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SYNTHESIS AND APPALICATION OF COMPLEX METAL OXIDE NANO-PARTICLE TO THE PHOTOCATALYTIC DECOLOURIZATION OF VIOLET GL2B AZO DYE

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ABSTRACT

Azo dyes present in textile wastewater require a proper technique for their removal, due to their negative environmental and health effects. Although there are several ways to treat such wastewater, this study is focused on photocatalytic degradation on $MgZnAl_2O_5$ nano-catalyst. Violet GL2B (VGL2B) dye was used for photocatalytic degradation studies at 30mg/L concentration. Colour degradation was monitored using UV-Vis spectroscopy. Maximum colour removal was observed for the azo dye. It is found that, degradation rate of VGL2B for $MgZnAl_2O_5$ (acetamide) the degradation was found to be 98.18% at pH 11 in 120 minutes for 0.7g/100ml. Also the results revealed that, the degradation facility is directly bear upon by the concentration of dye solution.

Keywords: Photocatalyst, Degradation, Nano-particles, $MgZnAl_2O_5$, Violet GL2B

I. INTRODUCTION

Different types of dyes are used in many industries such as textile, paint, ink, plastics and cosmetics [1]. About half of global production of synthetic textile dyes (7,00,000 tons per year) are classified into azo compounds that have the chromophore of -N=N- unit in their molecular structure and over 15% of the textile dyes are lost in wastewater stream during dyeing operation[2]. Dyes concentration in wastewaters is usually lower than any other chemical found in these wastewaters, but due to their strong colour they are visible even at very low concentrations, thus causing serious aesthetic and pollution problems in wastewater disposal [3] [4].

The problem of colour in textile dye house effluent and the possible problems associated with the discharge of dyes and dye degradation products are of concern. Traditional methods for dealing with this kind of wastewater

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are usually the biological, physical and chemical techniques. It has been widely reported that many dye chemicals are difficult to degrade using conventional biological treatment processes [5] [6].

In recent years, much attention is given to photocatalytic decolourization of azo dyes, which has been widely explored for the decolourization of various dyes using different nano-particles. Since, it is cost-effective alternate for the purification of dye containing wastewater [7]. Photocatalysis, which is one of the Advanced Oxidation Processes, is a new method used to mineralize dye compounds [8] and also semiconducting material absorbs light energy more than or equal to its band gap, thereby generating holes and electrons which further releases free-radicals in the system to oxidize the substrate. The resultant free-radicals are very efficient oxidizers of organic compounds [9] [10] [11]. The photocatalytic oxidation technology is frequently used for the complete degradation of organic micro- pollutants (dyes) in water, utilizing sunlight and UV radiation as energy sources [12].

The main objective of the present investigation is to study the efficiency of newly synthesized Magnesium zinc aluminate nano-particles in colour removal of Violet GL2B, an extensively used azo dye. The effect of pH and the different dosage of Magnesium zinc aluminate nano-particles as catalyst on the decolourization of Violet GL2B dye were also studied.

II. MATERIALS AND METHODS

2.1 Materials and Reagents

The 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 $Al_2(NO_3)_3\ 9H_2O$) (95% AR) and Acetamide (CH_3NOCH_2) (99% AR), are obtained from Hi-media chemicals Mumbai, and used without further purification. The Violet GL2B azo dye used for the photocatalytic study was purchased from Colourtex Limited, Surat, Gujarat. The structure of the azo dye is given in Fig 1.

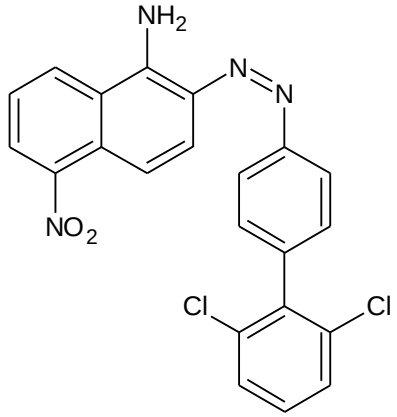

Fig 1: Chemical Structure of Violet GL2B dye

2.2. Synthesis of Magnesium Zinc Aluminate Nano-Particles

The Magnesium Zinc aluminate nano-particle was prepared by solution combustion method using procured Magnesium nitrate, zinc nitrate, aluminium nitrate, and acetamide has fuel. Stochiometric compositions of Magnesium nitrate (2.82g), zinc nitrate (3.27g), Aluminium nitrate (8.25g) and acetmide (2.95g) was taken in a

