https://doi.org/10.46344/JBINO.2022.v11i03.10

A PRELIMINARY INVESTIGATION ON PHOTOCATALYTIC DEGRADATION OF CORALENE BLUE BGFS DYE BY USING SYNTHESIZED MAGNESIUM ZINC ALUMINATE NANOPARTICLE IN PRESENCE OF UV LIGHT

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ABSTRACT

In the process of dyeing and finishing operations in industries, consumes considerable amount of water. Dyes extensively used are found to be toxic and considered to be resistant to biodegradation. A detailed investigation was done on photocatalytic degradation for selected dye solutions of Coralene Blue BGFS. The $MgZnAl_2O_5$ nanoparticles were synthesized by using fuel NH_2CONH_2 through solution combustion method. The synthesized nanoparticles were characterized by using X-ray diffraction (XRD), Scanning Electron Micrograph (SEM) and UV absorbance spectroscopy. The average nanoparticle size was found to be 23 nm. The band gap of the nanoparticle $MgZnAl_2O_5$ was found to be 3.0 eV. The application of the nanoparticle was tested for photocatalytic degradation by varying parameters such as catalyst concentration, pH and dye concentration and effect of UV-light at 254nm. The experimental results showed maximum photodegradation of Coralene Blue BGFS was found to be 98.12% at pH 10 in presence of UV light.

Keywords: Coralene Blue BGFS, $MgZnAl_2O_5$, Nanoparticle, photocatalyst, Photodegradation, UV light.

1.Introduction

Water is life and life on earth exists because of water. Our existence is dependent on water. Water accounts for two-third of human body weight. This indicates that water is a vital ingredient for human survival and attention to water pollution is important (Aghalari and Jafarian 2017; Dai *et. al.*, 2016). Rapid industrialization, urbanization, modern agricultural practices and population explosion increased the demand of water, which lead to water scarcity these days. In industries water utilization and wastewater generations are maximum. Moreover, wastewater generated in industries is the main reason for surface water pollution (Kumar, 2018). The pollutants alter the physical, chemical and biological nature of the surrounding water bodies, which leads to eutrophication. Industries play a major role in water pollution by producing billions of liters of wastewater every day. In India, 13,468 MLD of wastewater is generating (Britto Jeyakumar and Raju 2019). Most of the pollutants produced by the industries are non-biodegradable waste, which can induce long-term and short-term impacts on living organisms (Chaudhry and Malik 2017).

Textile effluents contain major content of dye molecules as well as toxic chemicals and contribute to water pollution. An average textile industry consumes 1.6 million liters of water to produce 8,000 kg of fabrics per day (Akarslana and Demiralay 2015; Toprak and Anis 2017). The textile effluent contains a wide range of pollutants which includes wastes like heavy metals, various acids, alkalis, solid wastes, pesticides, pharmaceuticals and dyes which affect the surrounding water bodies (Rana and Reddy 2016; Singh *et al,* 2018; Yadav *et al,* 2016). The untreated effluents from the textile industries are rich in colour, pH, suspended solids (SS), biological oxygen demand (BOD), salts, chemical oxygen demand (COD), metals and temperature (Lellis *et al,* 2019; Ho *et al,* 2019; Yaseen and Scholz 2019). The untreated effluents containing dye molecules damage the aquatic organisms present in the water bodies (Alahiane *et al,* 2014; Mia *et al,* 2019). The effluents not only pollute the surrounding water bodies, but also affect the soil, sediment, and surface water (Yaseen and Scholz 2019).

Dyes have a long history and constitute an important component in our daily lives. The dye industry began by using natural plant and insect sources, and then rapidly turned to synthetic manufacturing processes. Unfortunately, several of the synthetic dyes, especially azo dyes, have been found to be toxic and mutagenic and are banned throughout the world. However, because of their low cost and other desirable properties, the use and manufacture of azo dyes continues even today.

Since the coloured dye pollutants could be completely degraded into harmless matters by photocatalytic method under the normal temperature and air pressure, scientists have confirmed that in the near future photocatalysis would become one of the most effective means in dealing with various kinds of industrial wastewater. The initial step in the metal oxides for the

photocatalytic degradation is proposed to involve the generation of a (e^-/h^+) pair, leading to the formation of hydroxyl radicals (OH•), superoxide anion radical ($O_2^{\bullet-}$), and hydroperoxyl radicals (•OOH). These radicals are the oxidizing species in the photocatalytic oxidation processes. The efficiency of the dye degradation depends on the concentration of the oxygen molecules, which either scavenge the conduction band electrons (e^{-CB}) or prevent the recombination of (e^-/h^+). The adsorbed dye molecules, leading to the formation of dye radical anions and the degradation of the dye, can pick up the electron in the conduction band (Deepa *et. al*., 2014).

