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Photocatalytic Degradation of Coralene Red BEL dye by using Synthesized Magnesium Zinc Aluminate Nanoparticle under UV light

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Abstract

Colored dyes are the substances used to coloring the cloths and are increased in our environment, causing potential harm to environment. The textile industry is the largest consumer of the dye stuffs. The World Bank estimates that 17 to 20 % of industrial water pollution comes from textile dyeing and finishing treatment given to fabric. In the present study, the $MgZnAl_2O_5$ nanoparticles were prepared by solution combustion method using urea as a fuel. The prepared nanoparticles were characterized by XRD, UV-Vis absorbance Spectroscopy, SEM. The result suggested that, the average particle size was found to be 23nm and band gap was found to be 3.0 eV. The optimal catalyst concentration was found to be 0.09g/10ml with dye concentration 30ppm and the pH 9 was maintained by 0.1N HCl and 0.1N NaOH. The maximum degradation was found to be 97.83% in 300 minutes. The method of photocatalytic degradation of Coralene Red BEL is more helpful in treating Coralene Red BEL dye containing textile effluents.

Keywords: **Coralene Red BEL, $MgZnAl_2O_5$, Nanoparticle, Photodegradation, UV light.**

1. Introduction

Water is a transparent and colorless chemical substance. It is the main constituent of living organisms. Water moves ceaselessly through the natural and manmade environment. pollutants are directly and indirectly discharge into water bodies without adequate treatment to remove harmful compounds.

Dyes and pigments are the most important colorants used to add color or to change the color of something. They are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paints and paper industries [1]. Pigments are colored, colorless, or fluorescent particulate organic or inorganic finely divided solids which are usually insoluble.

Azo dyes are synthetic color that contain an azo group (-N=N-), as a part of the structure. Azo group do not occur naturally. Most of the azo-dyes contain only one azo group but some contain two or more azo dyes accounts approximately 60-70% of all the dyes used in textile manufacture.

World Bank estimates that textile dyeing and treatment contributes up to 17-20 % of total industrial water pollution. The textile dyeing and finishing industry has created huge pollution problem as it is one of the chemically intensive industries on earth, and the highest polluter of clean water (after agriculture). More than 3600 individual textile dyes are being manufactured by the industry today. The industry is using more than 8000 chemicals in various processes of textile manufacture including dyeing and printing. The daily water consumption of an average sized textile mill having a production of about 8000kg of fabric per day is about 1.6million liters. The 16% of this is consumed in dyeing and 8% in printing. The 72 toxic chemicals have been identified in water solely from textile dyeing 30 of which cannot be removed. This represents a terrible environmental problem for the clothing and textile manufacture.

Due to high chemical properties or strong chemical bonding dyes are not easily degraded by biological activity. Hence, many treatment methods have been developed to treat textile industry effluents.

2. Materials and Methods

2.1 Chemical Reagents

The Coralene Red BEL azo dye used for the photocatalytic study was procured from colurtex, Pvt. Ltd. Gujarat. 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 $Zn(NO_3)_2$. $6H_2O$ (99.0% AR)] [Aluminum Nitrate $Al(NO_3)_3$ (98.0% AR)] and fuel [Urea NH_2CONH_2 (99.5%)] was purchased from Hi-media Pvt. Ltd, Mumbai.

2.2 Synthesis of $MgZnAl_2O_5$

The nanoparticles were prepared by solution combustion synthesis. The residue or the ash that emerges after complete combustion is the oxide material. By use of the above flaming combustion, a number of useful oxide materials used for various applications such as refractory, magnetic, dielectric, semiconducting, insulators, catalysts, sensors, phosphors, *etc.*, have been identified [2]. 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 the propellant chemistry the reaction is as shown below [3].

$$3Mg(NO_3)_2+3Zn(NO_3)_2+6Al(NO_3)_3+25NH_2CONH_2 \rightarrow 3MgZnAl_2O_5 +50H_2O+25CO_2 +40N_2 \quad \text{(Eq.1)}$$

3. Characterization of Nanoparticles

3.1 X-ray Diffraction technique (XRD)

X-ray diffraction is a versatile; non-destructive that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD was performed by Rigaku diffractometer using Cu-Kα radiation (1.5406 Å) in a θ-2θ configuration [4]-[6].

According to the Debye Scherrer's formula:

$$D = K\lambda/\beta COS\theta \quad \text{(Eq.2)}$$

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.

