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Research Paper

Synthesis of Calcium Aluminate Nanoparticle and Its Application to Photocatalytic Degradation of Coralene Navy Blue 3G and Coralene Violet 3R

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Abstract: *The Calcium aluminate ($CaAl_2O_4$) nanoparticle was synthesized by solution combustion method using acetamide as fuel. Calcium aluminate ($CaAl_2O_4$) nanoparticle was characterized by Scanning Electron Micrograph (SEM), X-Ray Diffraction (XRD) and UV-absorption spectroscopy. The average crystallite size was found to be 42nm and the band gap energy of $CaAl_2O_4$ nanoparticle was 2.7eV. The photocatalytic degradation of Coralene Navy Blue 3G and Coralene Violet 3R in aqueous solution was investigated by using Calcium aluminate ($CaAl_2O_4$) nanoparticle by varying different parameters such as catalyst concentration, solution pH and dye concentration. All the experiments were conducted in presence of natural sun light. The highest degradation i.e., 86.52% (0.4g/100ml catalyst dose) and 87.94% (0.3g/100ml catalyst dose) was achieved at pH 3 for Coralene Navy Blue 3G and Coralene Violet 3R in aqueous medium at 30ppm concentration of dyes. After the degradation, 27.02mg/L and 28.58mg/L COD reduction was also recorded for Coralene Navy Blue 3G and Coralene Violet 3R.*

Keywords: Coralene Navy Blue 3G, Coralene Violet 3R, $CaAl_2O_4$, Photocatalyst, nanoparticle, COD.

Introduction

Synthetic dyestuffs are extensively used in textile, printing industries, paper, and dye houses due to their ease of production, variety of colors, and fastness compared to natural dyes [1]. Azo dyes with -N=N- unit as the chromophore in the molecular structure is the largest group of dyes and represents more than a half of the global dye production. Over 15% of overall azo dye production is lost during manufacturing and application processes[2, 3]. Wastewater from textile, paper and some other industries contain residual dyes, which are not readily biodegradable [4]. The non-biodegradable nature of dyes and their stability toward light and oxidizing agents complicate the selection of a suitable method for their removal. Moreover, toxicity bioassays have demonstrated that most of them are toxic [5].

Advanced oxidation processes (AOPs) are alternative techniques of destruction of dyes and many other organics in wastewater and effluents. These processes generally, involve UV/H_2O_2, UV/O_3 or UV/Fenton's reagent for the oxidative degradation of contaminants. Semiconductor photocatalysis is another developed AOP, which has attracted considerable attention among AOP as a promising tool for implementing the large-scale purification of wastewaters at low cost [6-10].

Advantages of the photocatalytic process include its mild operating conditions and the fact that it can be powered by sunlight, thus reducing significantly the electric power required and therefore the operating costs [11]. Among the semiconductors whose photocatalytic properties have been studied, TiO_2 is the most commonly used, because it is effective, stable, harmless, and inexpensive [12, 13]. Thus various metal oxide nanoparticles have been reported as photocatalysts in the degradation of azo dyes and nanoparticles such as calcium zincate ($CaZnO_2$),

composites of zinc oxide were found to be effective in the degradation of Coralene Dark Red 2B and Coralene Red F3BS azo dyes in the presence of sun light or under UV-irradiation [14,8].

Hence based on the literature report on the photocatalytic degradation Coralene Dark Red 2B, and Coralene Red F3BS azo dyes and while searching for new potential catalyst for degradation of various dyes in our lab [15-17], in this report we probe to obtain $CaAl_2O_4$ nanoparticle through simple and convenient method and was applied successfully as potential photocatalyst for the degradation of Coralene Navy Blue 3G and Coralene Violet 3R azo dyes in presence of sun light by varying parameters such as catalyst dosage, dye concentration and pH of the dye solution.

Material and Methods

The commercially available water soluble azo dyes Coralene navy Blue 3G (λmax 530nm) and Coralene Violet 3R (λmax 480nm) were obtained from Colortex Limited, Surat, Gujrat (Figure 1 and 2). The chemicals like Calcium nitrate ($Ca(NO_3)_2.4H_2O$) (99%, A. R.), Aluminium nitrate $Al(NO_3)_3.9H_2O$ (99%, A.R.), Acetamide (CH_3CONH_2) (99%, A.R.), were obtained from Hi-Media Chemicals, Mumbai and used as received without any further purification. The UV-VIS single beam spectrophotometer-119 (Systronics) has been used for recording absorbance at λmax. Later the absorbance was recorded in UV-VIS spectrophotometer 169 (Systronics).