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silica crucible (with volume of 100 cm3) using distilled water. Crucible was then introduced into the muffle furnace for calcination which was preheated to 500°C. According to propellant chemistry the reaction is as follows;

$11Mg(NO_3)_2 + 11Zn(NO_3)_2 + 22Al(NO_3)_3 + 50CH_3CONH_2 \rightarrow 11MgZnAl_2O_5 + 125\ H_2O + 100CO_2 + 55N_2$

2.3 Characterization of Synthesized $Mgznal_2o_5$ Nano-Particle

2.3.1 X-Ray Diffraction (XRD)

The XRD was performed by powder X-ray diffraction (Rigaku diffractometer) using Cu-Kα radiation (1.54 Å) in a θ-2θ configuration. The pattern obtained from the XRD analysis of the prepared $MgZnAl_2O_5$ nano-particle is presented in Figure 2. According to the Debye-Scherrer's formula D = Kλ/ (β Cosθ), where, K is the Scherrer's constant, λ the X-ray wavelength, β is the full width at half-maximum, and θ is the Bragg diffraction angle calculated using the Debye-Scherrer's formula. The average crystallite size of $MgZnAl_2O_5$ was found to be 10nm.

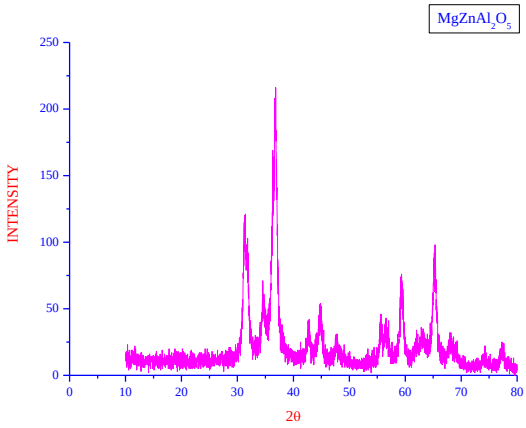

Fig 2: X-Ray Diffraction of $MgZnAl_2O_5$ (acetamide)

2.3.2. Scanning Electron Micrograph (SEM)

Scanning Electron Microscope pictures have been taken for the $MgZnAl_2O_5$ nano-particles. A crystal like structures was observed which are compactly packed in groups. Many uneven sized structures were observed by the SEM images. It is also observed that the particle structures are irregular with the average size 10nm (Fig. 3).

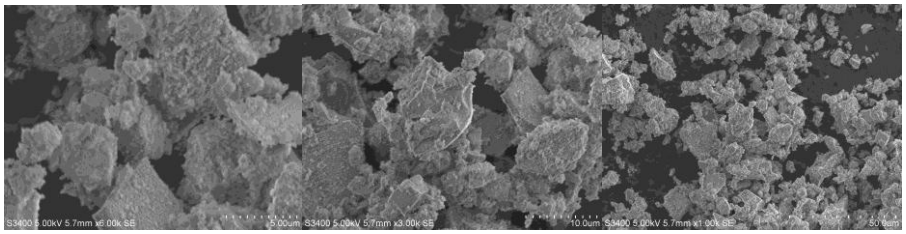

Fig 3: SEM Photograph of $MgZnAl_2O_5$ (acetamide)

2.3.3. UV-V is Absorption Spectroscopy

UV-Vis absorption spectra of as prepared $MgZnAl_2O_5$ were examined by using UV-Vis spectrophotometer of family Ocean Optics DH- 2000 by wavelength range from 200-800 nm at Research Laboratory, Department of

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Nanotechnology, Kuvempu University. According to the reflectance spectrum of $MgZnAl_2O_5$ photocatalyst the band edge was found to be at 386.08 nm and the band gap was calculated by Planck's equation as follows;

Band gap energy Eg = (h × C/λ); Where, h= Planks Constant; C= Velocity of light (Speed of light);

λ= Wavelength of light; h= 4.135×10^{-15} eV; C=3×10^{8} m/s, λ= ---------× 10^{-9} nm;

