



Photocatalytic Degradation of Violet GL2B Azo dye by using Calcium Aluminate Nanoparticle in presence of Solar light

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Abstract

The present study deals with the photocatalytic degradation of Violet GL2B an azo dye, using Calcium aluminate (CaAl_2O_4) nanoparticles. SEM and XRD studies were carried out to determine the size of the nanoparticle. UV-VIS spectroscopy method was selected to evaluate the degradation efficiency at 545nm. The results indicated that at all pH levels ~100% degradation was achieved in 120 minutes irrespective of amount of catalyst load. The results revealed the efficiency of the present photocatalytic process for the effective degradation of dye effluents.

Keywords: Violet GL2B, Degradation, Nanoparticle, Photocatalyst, Calcium aluminate

Introduction

Different types of dyes are used in many industries such as textile, paint, ink, plastics and cosmetics. About half of global production of synthetic textile dyes (700000 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 operation¹. It is well known that when accumulated into the body the soluble azo dyes split into corresponding aromatic amines by liver enzymes and intestinal flora, which can cause cancer in human. The textile industry produces large quantity of highly coloured effluents, which are generally toxic and resistant to destruction by biological treatment methods. Therefore, it is necessary to find an effective method to remove colour from textile effluents²⁻⁴.

Various chemical and physical processes such as coagulation, electro coagulation and adsorption on activated carbon are not destructive but only transfer dye from one phase to another; hence, there is a need for developing treatment technologies for eliminating contaminants from wastewater. Photocatalytic degradation by semiconductors is a new and effective technique for the removal of pollutants from water^{5,6}. Although the process of UV-irradiated photocatalytic decolourization of azo dyes has proved to be effective, the direct use of clean and renewable solar light and active photocatalysts for decolourization and degradation of azo dyes has attracted great interest in recent years⁷⁻⁹.

Very recently, Ali Mahyar *et al.*, reported the degradation of C.I. Basic Violet 2 (BV2; New Fuchsin) by preparing TiO_2 - SiO_2 nanoparticles by the sol-gel method using Titanium tetraisopropoxide as a titanium source and used as a

photocatalyst for the photodegradation of BV2¹⁰. In another research work, photocatalyst Zinc oxide (ZnO), which is one of the most important semiconductors with a direct wide band gap of ~3.37 eV and large excitation binding energy of 60 meV at room temperature¹¹. ZnO has promising applications in electrical engineering, catalysis, ultraviolet (UV) absorption, and optical and optoelectronic devices. One of the most important and surface-dependant properties of ZnO nanoparticles is their photocatalytic behavior under UV electromagnetic irradiation. Hence, ZnO can be used for degradation and removal of environmental pollutants, especially organic dye contaminants, from water¹².

Similar work has been reported such as, degradation of azo dyes by using synthesized nanoparticles (ZnO , CaAl_2O_4 , and CaZnO_2) as photocatalysts under natural sunlight¹³⁻¹⁵. These nanoparticles have been reported as efficient photocatalysts against Coralene Red F3BS and Coralene Dark Red 2B dyes at different conditions such as optimum catalyst dosage and effective pH level.

This study reports CaAl_2O_4 nanoparticles mediated photocatalytic destruction of dyes. The textile azo dye Violet GL2B is selected for the degradation studies under natural sunlight and it gives dark Violet colour when dissolved in water. The structure is as shown in figure 1.

Materials and Reagents: Metal nitrates were chosen for the preparation of the CaAl_2O_4 nanoparticle, as the NO_3 groups of metal nitrates act as oxidizing agents and also their high solubility in water allows a proper homogenization. Urea seems to be the most convenient fuel which can be used for the synthesis of CaAl_2O_4 . The commercially available azo dye Violet GL2B was procured. The chemicals like Calcium nitrate

(Ca (NO₃)₂. 4H₂O) (99%, AR), Aluminium nitrate (Al (NO₃)₃.9H₂O) (95%, AR), Urea (NH₂ CO NH₂) (99%, AR), were obtained from Hi-media chemicals, Mumbai and used as received.