MATERIALS AND METHODS

Chemical reagents:

The Coralene Blue BGFS azo dye used for the photocatalytic study was procured from colurtex, Pvt. Ltd. Gujarat.

Chemical reagents:

The chemicals used for the synthesis of Magnesium Zinc Aluminate ($MgZnAl_2O_5$) nanoparticles are [Magnesium Nitrate $Mg(NO_3)_2$. $6H_2O$ (99-102% AR)] [Zinc Nitrate $Zn(NO_3)_2$. $6H_20$ (99.0% AR)] [Aluminum Nitrate $Al(NO_3)_3$. (98.0% AR)] and fuel [Urea NH_2CONH_2 (99.5%)] purchased from Hi-media Pvt. Ltd, Mumbai.

Synthesis of $MgZnAl_2O_5$:

The nanoparticles were prepared by using solution combustion synthesis method. A mixture of stoichiometric amounts of Magnesium nitrate (7.69g), Zinc nitrate (8.92g), Aluminium nitrate (22.50g) and Urea (1.51g) was dissolved in a minimum quantity of water in a silica crucible (100 mm size). The mixture solution was introduced into the muffle furnace which was preheated at 600°C. The solution undergoes dehydration and catches fire by spreading throughout the mass, finally yielding $MgZnAl_2O_5$ nanoparticles. The obtained $MgZnAl_2O_5$ was crushed in a mortar and pestle to make the $MgZnAl_2O_5$ amorphous. Thus, $MgZnAl_2O_5$ is formed. According to propellant chemistry the reaction is as shown. (Madhusudhana *et al,* 2011).

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

(Eq.1)

Characterization of nanoparticles

X-ray diffraction technique (XRD) :

X-ray diffraction is a versatile, nondestructive that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD was performed by Rigaku diffractometer using Cu-K_α radiation (1.5406 Å) in a θ-2θ configuration (Girase *et al,* 2011). According to the Debye Scherrer's formula;

$$D = K\lambda/\beta COS\theta$$

(Eq.2)

Where D = Thickness of the crystallite

K = 0.90 the Scherrer's constant (dependent on crystallite shape)

λ = X-ray wavelength

β = the peak width at half-maximum (FWHM)

θ = the Bragg diffraction angle.

According to the XRD the average crystallite size of $MgZnAl_2O_5$was found to be 23nm

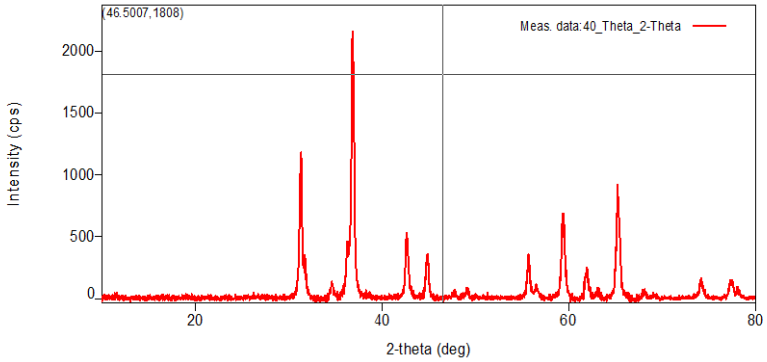

Fig 1: X-Ray diffraction of $MgZnAl_2O_5$

Scanning Electron Microscope (SEM):

The SEM is a microscope that uses electrons instead of light to form an image. The technique in which SEM is used to characterize the materials is called Scanning Electron Microscopy.

SEM study of $MgZnAl_2O$

Photo 1 illustrates SEM photographs of single crystals of $MgZnAl_2O_5$. The photographs revealed combination of cluster structure morphology with plate like structures, which looks like a colony. The enlarged image shows the uneven size and shape of the different nanoparticles, which also revels the thick attachment and agglomeration of nanoparticles over one another.