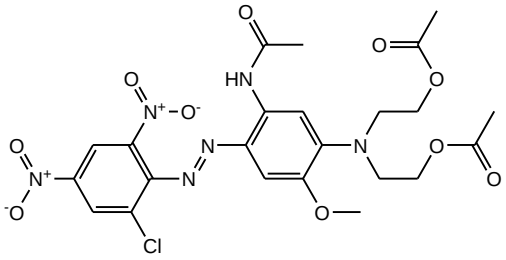

Figure 1: Chemical structure of Coralene Navy Blue 3G

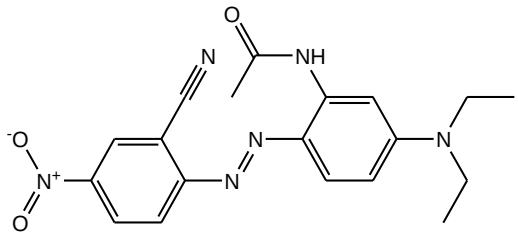

Figure 2: Chemical structure of Coralene Violet 3R

Synthesis of $CaAl_2O_4$ nanoparticle

The Calcium aluminate nanoparticle was prepared by solution combustion method [18, 19], using procured calcium nitrate, aluminium nitrate and acetamide (as fuel). Stoichiometric amounts of calcium nitrate, aluminium nitrate, and fuel acetamide were calculated using the total oxidizing and reducing valencies of the compounds which serve as numerical coefficients for stoichiometric balance. Initially $Ca(NO_3)_2.4H_2O$ (6.49 g) and $Al(NO_3)_3.9H_2O$ (20.63 g) were dissolved in a minimum quantity of water along with acetamide (5.90 g) in a silica crucible (with a volume of $100cm^3$). The crucible was introduced into the muffle furnace which was preheated to 600° C. The product obtained after calcinations is crushed in a mortar and used for the photocatalytic degradation study of Coralene navy Blue 3G (λ_{max} 530nm) and Coralene Violet 3R (λ_{max} 480nm) aqueous suspensions. According to the propellant chemistry, the following reaction takes place during combustion.

$$11Ca(NO_3)_2+22Al(NO_3)_3+40CH_3CONH_2 \longrightarrow 11CaAl_2O_4 + 80CO_2 + 100H_2O + 64\ N_2$$

Characterization of $CaAl_2O_4$ nanoparticles: $CaAl_2O_4$ nanoparticle was characterized by SEM, XRD and UV absorption spectroscopy.

Scanning Electron Micrograph (SEM): The powdered sample was examined by SEM technique which helps to predict the structure of the synthesized $CaAl_2O_4$. Images obtained by SEM analysis reveal the crystal and plate like structures for synthesized $CaAl_2O_4$ presented in Figure 3.

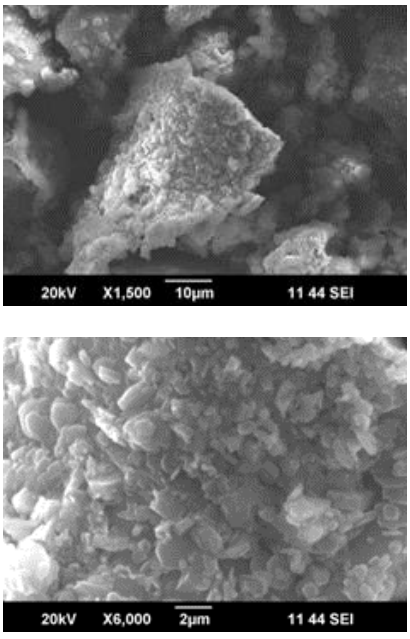

Figure 3: SEM micrographs of synthesized $CaAl_2O_4$

X-Ray Diffraction (XRD): The XRD was performed by powder X-ray diffraction (Rigaku diffractrometer) using Cu-Kα radiation (1.5406 Å) in a θ-2θ configuration. The pattern obtained from the XRD analysis of the prepared $CaAl_2O_4$ nanoparticle is presented in Figure 4.

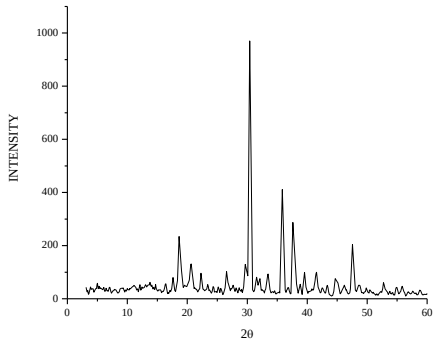

Figure 4: XRD of the synthesized $CaAl_2O_4$

According to the Debye Scherrer's formula:
$D=K\lambda/\beta \cos\theta$ (1)

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

In the present work, the powdered sample of newly synthesized $CaAl_2O_4$ nanoparticle was examined by XRD studies and the average crystallite size of $CaAl_2O_4$ was found to be 42nm.

