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Photocatalytic degradation of Coralene dark red 2B dye using calcium aluminate ($CaAl_2O_4$) catalyst

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ABSTRACT

Photocatalytic activity of the synthesized Calcium aluminate ($CaAl_2O_4$) nanoparticle with average size of 8.34 nm was assessed on Coralene Dark Red 2B azo dye in an aqueous solution under solar irradiation. The nanoparticles were characterized by X-Ray Diffraction (XRD) and scanning electron microscopy (SEM). The effect of various parameters, such as effect of pH and catalyst loading on Coralene Dark Red 2B azo dye degradation was investigated. The degradation efficiency was studied by using spectrophotometer (473nm) with the addition of Calcium aluminate ($CaAl_2O_4$) nanoparticles (average size of 8.34nm) against Coralene Dark Red 2B azo dye (30 mg/L) and found to be very efficient in the degradation of the dye.

KEYWORDS

Calcium aluminate;
Coralene dark red 2B;
Photocatalytic activity;
Degradation;
Nanoparticle.

INTRODUCTION

Azo dyes are widely used synthetic dyes and are major pollutants in dye wastewaters. Azo dyes are having one or more azo bonds and are responsible for the intense colour. These dyes are classified as environmentally hazardous due to their toxicity and slow degradation[1,2]. Varity of synthetic complex organic dyes are often used by the textile industries for colouring materials of the textile goods for their creative and attractive look[3,4]. Thus, research is underway for appropriate treatment to remove impurities and obtain decolorization of different dyes[5]. The current existing techniques (both physical and chemical) for the treatment of wastewater containing dyes are cost effective but, forms hazardous by-products and require more energy. Similarly the biological treatment takes a long time to reach the required standards, which produces large quantity of sludge that cannot be reused[6]. Thus, there is an urgent need to develop effective alternative methods to treat these toxic textile industry effluents.

Photocatalytic degradation process is an advanced technology and is widely used in the destruction of organic pollutants in wastewater and effluents[7,8]. The photocatalytic degradation of textile azo dyes by using nanoparticles such as TiO_2 and ZnO are most widely studied in recent years[9,10]. The usage of semiconductor nanoparticle under UV light illumination have proved

to be advantageous and useful in degrading dyes in effluents[11,12]. Further, the nanoparticles such as CuO/MgO doped with Cr_2O_3 initiated significant increase in the catalytic activity[13].

In the present study, the photocatalytic activity of synthesized (low cost) Calcium aluminate ($CaAl_2O_4$) nanoparticles was investigated under natural sunlight for the degradation of an azo dye Coralene Dark Red 2B, which is widely used in textile industry.

EXPERIMENTAL

Materials and reagents

The nanoparticles were prepared by using solution combustion method[14,15]. The commercially available water soluble azo dye Coralene Dark Red 2B was obtained from Colourtex Limited, Surat, Gujarat. The Calcium nitrate ($Ca(NO_3)_2.4H_2O$) (99%, AR), Aluminium Nitrate ($Al_2(NO_3)_3.9H_2O$) (95%, AR), Acetamide (C_2H_5NO) (99%, AR), were obtained from Hi-Media Chemicals, Mumbai, India and used as received without purification. Metal nitrates allow proper homogenization, $Al_2(NO_3)_3.9H_2O$ and $Ca(NO_3)_2.4H_2O$ were selected as starting materials. Acetamide, the cheap and easily available in the market was used as fuel. Chemical structure of this dye is given in Figure 1. The UV-VIS spectrophotometer 119 (Systronics Company), single beam, has been used for recording absorbance at λ_{max} for the azo dye Coralene Dark Red 2B and the absorbance was recorded by using UV-VIS spectrophotometer 169 (Systronics).

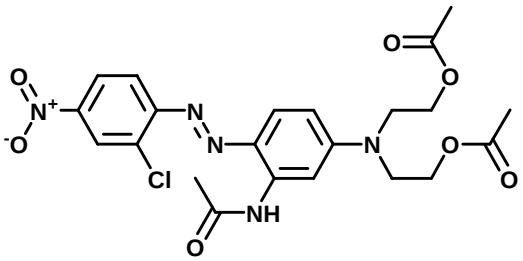

Figure 1 : Chemical structure of Coralene dark red 2B dye.