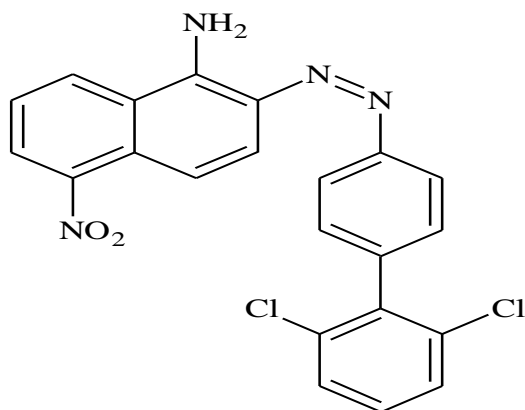
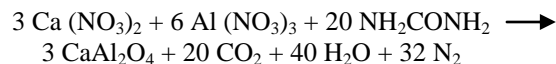


Figure-1
Chemical structure of Violet GL2B

The UV-VIS single beam spectrophotometer 119 (Systronics) has been used for recording absorbance at λ_{max} . Later the absorbance was recorded in UV-VIS spectrophotometer 169 (Systronics).

Synthesis of Calcium aluminate nanoparticle: The Calcium aluminate nanoparticle was prepared by solution combustion method, using procured calcium nitrate, aluminium nitrate, and Urea (Fuel). Stoichiometric amounts of calcium nitrate, aluminium nitrate and fuel Urea were calculated using the total oxidizing and reducing valencies of the compounds which serve as numerical coefficients for Stoichiometric balance. Here Ca (NO₃)₂.4H₂O (3.54 g) and Al (NO₃)₃. 9H₂O (11.255 g) were dissolved in minimum quantity of water along with Urea (24 g) in a silica crucible (with volume of 100 cm³). The resulting mixture was introduced into the muffle furnace which was preheated to 600^oC. The solution boils and undergoes dehydration followed by decomposition along with the release of certain amounts of gases it froths and swells forming foam which ruptures with a flame and glows to incandescence^{16,17}. The product after combustion is a voluminous and foamy

CaAl₂O₄. The obtained Calcium aluminate was crushed in a mortar to make it amorphous. According to propellant chemistry the reaction is as shown.



SEM and XRD of prepared Calcium Aluminate Nanoparticles: XRD analysis was carried out on fresh sample to assess the purity of the expected phases and the degree of crystallization, i.e., size, composition and crystal structure. XRD was performed by Rigaku diffractometer using Cu-K_α radiation (1.5406 Å) in a θ -2 θ configuration. The XRD pattern of the prepared CaAl₂O₄ nanoparticle was as shown in Figure 2. According to the Debye-Scherrer's formula ($D = K\lambda / (\beta \cos\theta)$), where K is the Scherrer's constant, λ the X-ray wavelength, β is the peak width at half-maximum and θ is the Bragg diffraction angle) the average crystallite size D is 38.55 nm.

The SEM images of prepared CaAl₂O₄ nanoparticle have shown the typical texture and morphology. SEM images obtained were depicted that the synthesized nanoparticles were crystal like structures.