UV Absorption spectroscopy: The absorbance spectrum of synthesized $CaAl_2O_4$ was recorded using UV-VIS spectrophotometer (Ocean Optics DH-2000) over the wavelength range 200-1200nm.The band gap energy of the $CaAl_2O_4$ nanoparticle was calculated using the following simple conversion equation. The band gap equation is calculated using the Planck's equation as follows.

$E = hC/\lambda$
h = Planck's constant,
C = Velocity of light,
λ = wavelength,
h = 4.135×10−15 eV,
C = 3×10^8 m/s, λ= −−−×10^{-9}nm
Band gap energy (eV) = $4.135\times10^{-15}\times3\times10^8\times10^9$
Band gap energy (eV) = 1240/wavelength (nm)

The band gap energy of $CaAl_2O_4$ particle was 2.7eV. The UV-absorbance spectra of synthesized $CaAl_2O_4$ presented in Figure 5.

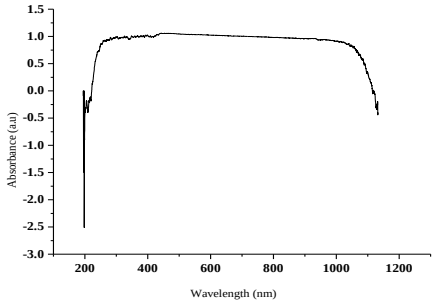

Figure 5: UV-absorption spectra of synthesized $CaAl_2O_4$

Experimental procedure: The UV-VIS spectrophotometer 119 (Systronics) was used for the determination of absorbance. The λ_{max} value of Coralene navy Blue 3G and Coralene Violet 3R was found to be 530nm and 480nm respectively. The photocatalytic experiments were carried out under direct sunlight. The known concentration of dye solutions were prepared by dissolving 30mg of Coralene navy Blue 3G and Coralene Violet 3R separately in 1000ml double distilled water and investigated for its decolorization in the presence of Calcium aluminate nanoparticle at different catalyst dosages and pH levels. Initially, 10ml of 30 mg/L dye samples were tested with different catalyst dosage (from 0.01g to 0.1g) in the presence of direct sunlight. After the photocatalytic decolorization, the extent of decolorization 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 degradation was determined by using the following equation,

The percentage of decolourization,

$$D = ((Ao - At) \div Ao) \times 100$$

Where, $\mathbf{A_0}$ is the initial absorbance of the dye solution
$\mathbf{A_t}$ is absorbance at time interval't' i.e., after 120 minutes.

Mechanism of the photocatalytic degradation: The mechanism of photocatalytic activity of nanoparticles can be predicted as below.

Step-1: Under sunlight irradiation, nanoparticle molecules get excited and transfer electrons to the conduction band.

$$CaAl_2O_4 + h\nu \rightarrow (e^-_{CB} + h^+_{VB}) \quad (1)$$

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

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

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

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

$$2OOH^{\bullet} \rightarrow O_2 + H_2O_2 \quad (4)$$

$$O_2^{\bullet -} + \text{dye} \rightarrow \text{dye-}OO^{\bullet} \quad (5)$$

Hydrogen peroxide can be generated in another path.

$$OOH^{\bullet} + H_2O + e^-_{CB} \rightarrow H_2O_2 + OH^- \quad (6)$$

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

$$H_2O_2 + e^-_{CB} \rightarrow OH^{\bullet} + OH^- \quad (7)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^{\bullet} + OH^- + O_2 \quad (8)$$

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

$$OH^{\bullet} \ / \ O_2^{\bullet -} / \ CaAl_2O_4^{\bullet +} + \text{dye} \rightarrow \text{Dye degradation} \quad (9)$$

Results and Discussion

Effect of catalyst dosage: To study the effect of catalyst load, the Calcium aluminate dosage was varied from 0.01g to 0.1g for 30 mg/L of Coralene navy Blue 3G and Coralene Violet 3R dye solutions keeping all other parameters constant and the results are presented in Figure 6. On the exposure of the reaction volume to sunlight after adding the catalyst, the dye color started to fade showing the visible signs of decolorization. The highest degradation 85.46% (C. Navy Blue 3G) and 85.52% (C. Violet 3R) was recorded for 0.4g/100ml and 0.3g/100ml of catalyst which was sufficient to degrade Coralene navy Blue 3G and Coralene Violet 3R dye solutions within 120minutes.