Synthesis of calcium aluminate nanoparticle

A mixture of stoichiometric amounts of Calcium nitrate (2.59 gm), Aluminium nitrate (8.25 gm), and fuel Acetamide (2.36 gm) was dissolved in approximately 15 ml of distilled water in a silica crucible (100 cm^3 capacity). The mixture solution was introduced into the muffle furnace which was preheated at 500^0 C. The solution undergoes dehydration and catches fire by spreading throughout the mass, finally yielding calcium aluminate nanoparticles. The obtained calcium aluminate was crushed in a mortar to make the Calcium aluminate amorphous. Thus, Calcium aluminate is formed. According to propellant chemistry the reaction is as shown[16].

$$11\ Ca(NO_3)_2 + 22\ (Al(NO_3)_3^{+}\ 40\ C_2H_5NO \rightarrow 11\ CaAl_2O_4 + 80\ CO_2 + 100\ H_2O + 64\ N_2$$

Procedure

All solar photocatalytic experiments were carried out in the borosil beakers of 500 ml capacity and was performed during the sunny days between 11:00 am to 3:00 pm when solar intensity fluctuations were less, the solar intensity was found to be 423 lux during these periods. The absorbance of the samples were immediately checked at regular intervals of time by using spectrophotometer 169 (Systronics) before and after reaction at wavelength 473 nm (λ_{max}). Experiments were repeated to get better results. The newly synthesized nanoparticles were characterized by XRD and SEM studies.

The known concentration dye solution was prepared by dissolving 30 mg of Coralene Dark Red 2B dye in 1000 ml distilled water and it was used for the degradation. Initially 300 ml of 30 mg/L dye sample was tested with different catalyst dosage such as 300, 600, 900, 1200 and 1500 mg in presence of direct sunlight. After the photocatalytic degradation, the extent of decolorization was estimated by recording absorbance of the dye solution with respective to 30 min time interval. The experiments were repeated for different pH of 2, 5, 9 and 12 for the same standard solution. The decolorization efficiency of Calcium aluminate nanoparticles is shown in Figure 4. The percentage of decolorization was determined by using the following equation.

$$\text{Decolorization} = \frac{(A_0 - A_t)}{A_0} \times 100$$

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

XRD and SEM of the prepared calcium aluminate

nanoparticle

The XRD was performed by powder X-ray diffraction (Rigaku diffractrometer) using Cu-K_α radiation (1.5406 Å) in a θ-2θ configuration. The output from XRD analysis of the prepared Calcium aluminate nanoparticle sample yields a plot of intensity versus angle of diffraction as shown in Figure 2. Thus various reflections of Calcium aluminate nanoparticles are observed which indicate that the product is amorphous (JCPDS card no: 70-0134). In addition, the particle size is very small 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 full width of half-maximum, and θ is the Bragg diffraction angle calculated using the Debye–Scherrer's formula. The average crystallite size D is 8.34 nm.

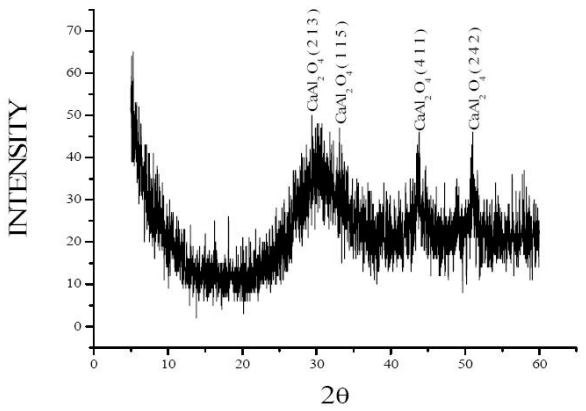

Figure 2 : XRD of the calcium aluminate nanoparticle.

The SEM images of prepared Calcium aluminate nanoparticles have shown a typical texture and morphology. The Figure 3 has shown evenly distributed amorphous nature of the Calcium aluminate in the SEM images.