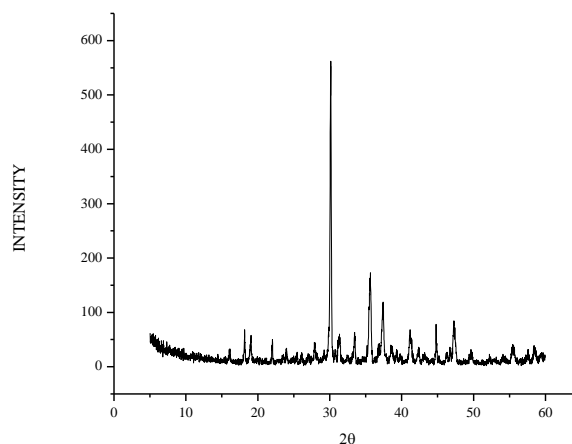


Figure-2
X-ray diffractograms of the nanoparticle CaAl₂O₄

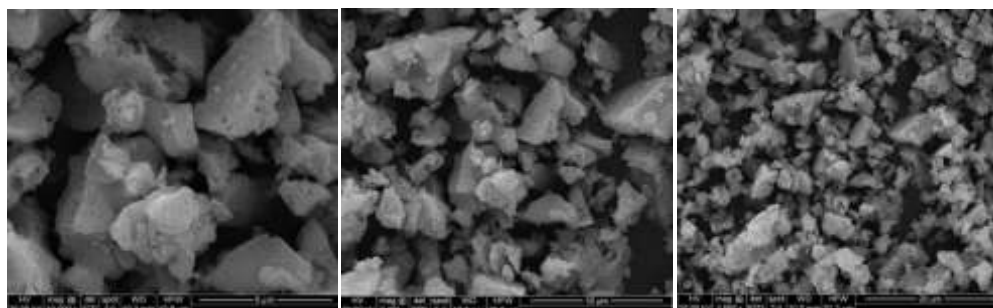


Figure-3
SEM micrographs of the nanoparticle CaAl₂O₄

Material and Methods

Experimental Procedure: The photocatalytic experiments were carried out in presence of direct sunlight of intensity at 1125 lux (using Lux meter). The experiments were carried out between 10.30 am to 1.30 pm. In all photocatalytic experiments, 100 ml of 30 ppm Violet GL2B solution was taken in 100 ml Borosil beakers. The UV-VIS spectrophotometer 119 (Systronics) was used for the determination of absorbance in the range of 200 to 800 nm. The λ_{max} of Violet GL2B was found to be 545 nm. The photocatalytic suspensions of 100 mg, 200 mg, 300 mg, 400 mg and 500 mg were tested on the dye samples. The suspension pH values were adjusted by using NaOH/ HCl solutions using pH meter. Before irradiation, photocatalyst suspension was stirred in the dark to ensure the adsorption equilibrium and it was kept in sunlight for the photocatalytic degradation. The suspension was sampled at regular time intervals of 30 minutes and centrifuged using (EBA-Hetlich) at 2500 rpm for 10 min to remove photocatalyst particles. The residual concentration of the solution samples was monitored by using UV-VIS spectrophotometer 169 (Systronics) at 545 nm. The violet GL2B experiments were conducted at pH range of 2.5 to 9.5 in order to study the efficiency of the nanoparticle on Acidic, alkaline and neutral conditions. The data obtained from the photocatalytic degradation experiments were then used to calculate the degradation efficiency D.

$$D = [(A_0 - A_t) \div A_0] \times 100$$

Where, A_0 is the initial absorbance of dye solution and A_t is absorbance at time 't'.

Results and Discussion

Effect of Sunlight and Catalyst: Figure 4 illustrate the photocatalytic degradation of Violet GL2B dye in aqueous solution under three different experimental conditions; Sunlight alone, Dark/ CaAl_2O_4 and Sunlight/ CaAl_2O_4 . The degradation rate was found to increase with increase in irradiation time and 100% degradation was achieved within 120 min for Violet GL2B. When 30 ppm of the dye along with CaAl_2O_4 was magnetically stirred for the same optimum dosage in the absence of sunlight, for pH 7 achieved degradation was 38.56%, whereas, when the dye was directly exposed to the sunlight without adding the photocatalyst decolorization was not observed. Similar results have been reported for ZnO-assisted photocatalytic degradation of azo dyes such as Red 3BL and Remazol Red RR¹⁸⁻²⁰.

