 70) ppm]

These experiments illustrated that the degradation efficiency was directly affected by the concentration. The decrease in the degradation with an increase in dye concentration was ascribed to the equilibrium adsorption of dye on the catalyst surface which results in a decrease in the active sites [17]. According to Beer Lambert law, as the initial dye concentration increases, the path length of photons entering the solution decreases. This results in the lower photon absorption of the catalyst particles, and consequently decrease photocatalytic reaction rate [18].

3.9 EFFECT OF SUNLIGHT IRRADIATION ON VIOLET GL2B

The photocatalytic degradation of Violet GL2B azo dye (30mg/L) under two different experimental conditions were examined, i.e., through sunlight alone, dye/dark/catalyst, and dye/sunlight/catalyst. Violet GL2B azo dye solution when exposed directly to the sunlight without the catalyst, the degradation was found to be zero during the entire experiments. The degradation rate was found to increase with increase in irradiation time, for dye/sunlight/ $MgZnAl_2O_5$ showed 97.09%, and for dye/dark/ $MgZnAl_2O_5$ 38.90% was recorded (Figure 9). These results clearly indicate that photodegradation occurs most efficiently in the presence of sunlight (Photo 4) [19, 20].

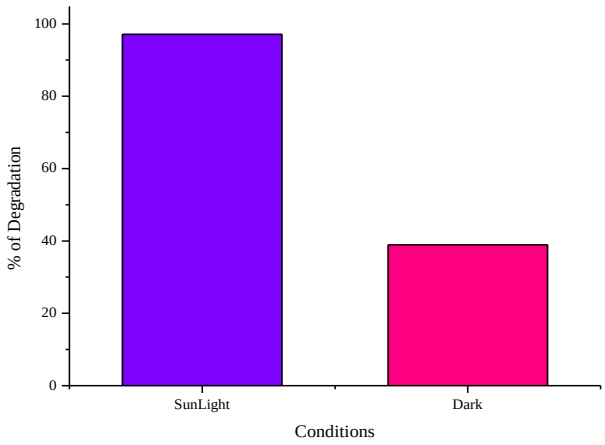

Figure 9: Effect of sunlight irradiation with respect to Dark condition on photocatalytic degradation of Violet GL2B in 120 minutes

Photo 4: Effect of sunlight irradiation with respect to Dark condition on photocatalytic degradation of Violet GL2B in 120 minutes

4. CONCLUSIONS

Photocatalysis is a very effective method for the degradation of azo dyes. In this study, Magnesium zinc aluminate nanoparticles were synthesized and characterized by SEM and XRD studies. It was observed that the synthesized Magnesium zinc aluminate (average particle size 25 nm) is photosensitive and effective in degrading selected azo dye (Violet GL2B) completely in a short interval of time (120 minutes). From this experiment, we can conclude that the $MgZnAl_2O_5$ did in fact degrade the dye over short interval of time with the help of sunlight. Even though the result was achieved more than 97%, we still believe that if this experiment was done over a longer period of time that the concentration of the dyes would have been zero. This protocol developed may be employed effectively in the treatment of textile dye effluents which are hazardous to the environment.

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