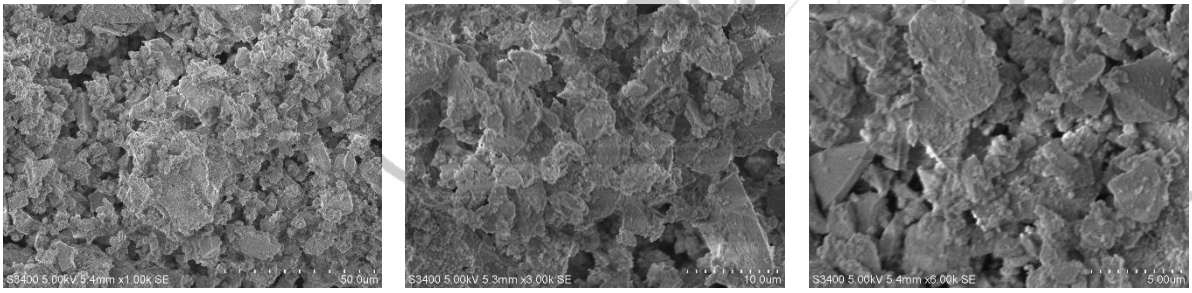

Photo 1: SEM photographs of $MgZnAl_2O_5$ nanoparticles

UV absorbance spectroscopy

Absorption spectra of the $MgZnAl_2O_5$ metal oxide nanoparticle was recorded using UV-Vis spectrophotometer (Systronics–169) over the wavelength range 200-800 nm at Nano Research Laboratory, Department of Nanotechnology, Kuvempu University. From this spectrum, it has been inferred that, the nanoparticles have sufficient transmission in the entire visible and IR region. The band gap energy of the $MgZnAl_2O_5$ nanoparticle was calculated using the following simple conversion equation. The band gap equation is calculated using the Planck's equation as follows.

Band Gap Energy $E = h \times C/\lambda$ (Eq.3)

Where,

h= Planck's 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 × 10^{-15} eV × 3 × 10^{8} × 10^{9}

Band gap energy (eV) = (1240/ wavelength (nm))

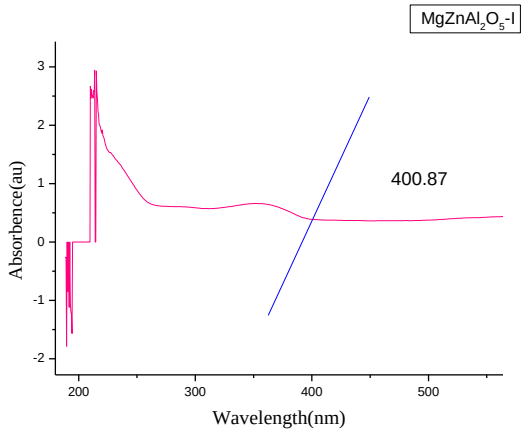

Fig 2: UV absorbance spectroscopy

The band gap energy of $MgZnAl_2O_5$ is found to be 3.0 eV with this we can say that the band gap of the semiconductors has been found to be particle size dependent

Results and Discussion

Experimental Procedure

Coralene Blue BGFS dye has the appearance of Blue in color. An azo dye, Coralene Blue BGFS (Cationic dye) are widely used in the biological staining, printing and dyeing, leather, ink, lithography *etc*. (Chaudhary, *et al,* 2013).

Based on the references from the previous studies, we have synthesized $MgZnAl_2O_5$ nanoparticle & selected this for study. Photocatalytic dosages from 0.01g, 0.02g, 0.03g upto 0.1g were tested on the Coralene Blue BGFS dye sample of 30ppm concentration and 10ml quantity. The suspension pH values were adjusted by using 0.1N NaOH and 0.1N HCl solutions using pH meter. Before irradiation, photocatalyst suspension was stirred in the dark to ensure the adsorption equilibrium and it was kept in UV chamber for the photocatalytic degradation. After every 60 minutes the suspension was sampled and centrifuged and the process was repeated at 60, 120, 180, 240 and 300 minutes. The residual concentration of the solution sample was monitored by using spectrophotometer at 540nm. The experiments were conducted in different pH range from 2 to 11 in order to study the efficiency of nanoparticle in acidic, alkaline and neutral conditions. The data obtained from the photocatalytic degradation experiments were used to calculate the degradation efficiency 'D' using (Eq. 04).

$$D= (A_0-A_t/A_0) \times 100 \quad \text{(Eq.04)}$$

Where, A_0 is the initial absorbance of dye solution

A_t is absorbance at time 't'.