Effect of catalyst loading on the rate of degradation: The catalytic dosage was varied from 100 mg - 500 mg for 30 ppm (30 mg/L) against Violet GL2B at three different pH levels. After adding the catalyst, the solution was stirred to disperse the catalyst throughout the solution and kept in sunlight and immediately it started degrading. For all the pH levels in the first 30 minutes the average percentage of degradation was found to be 53.34% for minimum dosage and 83.71% for the

maximum dosage (Figure 5), after 120 min it was degraded upto ~100 % for minimum dosage and ~100% for maximum dosage (Figure 6). Degradation efficiency was equal for all the catalytic dosages at 120 minutes. The photonic absorption has helped the reaction to a great extent and an increase in catalyst loading greatly enhances the process performance with respect to time.

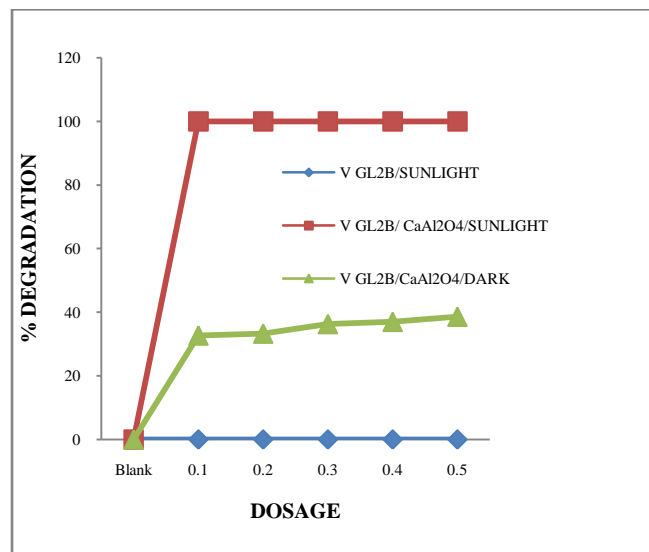


Figure-4

Photocatalytic degradation of Violet GL2B under different experimental conditions ($[\text{CaAl}_2\text{O}_4]=0.1\text{gm}, 0.2\text{ gm}, 0.3\text{ gm}, 0.4\text{ gm}$ and 0.5gm , $[\text{Violet GL2B}]=30\text{ ppm}$, neutral pH =7, $T=1125\text{ lux}$, $\lambda_{max}=545\text{ nm}$)

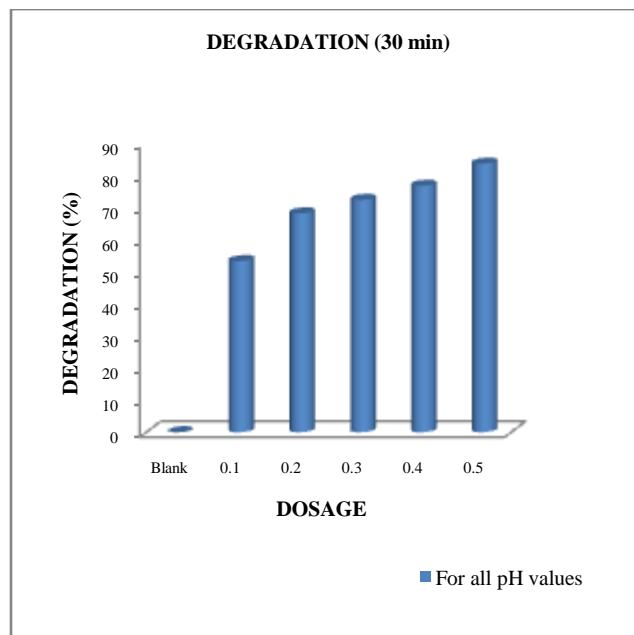


Figure-5

The average percentage of degradation at the first 30 minutes time interval for all the pH parameters