Band gap energy (eV) = $4.135 \times 10^{-15} \times 3 \times 10^{8} \times 10^{9}$; eV= (1240/ Wavelength (nm));

eV = (1240/ 386.08) = 3.2 eV

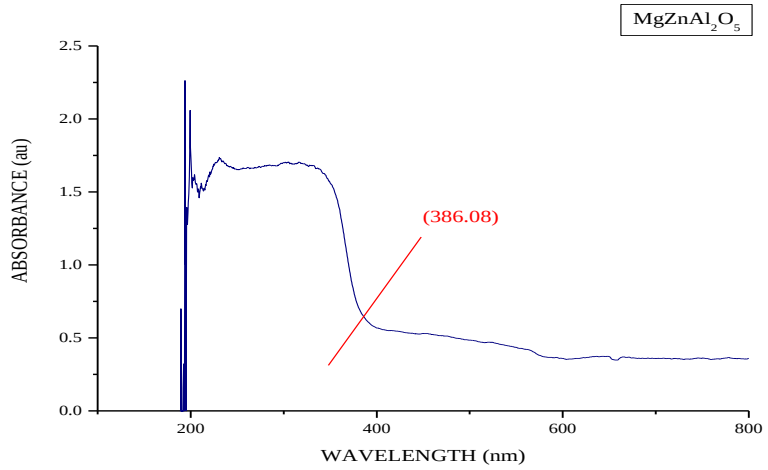

Fig. 4: UV-Vis absorption spectra of $MgZnAl_2O_5$

The band gap of $MgZnAl_2O_5$ is 3.2 eV. Hence band gap of the semiconductor is particle size dependent.

III. RESULT AND DISCUSSION

3.1. Experimental Procedure

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,

$$\text{Decolourization} = (A_0 - A_t)/ A_0 \times 100$$

Where, A_0 is the initial absorbance of the dye solution

A_t is absorbance at time interval 't' i.e., after 120 minutes.

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3.2 Mechanism Of the Photocatalytic Degradation

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

Step 1: Nano-particle 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 nano-particles 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 [13]. 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.

$O\ OH^{\bullet} + H_2O + e^-_{CB} \rightarrow H_2O_2 + OH^-$ (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.

3.3. 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 nano-particles have shown appreciable results. The $MgZnAl_2O_5$ (acetamide) with the nano-particle size 10 nm has shown 96.72% degradation. Since, the photodegradation was most effective at 0.7g/100ml in 120 minutes for $MgZnAl_2O_5$ (acetamide) nano-particle dosages showed in (Fig. 5) (Photo 1), further experiments were continued with same dosages.

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 [14].

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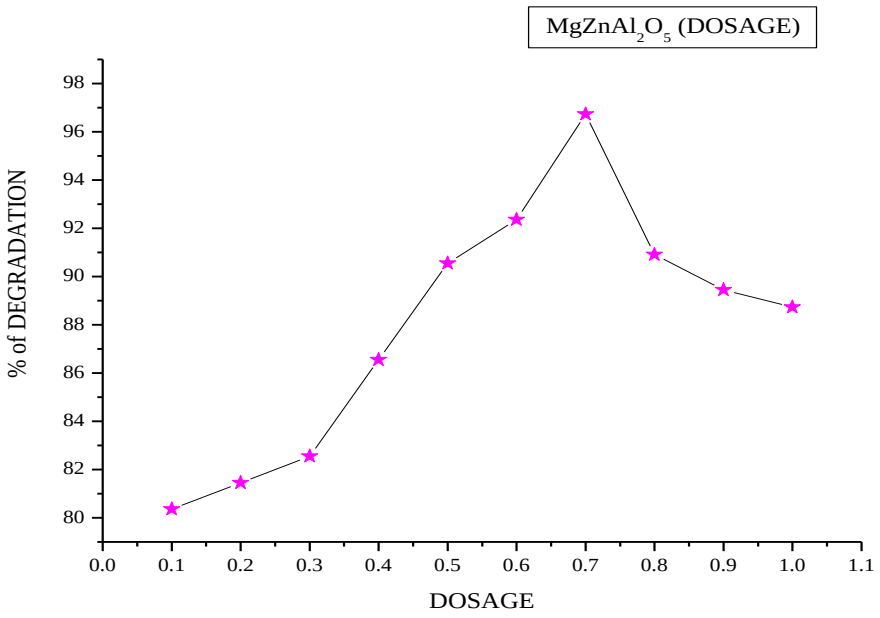

Fig. 5: Effect of catalyst concentration on Violet GL2B at 120 minutes [Violet GL2B =30 ppm, pH=7, $MgZnAl_2O_5$ (acetamide)]

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

3.4 Effect of pH on Violet GL2B

In order to study the effect of pH on the degradation efficiency of $MgZnAl_2O_5$ (acetamide) as catalyst, the experiments were carried out at pH ranging from 2 to11. The results showed that pH significantly affected the degradation efficiency (Fig. 6) (Photo 2). The degradation rate of Violet GL2B for $MgZnAl_2O_5$ (acetamide) the degradation of the Violet GL2B increased from 38.90% to 98.18% from pH 2 to 11 in 120 minutes for 0.7g/100ml.