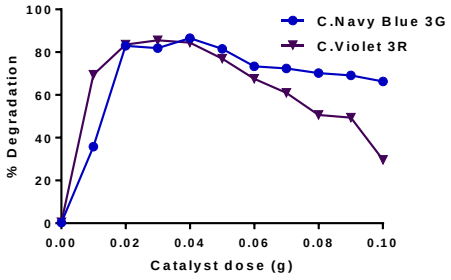

Figure 6: Effect of catalyst dose on the decolourization of Coralene navy Blue 3G and Coralene Violet 3R dye solutions at concentration 30mg/L, at pH 7 with respect to time interval of 120minutes

Effect of pH: The photocatalytic experiments were conducted at different pH from 2 to 11 by keeping the catalyst dosage constant (0.4g/100ml and 0.3g/100ml) for 30 mg/L of Coralene navy Blue 3G and Coralene Violet 3R dye solutions. pH of the solution was adjusted by using 0.2N HCl/NaOH solution and the results are presented in Figure 7. On the exposure of the reaction volume to sunlight, the highest degradation of 86.52% (Coralene navy Blue 3G) and 87.94% (Coralene Violet 3R) was recorded at pH 3 which was optimum to degrade the dye solutions within 120minutes.

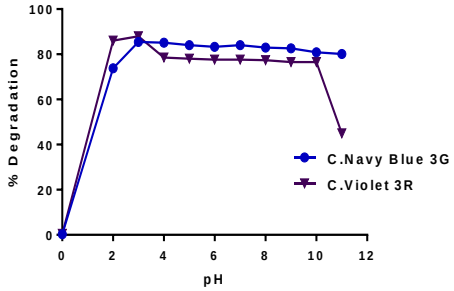

Figure 7: Effect of optimum catalyst dosage on the decolourization of Coralene navy Blue 3G and Coralene Violet 3R dye solutions at concentration 30mg/L, at different pH levels with respect to time interval of 120minutes

Degradation efficiency of $CaAl_2O_4$ at different dye concentrations: To study the effect of initial dye concentration on the photocatalytic efficiency of $CaAl_2O_4$ nanoparticles the initial dye concentrations were varied from 30ppm to 60ppm, 90ppm and 120ppm and experiments were conducted at optimum catalyst dosage and pH. The highest degradation of 86.52% and 87.94% was recorded for the concentration of 30ppm Coralene navy Blue 3G and Coralene Violet 3R dye solution respectively. The experiment result depicts that, as the concentration of the dye solution increases, degradation efficiency decreases. Results are presented in Figure 8.

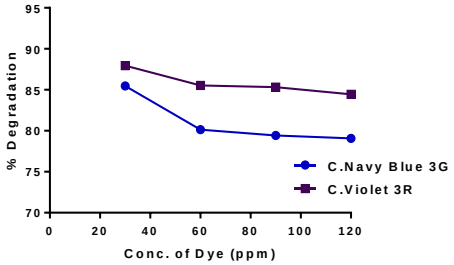

Figure 8: Effect of optimum catalyst dose and pH on the decolourization of Coralene navy Blue 3G and Coralene Violet 3R dye solutions at different concentrations (30ppm, 60ppm, 90ppm and 120ppm) with respect to time interval of 120minutes

Chemical Oxygen Demand (COD): COD analysis conducted to the dye samples to know the reduction in COD level after the degradation experiments. The result obtained reveals that, the rate of COD reduction is less compared to the rate of colour degradation. After degradation, 27.02mg/L and 28.58mg/L COD reduction was recorded for Coralene Navy Blue 3G and Coralene Violet 3R respectively.

Conclusion

In the present study, a simple and convenient synthesis of $CaAl_2O_4$ nanoparticle was reported. The $CaAl_2O_4$ nanoparticle was characterized by SEM, XRD and UV-absorption studies. The average crystallite size was found to be 42nm and the band gap energy of $CaAl_2O_4$ particle was 2.7eV. The photocatalytic degradation of Coralene navy Blue 3G and Coralene Violet 3R by $CaAl_2O_4$ nanoparticle under natural solar irradiation shows that maximum of 86.52% (0.4g/100ml catalyst dose) and 87.94% (0.3g/100ml catalyst dose) degradation efficiency when exposed to sunlight irradiation for Coralene navy Blue 3G and Coralene Violet 3R at 120minutes respectively. It was also noticed from the results that, 27.02mg/L (Coralene navy Blue 3G) and 28.58mg/L (Coralene Violet 3R) COD reduction was recorded after degradation. Further the extent of degradation was found to depend on concentration of the photocatalyst, pH of the dye solutions and the solution concentration (30ppm, 60ppm, 90ppm and 120ppm). Since the degradation was achieved in presence of solar energy, the present protocol can be adapted to the large scale industrial decoloration processes.

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