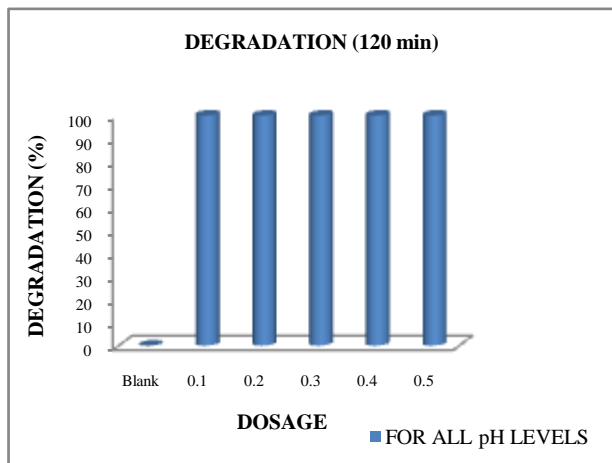
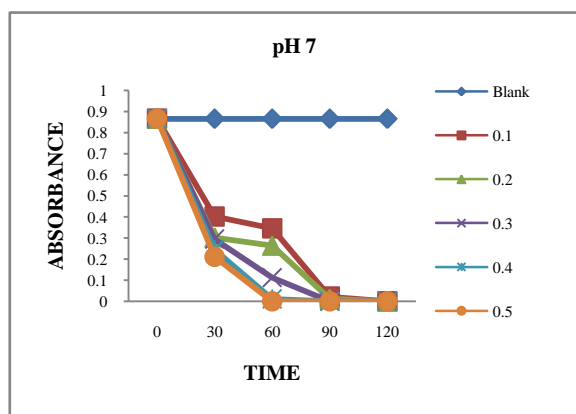


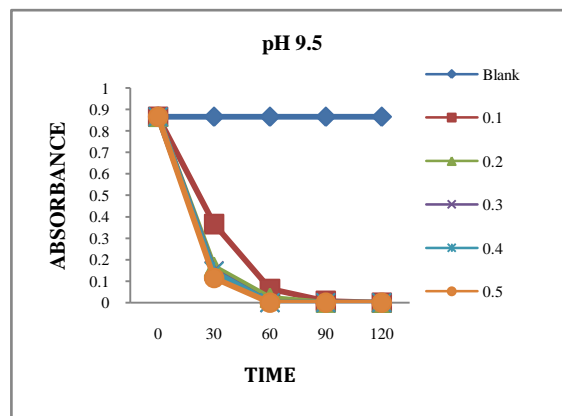
Figure-6

The average percentage of degradation at 120 minutes time interval for all the pH parameters

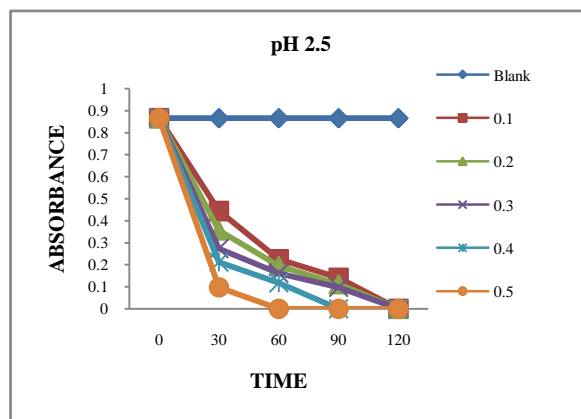
Effect of pH Solution: In order to study the effect of pH on the degradation efficiency of CaAl_2O_4 catalyst on photocatalytic degradation of violet GL2B dye, experiments were carried out at varied pH ranging from 2.5 to 9.5. As shown in figure 7, for Violet GL2B, the degradation rate increased to 100% for 300 mg, 400 mg and 500 mg in 60 minutes as the pH was increased from 7 to 9.5. The maximum degradation rate of violet GL2B (100%) was achieved at all pH ranges at the end of 120 minutes. The experimental data revealed that higher degradation rate of violet GL2B was observed in all the pH conditions. However in alkaline medium, the maximum colour degradation was attained at 60 minutes for 300mg, 400mg and 500mg dosages. In alkaline medium, excess of hydroxyl ions facilitate photogeneration of OH radicals which is accepted as primary oxidizing species responsible for photocatalytic degradation, resulting in enhancement of the efficiency of the process.