The maximum degradation rate for $MgZnAl_2O_5$ nano-particle was achieved at pH 11. 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 [15].

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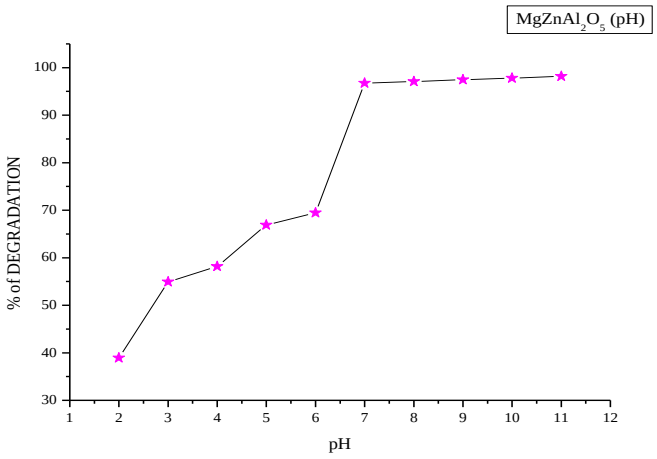

Fig. 6: Effect of pH on Violet GL2B at 120 minutes [Violet GL2B =30 ppm, $MgZnAl_2O_5$ (acetamide)]

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

3.5 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 $MgZnAl_2O_5$ (acetamide) is 98.18% for 30ppm, 90.35% for 50ppm and 85.43% for 70ppm respectively (Fig 7). 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 [16]. 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 [17].

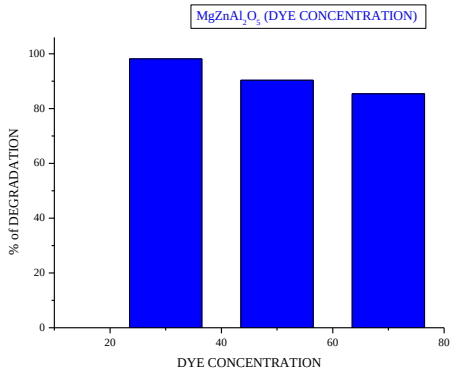

Fig 7: Effect of initial dye concentration on the photocatalytic degradation of Violet GL2B [$MgZnAl_2O_5$ (acetamide) g/pH=0.7/11 and Violet GL2B = (30, 50 and 70) ppm]

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Photo 3: Effect of initial dye concentration on the photocatalytic degradation of Violet GL2B [$MgZnAl_2O_5$ (acetamide) g/pH=0.7/11 and Violet GL2B = (30, 50 and 70) ppm]

3.6 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 for the 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/ $MgZnAl_2O_5$ (acetamide) showed 98.18%, dye and for dye/dark/ $MgZnAl_2O_5$ (acetamide) 72.72% was recorded (Fig 8). These results clearly indicate that photodegradation occurs most efficiently in the presence of sunlight (Photo 4) [18] [19].

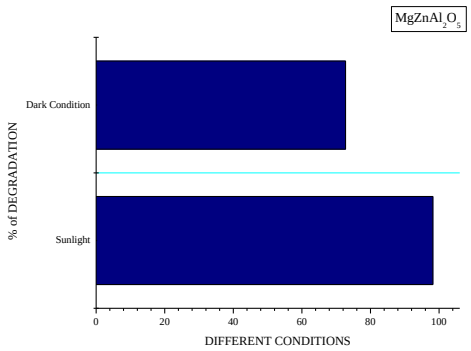

Fig. 8: Effect of sunlight irradiation with respect to Dark condition on photocatalytic degradation of Violet GL2B in 120 minutes.

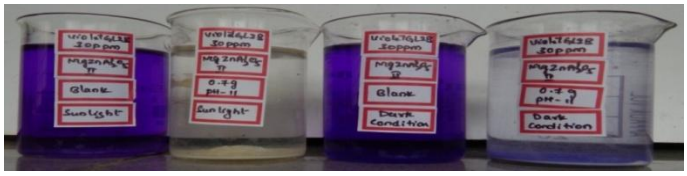

Photo 4: Effect of sunlight irradiation with respect to Dark condition on photocatalytic degradation of Violet GL2B in 120 minutes.

IV. CONCLUSION

Photocatalysis is a very effective method for the degradation of azo dyes. In this study, Magnesium zinc aluminate nano-particles were synthesized and characterized by SEM and XRD studies. It was observed that the synthesized Magnesium zinc aluminate (average particle size 10 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 98%, we still believe that if this experiment

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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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