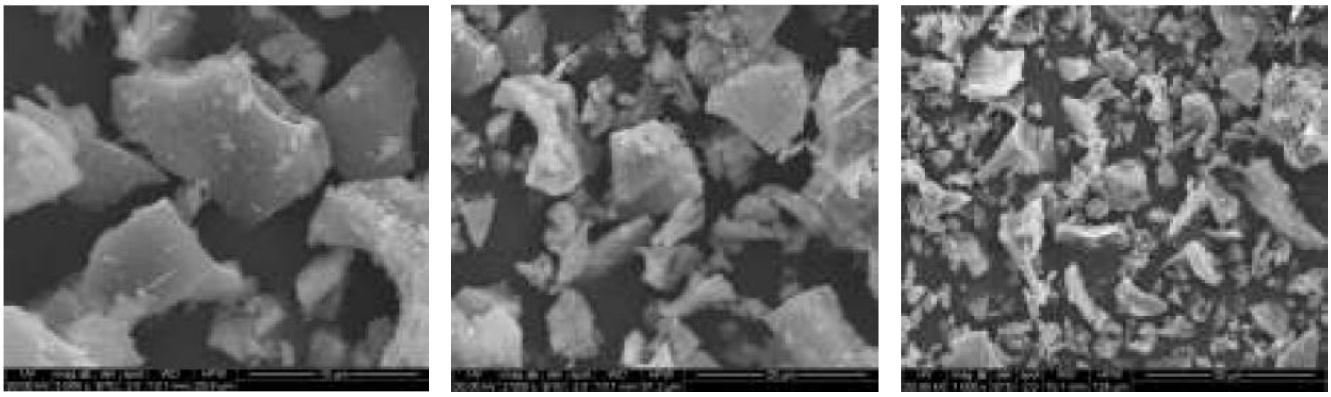

Figure 3 : SEM micrographs of the calcium aluminate nanoparticle.

RESULTS AND DISCUSSIONS

Effect of catalyst loading

The catalytic dosage was varied from 300 mg, 600 mg, 900 mg, 1200 mg and 1500mg for 30 (mg/L) of Coralene Dark Red 2B dye mg/L in the neutral condition. For the first 30 min, it was 79.78 % for minimum dosage and 83.68 % for the maximum dosage decolorized, after 120 min it was degraded up to 84.04 % for minimum dosage and 86.87 % for maximum dosage. Decolorization efficiency was same and maximum for all the catalyst dosages of 300 mg, 600 mg, 900 mg, 1200 mg and 1500 mg/300ml. The catalyst loading levels in photonic adsorption has helped the reaction to a great extent, and the catalyst loading has significantly enhanced the degradation performance[17]. In all the dosages the rate of decolorization is fast in the first 30 min and slightly slow in the later one and half an hour or the initial decolorization rate is very fast and decreases exponentially with time.

The mechanism of the photocatalytic degradation of Coralene Dark Red 2B dye is as follows[18].

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

$$h^+_{VB} + H_2O \rightarrow H^+ + OH^- \quad (2)$$

$$h_{VB} + OH^- \rightarrow O^-H \quad (3)$$

$$OH^- + \text{Coralene Dark Red 2B} \rightarrow \text{decomposed Coralene Dark Red 2B} \quad (4)$$

$$CaAl_2O_4 + 2\,h^+_{VB} \rightarrow Ca^{2+} + 2Al^{3+} + 4O^* \text{ (active oxygen)} \quad (5)$$

Upon exposure to UV-irradiation, the $CaAl_2O_4$ is photoexcited and an electron–hole pair is formed (1), where e^-_{CB} is the electron in the conduction band, h^+_{VB} is the hole in the valence band $CaAl_2O_4$ ($e^-_{CB} + h^+_{VB}$). Due to the amphoteric property of $CaAl_2O_4$ semiconductor

nanoparticle, water molecules in acidic condition were adsorbed on its excited surface and decomposed by oxidative potential of the hole (2). The formed OH^- ions are further oxidized by the hole to produce $OH^{\cdot}$ radicals (3) and lead to partial or complete dye decomposition (4). On the other hand, in acidic solution $CaAl_2O_4$ reacts with the photogenerated holes and undergoes self-oxidation (5). Thus, the Coralene Dark Red 2B dye will also be further decomposed by the action of the more number of newly generated active oxygen.

Effect of pH on the dye samples

The rate of degradation was found to be less in neutral condition as compared to other pH ranges with the degradation of approximately 87% in 120 minutes. When the pH increased to 9 and 12 the rate of degradation was increased with the degradation of approximately 90% in 120 minutes. Also when pH decreased to pH 2 and 5 the degradation rate was high. Hence it is concluded that the degradation in acidic medium, basic medium is higher than that of neutral medium. The increase in rate of photocatalytic degradation may be due to the more availability of OH^- ions. In pH range between 2 to 12 more $O^{\cdot}H$ radicals may be generated due to electronic excitation in catalyst. Formation of

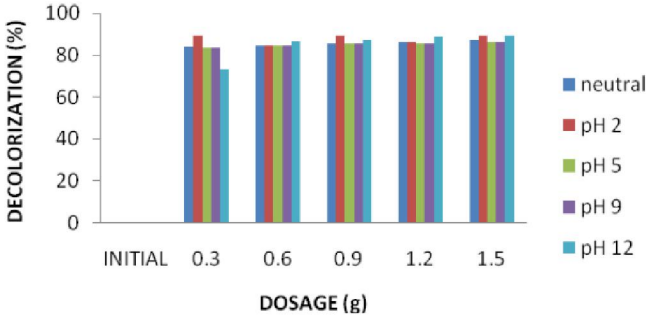

Figure 4 : Effect of pH on decolorization efficiency of calcium aluminate nanoparticle against Coralene dark red 2B azo dye.