7(a)



7(b)



7(c)

Figure-7

Effect of catalyst loading on Violet GL2B 30mg/L at different pH levels, pH 7 7(a), pH 9.5 7(b) and pH 2.5 7(c) with respect to time interval 120 minutes

COD removal: It is observed that the COD decreases slower than the decolourization of the solution (figure 8). This is because of the fact that the dyes are not directly mineralized, but transformed in intermediate photoproducts. These generated photoproducts may submit other cycles of degradation to complete total mineralization. The initial COD of the dye was found to be 39.9 mg/L and after degradation the final COD was found to be 34.3 mg/L.

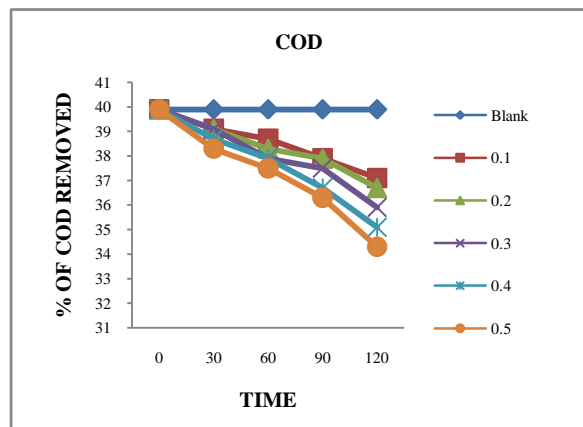
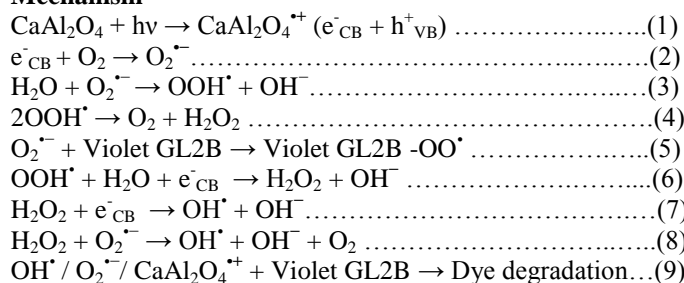


Figure-8

Percentage of COD removal by photocatalytic activity

Mechanism



The mechanism of photocatalytic activity of CaAl₂O₄ nanoparticle can be explained as shown above. Under sunlight irradiation CaAl₂O₄ molecules get excited and transfer electron to the conduction band (equation 1). Electron in the conduction band of CaAl₂O₄ can reduce molecular oxygen and produce the super oxide radical (equation 2). This radical may form hydrogen peroxide or organic peroxide in the presence of oxygen and organic molecule (equation 3,4,5). Hydrogen peroxide can be generated in another part (Equation 6). Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents (equation 7,8). The radicals produced are capable of attacking dye molecules and degrade them (equation 9).

Conclusion

Photocatalysis is a very effective method for the degradation of azo dyes. In this study, Calcium aluminate nanoparticles were synthesized and characterized by SEM and XRD studies. It was

observed that the synthesized Calcium aluminate (average particle size 38.55 nm) is photosensitive and effective in degrading selected azo dye (violet GL2B) completely in a short interval of time (120 minutes). The protocol developed may be employed effectively in the treatment of textile dye effluents which are hazardous to the environment. It is also economically feasible compared to other oxidative processes since it involves natural sunlight for photodegradation of dyes thereby saving energy.

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