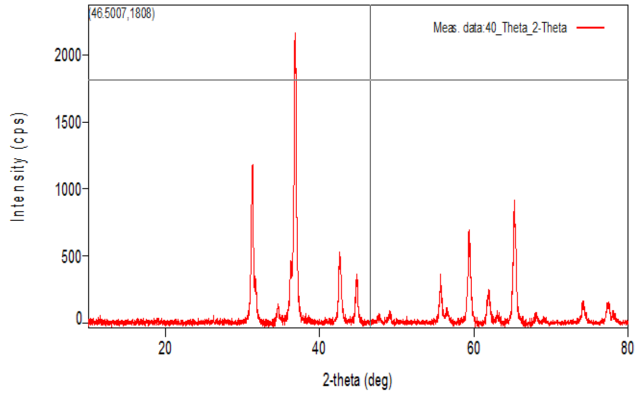

Fig. 1 X-Ray diffraction of $MgZnAl_2O_5$

3.2 Scanning Electron Microscope (SEM) of $MgZnAl_2O_5$

The Scanning Electron Microscope (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.

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

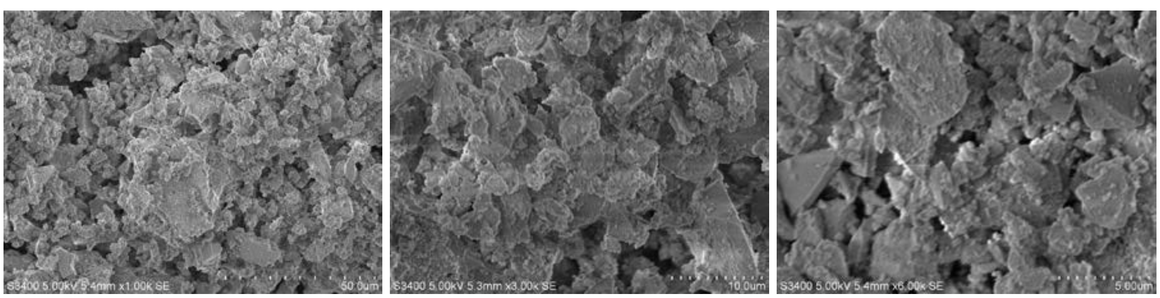

Photo 1 SEM photographs of $MgZnAl_2O_5$ nanoparticles.

3.3 UV absorbance spectroscopy of $MgZnAl_2O_5$

Absorption spectra of the $MgZnAl_2O_5$ metal oxide nanoparticle was recorded using UV-Vis spectrophotometer over the wavelength range 200-800 nm. 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.

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

Where,

h = Planck's constant,

C = Velocity of light (speed of light),

λ = Wavelength of light

$h = 4.135 \times 10^{-15}$ eV, $C = 3 \times 10^{8}$ m/s, λ= ---------$\times 10^{-9}$ nm

Band gap energy (eV) = 4.135×10^{-15} eV $\times 3 \times 10^{8} \times 10^{-9}$

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

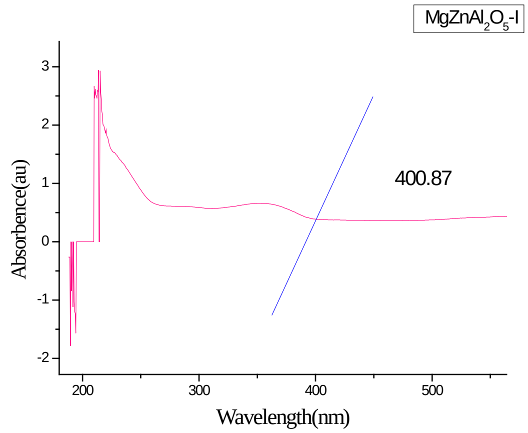

Fig. 2 UV absorbance spectroscopy.

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.

4. Results and Discussions

4.1 Experimental Procedure

Coralene Red BEL dye has the appearance of red in color. An azo dye, Coralene Red BEL are widely used in the biological staining, printing and dyeing, leather, ink, lithography *etc*. [7]. From these earlier studies we synthesized $MgZnAl_2O_5$ nanoparticle which was selected for this study. Photocatalytic dosages of 0.01g, 0.02g, 0.03g upto 0.1g were tested on the Coralene Red BEL 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, photo catalyst suspension was stirred in the dark to ensure the adsorption equilibrium and it was kept in UV Chamber for the photocatalytic degradation. After every 30 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 537 nm. 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.4).

$$D = (A_0 - A_t / A_0) \times 100 \qquad \text{(Eq.4)}$$

Where, A_0 is the initial absorbance of dye solution

A_t is absorbance at time 't'.