Effect of Catalyst Concentration under UV light

The effect of catalyst concentration on the photocatalytic degradation was studied over a range of the catalyst amount from 0.01 to 0.1g/10ml of Coralene Blue BGFS dye. The synthesized nanoparticle shows appreciable results. The magnesium zinc aluminate with the nanoparticle size 23 nm has shown 96.71% degradation. Since, the photodegradation was very efficient at 0.08g/10ml in 300 minutes for $MgZnAl_2O_5$ nanoparticles concentration showed in (Fig.3) (Photo 2).

The increase in degradation rate can be explained in terms of availability of active sites on the catalyst surface and UV light penetration into the suspension as a result of increased screening effect and scattering of light. A further increase in the catalyst amount beyond the optimum dosage for all the nanoparticles decreases the photodegradation by some margin. This may be due to overlapping of adsorption sites as a result of overcrowding owing to collision with ground state catalyst (Madhusudhana *et al,* 2017 and Byrappa *et al,* 2006).

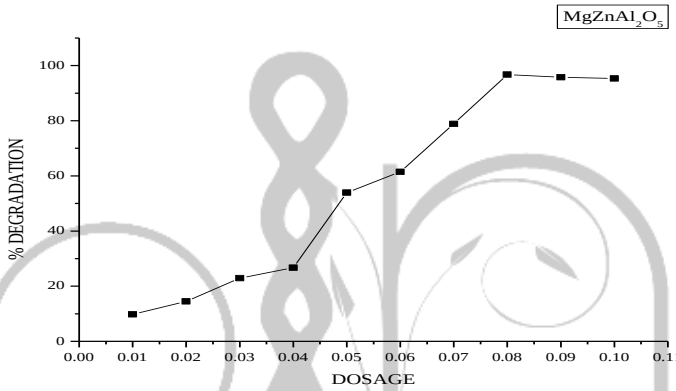

Fig 3: Effect of catalyst concentration on dye solution at 300 minutes=30 ppm, pH=7

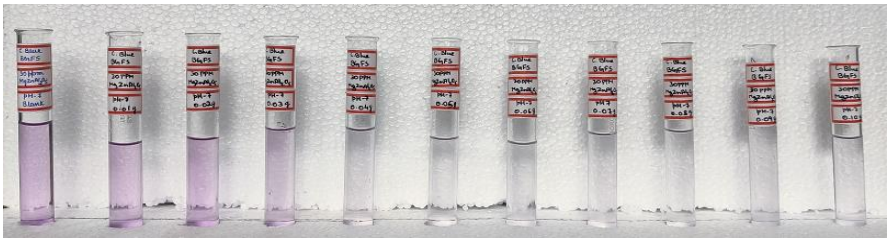

Photo 2: Effect of catalyst concentration on Coralene Blue BGFS dye at 300minutes=30 ppm, pH=7

Mechanism of Photocatalytic Activity

$MgZnAl_2O_5 + h\upsilon \rightarrow (e^{-CB} + h^{+VB})$ (Eq. 05)

Step 1: The nanoparticles under sunlight irradiation get excited and transfer electrons to the conduction band.

$e^{-}_{CB} + O_2 \rightarrow O_2^{\bullet -}$ (Eq. 06)

Step 2: It can reduce molecular oxygen and produce the super oxide radical.

$H_2O + O_2^{\bullet -} \rightarrow OOH^{\bullet} + OH^{-}$ (Eq. 07)

$2OOH^{\bullet} \rightarrow O_2 + H_2O_2$ (Eq. 08)

$O_2^{\bullet -}$ + Corelene Blue BGFS→ Corolene Blue BGFS-$OO^{\bullet}$ (Eq. 09)

Step 3: Molecular oxygen, adsorbed on the surface of the photocatalysts prevents the hole-electron pair recombination process (Madhusudhana *et al,* 2014). 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. 10)

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

$H_2O_2 + e^{-CB} \rightarrow OH^{\bullet} + OH^-$ (Eq. 11)

$H_2O_2 + O_2^{\bullet -} \rightarrow OH^{\bullet} + OH^- + O_2$ (Eq. 12)

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

$OH^{\bullet}$ / $O_2^{\bullet -}$/ $MgZnAl_2O_5^{\bullet +}$ + Corolene Blue BGFS→ Corolene Blue BGFS degradation (Eq. 13)