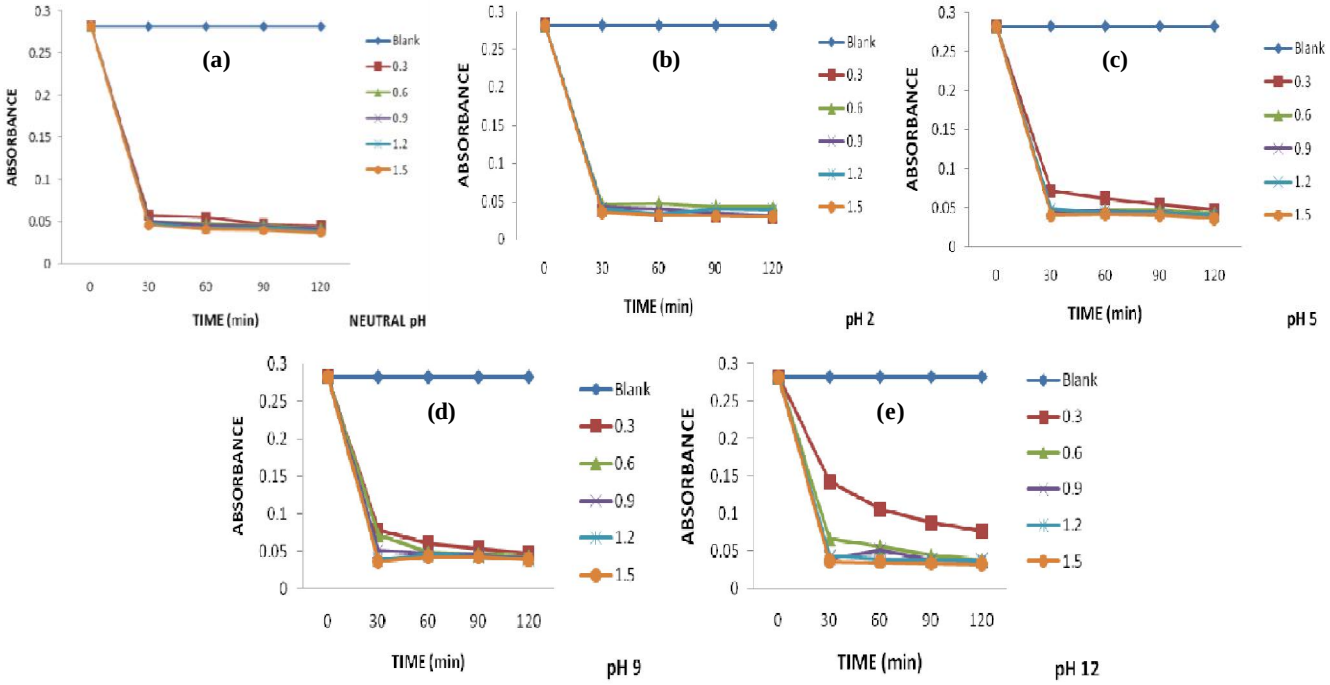

Figure 5 : Effect of catalyst load on the decolorization of coralene dark red 2B dyes at concentration 30mg/L, on 5(a) Neutral, 5(b) pH 2, 5(c) pH 5, 5(d) pH 9, and 5(e) pH 12.

these hydroxyl radicals is responsible for the high photocatalytic degradation. The pH effect is shown in Figure 4 and Figure 5.

CONCLUSION

It was observed that the synthesized Calcium aluminate is solar photosensitive and effective in degrading selected model azo dye completely in a short interval of time. Photocatalytic decolorization of water soluble azo dye is dependent on irradiation time and catalyst loading i.e higher the irradiation time and catalyst dosage high will be the degradation and viceversa. The protocol developed may be employed effectively in treatment of textile dye effluents which are causing pollution in the environment, as the catalyst found to

be eco-friendly and economically cheap compared to other oxidative processes. Further research work is under progress.

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