4.2 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 Red BEL dye. The synthesized nanoparticle shows appreciable results. The $MgZnAl_2O_5$ with the nanoparticle size 23nm has shown 96.53% degradation. Since, the photodegradation was very efficient at 0.09g/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 [8],[9].

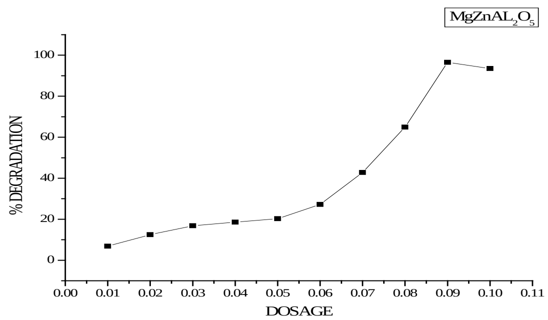

Fig. 3 Effect of catalyst concentration on dye solution at 300 minutes = 30 ppm, pH = 7.

Photo 2 Effect of catalyst concentration on Coralene Red BEL dye at 300 minutes=30 ppm, pH=7.

4.3 Mechanism of Photocatalytic Activity

$MgZnAl_2O_5 + h\upsilon \rightarrow (e^{-CB} + h^{+VB})$ (Eq.5)

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

$e^{-CB} + O_2 \rightarrow O_2^{\bullet -}$ (Eq.6)

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

$H_2O + O_2^{\bullet-} \rightarrow OOH^{\bullet} + OH^{-}$ (Eq.7)

$2OOH^{\bullet} \rightarrow O_2 + H_2O_2$ (Eq.8)

$O_2^{\bullet-}$ + Coralene Red BEL→ Coralene Red BEL-OO$^{\bullet}$ (Eq.9)

Step 3: Molecular oxygen, adsorbed on the surface of the photocatalysts prevents the hole-electron pair recombination process [10]. 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)

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

$OH^{\bullet} / O_2^{\bullet-} / MgZnAl_2O_5^{\bullet++}$ Coralene Red BEL→ Coralene Red BEL degradation (Eq.13)

Step 5: The radicals produced are capable of attacking dye molecules and degrade them.

4.4 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 Red BEL was obtained from 51.47% to 96.96% from pH 2to 8, similarly the degradation decreases to 91.76% at pH 11in 300 minutes for 0.09g/10ml. The maximum degradation was found at pH 9 of 97.83%. The experimental results show that, the degradation was effective in pH9 due to the interaction between the dye and nanoparticles lead to the generation of OH• in the alkaline medium and these hydroxyl radicals are the critical species responsible for the photodegradation. Above the pH 9 the degradation decreased due to the amphoteric nature of the catalyst and electrostatic repulsion between negatively charged dye molecules and the catalyst [11]. Thus, the adsorption is mainly depending on the pH of the solution.

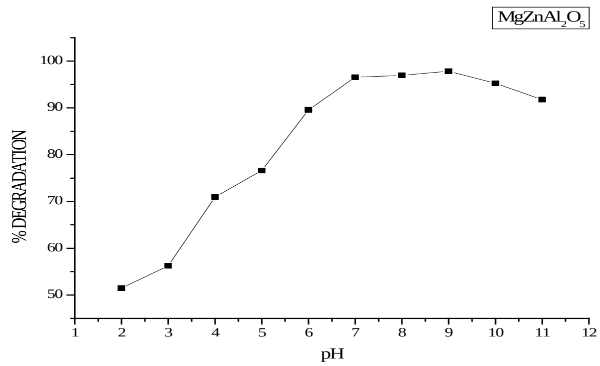

Fig. 4 Effect of pH on dye at 300 minutes

Photo 3 Effect of pH on dye at 300 minutes

4.5 Effect of Initial Dye Concentration under UV light

The experiments were conducted to study the effect of initial dye concentration by varying the Coralene Red BEL dye concentration from 30 ppm to 60 ppm. The results obtained for $MgZnAl_2O_5$ (Fig.5) (Photo 4) is 97.83% for 30ppm,62.03% for 40ppm 32.62% for 50 ppm and 15.49% for 60ppm, 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. This phenomenon results in the lower formation of OH· radicals which were considered as primary oxidizing agents of the dye [12]. 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 [9].