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

Effect of pH under UV light

In order to study the effect of pH on the degradation efficiency of $MgZnAl_2O_5$ catalyst, the experiments were carried out at pH ranging from 2 to11. The results showed that pH significantly affected the degradation efficiency. The percentage of degradation of Coralene Blue BGFS for $MgZnAl_2O_5$ (Fig 4) (Photo 3) nanoparticles increased from 33.74% to 97.65% from pH 2 to 9 decreases to 92.95% at pH 11 in 300 minutes for 0.08g/10ml. The maximum degradation was found at pH 10 of 98.12%. The experimental results show that, the degradation was effectively in pH 10 due to the interaction between the dye and nanoparticles leads to generation of $OH^{\bullet}$ in the alkaline medium and these hydroxyl radicals are the critical oxidizing species responsible for the photodegradation. Above the pH 10 the degradation is decrease due to amphoteric nature of the catalyst and electrostatic repulsion between negatively charged dye molecules and the catalyst (Sobana *et al,* 2016.). Thus, the adsorption mainly depends on the pH of the solution.

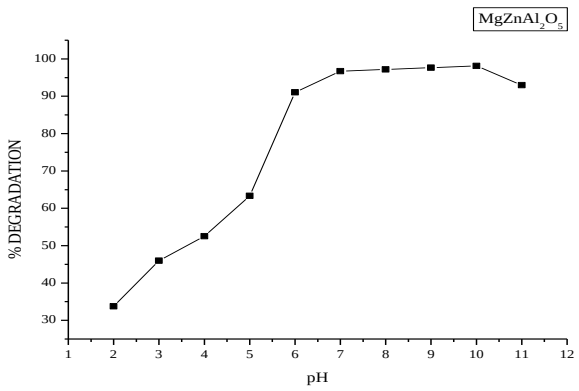

Fig 4: Effect of pH on dye at 300 minutes

Photo 3: Effect of pH on dye at 300 minutes

Effect of Initial Dye concentration

The experiments were conducted to study the effect of initial dye concentration by varying the Coralene Blue BGFS concentration from 30 ppm to 60 ppm. The results obtained for $MgZnAl_2O_5$ (Fig. 5) (Photo 4) is 98.12% for 30ppm, 54.60% for 40ppm 44.67% for 50ppm and 29.52% for 60ppm. The experiments illustrated that the degradation efficiency was directly affected by the concentration. The decrease in the degradation with an increase in dye concentration was described to the equilibrium adsorption of dye on the catalyst surface which results in a decrease in the active sites. This phenomenon results in the lower formation of $OH^{\cdot}$ radicals which were considered as primary oxidizing agents of the dye (Gopalappa *et al,* 2012). 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 adsorption of the catalyst particles, and consequently decrease photocatalytic reaction rate. (Byrappa *et al,* 2006).

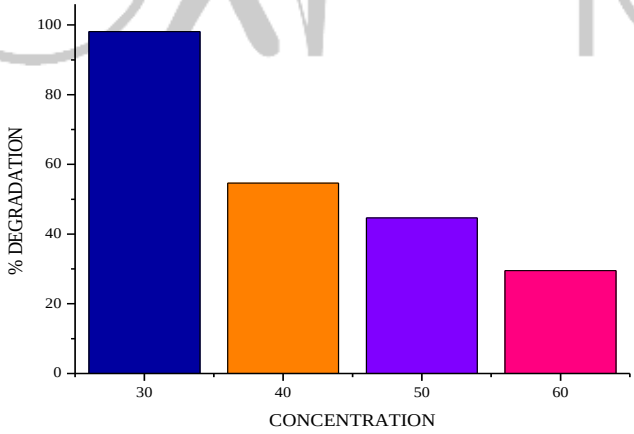

Fig 5: Effect of initial dye concentration on the photocatalytic degradation of Coralene Blue BGFS [$MgZnAl_2O_5$ pH = 10 and Corolene Blue BGFS = 30, 40, 50, 60ppm]