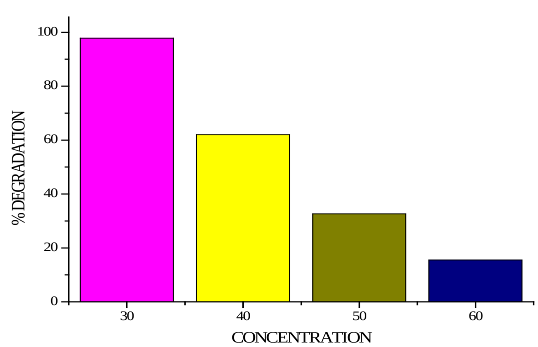

Fig. 5 Effect of initial dye concentration on the photocatalytic degradation of Coralene Red BEL [$MgZnAl_2O_5$ pH = 9 and Corolene Red BEL = 30, 40, 50, 60ppm]

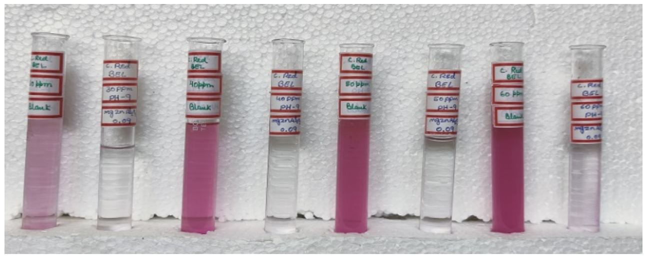

Photo 4 Effect of initial dye concentration on the photocatalytic degradation of Coralene Red BEL
[$MgZnAl_2O_5$ pH = 9 and Corolene Red BEL = 30, 40, 50, 60ppm]

4.6 Effect of UV light

The photocatalytic degradation of Coralene Red BEL dye (30mg/L) under two different experimental conditions were examined, *i.e.*, through dye/dark/catalyst and dye/UV/catalyst Coralene Red BEL 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/$MgZnAl_2O_5$ showed 97.83%, and for dye/dark /$MgZnAl_2O_5$ 5.24% was recorded (Fig 6) (Photo 5). These results clearly indicate that photodegradation occurs most efficiently in the presence of UV light (Photo 10). Under UV light, excitation of electrons from the catalyst surface takes place more rapidly than in the absence of light [13].

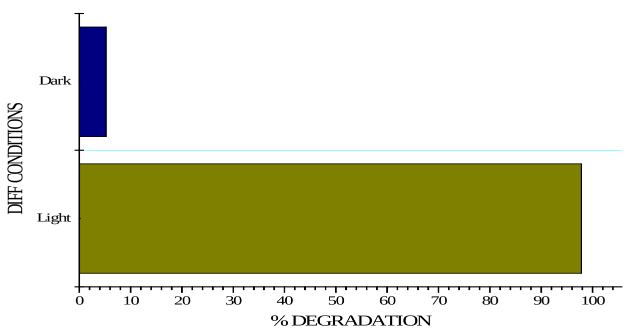

Fig. 6 Effect of light irradiation with respect to Dark condition and UV condition on photocatalytic degradation of Coralene Red BEL in 300 minutes

Photo 5 Effect of light irradiation with respect to Dark condition and UV condition on photocatalytic degradation of Coralene Red BEL in 300 minutes

5. 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 dyes 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 dye 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 naturally is very difficult so it causes more pollution in 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 applications. The photocatalytic activity of synthesized nanoparticles was used to degrade the Coralene Red BEL under artificial UV light and by varying the parameters such as, pH of dye, dye concentration and catalyst concentration. The optimal catalyst concentration was found to be 0.09g/10ml with dye concentration 30ppm and the pH 9 was maintained by 0.1N HCl and 0.1N NaOH. The maximum degradation was found to be 97.83% in 300min. The method of photocatalytic degradation of Coralene Red BEL is more helpful in treating Coralene Red BEL dye containing textile effluents. This method does not cause any harm to the environment and easily adoptable dye degradation techniques under UV light and this can be applicable in large scale.

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