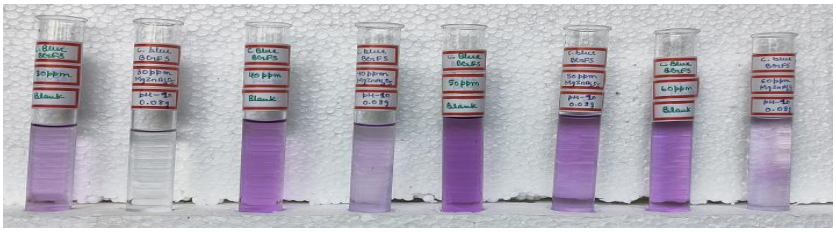

Photo 4: Effect of initial dye concentration on the photocatalytic degradation of Coralene Blue BGFS [$MgZnAl_2O_5$ pH = 10 and Corolene Blue BGFS = 30, 40, 50, 60ppm]

Effect of UV light

The photocatalytic degradation of Coralene Blue BGFS dye (30mg/L) under two different experimental conditions were examined, *i.e.*, through dye/dark/catalyst, and dye/UV/catalyst. Coralene Blue BGFS dye solution when exposed directly to the UV light 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/UV light/$MgZnaAl_2O_5$ showed 98.12%, and for dye/dark/$MgZnAl_2O_5$ 6.06% was recorded (Fig 6) (Photo 5). These results clearly indicate that photodegradation occurs most efficiently in the presence of UV light (Photo 5). Under UV light, excitation of electrons from the catalyst surface takes place more rapidly than in the absence of light (Guillen *et al*, 2010).

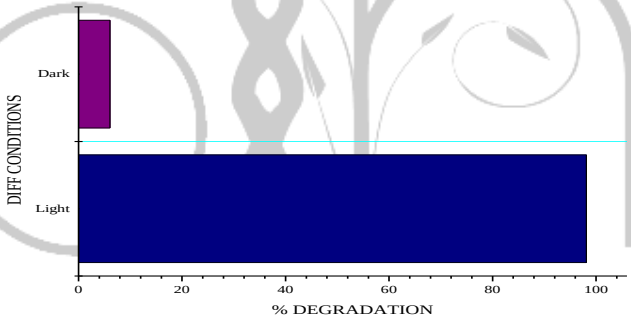

Fig 6: Effect of light with respect to Dark condition and UV condition on photocatalytic degradation of Coralene Blue BGFS in 300 minute

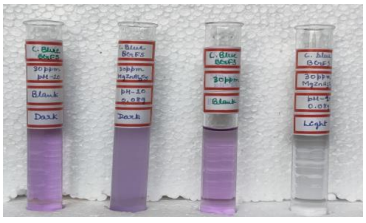

Photo 5: Effect of light with respect to Dark condition and UV condition on photocatalytic degradation of Coralene Blue BGFS in 300 minutes

Summary and Conclusion

Colored dyes are the substances used to coloring the cloths and are increased in our environment, causing potential harm to environment. Different kinds of dyes are used in textile industries they are natural dye and even synthetic dyes. The natural dyes that are not harmful because it is extracted from plants, animals but synthetic dyes are causing effects to the environment due to their non-biodegradability and toxicity. During the coloring process, the large percentage of synthetic azo dyes is lost in water through effluent and effects on aquatic bodies and plants. Nowadays most of dyes available in market are azo dyes. The breaking of these bonds by naturally is very difficult so it causes more pollution to the environment. Hence the treatment of these colored dyes is most important to protect our environment from pollution.

In the present study, the $MgZnAl_2O_5$ nanoparticles were prepared by solution combustion method using urea as a fuel and the result suggested that, the average particle size was found to be 23nm and band gap was found to be 3.0eV and these nanoparticles have been used in industries and medical application. The Photocatalytic Activity of synthesized nanoparticles was used to degrade the Coralene Blue BGFS under artificial UV light and by varying the parameters such as, pH of the dye, dye concentration and catalyst concentration. The optimal catalyst concentration was found to be 0.08g/10ml with dye concentration 30ppm and the pH 10 was maintained by 0.1N HCl and 0.1 N NaOH. The maximum degradation was found to be 97.65% in 300min. The method of photocatalytic degradation of Coralene Blue BGFS is more helpful in treating Coralene Blue BGFS dye containing textile effluents. This method do not cause any harm to the environment and easily adoptable dye degradation techniques under UV light and this can be applicable in large scale.

Acknowledgement

The authors are grateful to Vision Group of Science and Technology, Department of Information Technology, Biotechnology and Science & Technology, Government of Karnataka, for their financial support under the scheme of establishment of Center of Innovative Science Engineering and Education (CISEE) (GRD number-859/2019-2020).

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