STUDY ON PHOTOCATALYTIC DEGRADATION CORALENE RED F3BS BY USING SYNTHESIZED Al_2O_3 NANOPARTICLES

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ABSTRACT

In this study, Al_2O_3 nano-particle was synthesized by solution combustion method using the acetamide as fuel and was used for the degradation of selected Coralene Red F3BS azo dye. This nano-particle was characterized by using X-ray diffraction (XRD), UV-absorbance studies and Scanning Electron Micrograph (SEM). The average size was found to be 56 nm. The experiments were carried out by varying parameters such as catalyst concentration, pH, varying dye concentration and effect on sunlight. The experimental results demonstrated that, the synthesized Al_2O_3 nano-particles achieved maximum degradation of 96%.

Key words - Al_2O_3, Coralene Red F3BS, Decolourization, , Nano-particles, Photocatalyst.

I.INTODUCTION

Azo dyes are synthetic colours that contain an azo group, -N=N-, as a part of the structure. Azo group do not occur naturally. Most of the azo dye contains only one azo group but some contain 2, 3 or more [1].

Azo dye accounts for approximately 60 – 70 % of all the dyes used in textile manufacture. In theory azo dyes can supply a complete rainbow of colours, but the different, mainly aromatic side groups around the azo bond help to stabilize the N=N group by making it part of an extended decolorized system [2].

A major challenge we deal with in industries such as textiles, food, paper, cosmetics and so on has always been refining toxic contaminants before discharging them into the environment [3].

Since the beginning of humankind, people have been using colorants for painting and dyeing of their surroundings, their skins and their clothes. Until the middle of the 19^{th} century, all colorants applied were from natural origin. Organic natural colorants have also a timeless history of application, especially as textile dyes. These dyes are all aromatic compounds, originating usually from plants (e.g. there dye alizarin from madder and indigo from wood) but also from insects, fungi and lichens. Synthetic dye manufacturing started in 1856, when the English chemist W.H. Perkin, in an attempt to synthesize quinine, obtained instead a bluish substance with excellent dyeing properties that later became known as aniline purple. In the beginning of the 20th century, synthetic dyestuffs had almost completely supplanted natural dyes. Economic [4]

In textile industry, dyes and their intermediates with high aromaticity and low biodegradability have emerged as major environmental pollutants and nearly 10-15% of the dye is lost in the dyeing process and released into the effluent which is an important source of environmental contamination. Huge amount of water is used for dyeing and finishing of fabrics in the textile industries [5,6].

Synthetic dyes are extensively used in different industries. The discharge of little amounts of dyes can harm the environment especially the aquatic ecosystem. Coloured effluents released by different industries may be mutagenic, carcinogenic and toxic. Synthetic dyes are usually treated by physical or chemical methods.

In recent years, photocatalytic degradation by semiconductors is emerged as a new and effective technique for the removal of pollutants from water. The discharge of highly coloured dye wastewater impedes light penetration, which disturbs the various biological reactions within a stream. Dyes can cause allergic dermatitis, skin irritation, cancer, genetic mutation etc., [7,8].

Recently the field of photocatalysis is developing fast because; solar energy is a renewable source of energy which is abundant and freely available for almost eight to nine months in a year over most part of the world [9]. This research article is focused on Solution combustion method of Al_2O_3 nanoparticle and its photocatalysis against colour induced by Coralene Red F3BS in lab scale which will combine effectiveness and cheapness in treating these coloured effluents.

II.MATERIAL AND METHODS

2.1 CHEMICAL REAGENTS

The chemicals used for the synthesis of aluminium nitrate (Al_2O_3) nanoparticles were from Hi-media Chemicals Mumbai [Aluminium Nitrate $Al_2(NO_3)_3 9H_2O$) (95% AR) and [Acetamide (CH_3CONH_2) (99% AR)] India. The Coralene Red F3BS dye used for the photocatalytic study was purchased from Colourtex Limited, Surat, Gujarat.

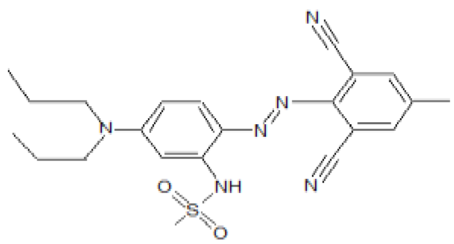

Fig 1: Chemical Structure of Coralene Red F3BS

2.2SYNTHESIS ALUMINIUM NITRATE NANOPARTICLES

A stoichiometric amount of Aluminium nitrate (16.504g) and Acetamide (3.542 g) was dissolved in ~25 ml of distilled water in a silica crucible (100 cm^3 capacity). The Silica crucible was then kept for calcination in the muffle furnace (preheated to 500 C°) till the complete combustion of Aluminium nitrate with the fuel acetamide

[10,11]. The obtained Aluminium nitrate, nanoparticles were crushed in a mortar to make it amorphous. According to propellant chemistry the reaction is as follows [12].

$$22\ Al(NO_3) + 30\ CH_3CONH_2 \rightarrow 11\ Al_2O_3 + 60\ CO_2 + 75\ H_2O + 48\ N_2 \text{ …….. (Eq 1)}$$

2.3XRD OF ALUMINIUM NITRATE NANOPARTICLES

The powdered sample of Al_2O_3 (Acetamide) nanoparticle was examined by XRD and 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 (1.5406Å) in a θ-2θ configuration. According to the XRD the average crystallite size of Al_2O_3 was found to be 56 nm.

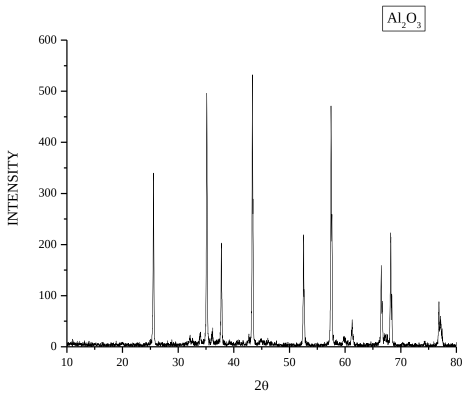

Fig 2: X-Ray diffraction of Al_2O_3

2.4SCANNING ELECTRON MICROSCOPE OF Al_2O_3

SEM images of single crystal Al_2O_3 (Acetamide) represents a combination of scattered crystals, Sharpe edged, and plate like structures which looks like a colony. The enlarged image shows the uneven size and shape of the different nano-particles, which also revels the thick attachment of nano-particles over one another.

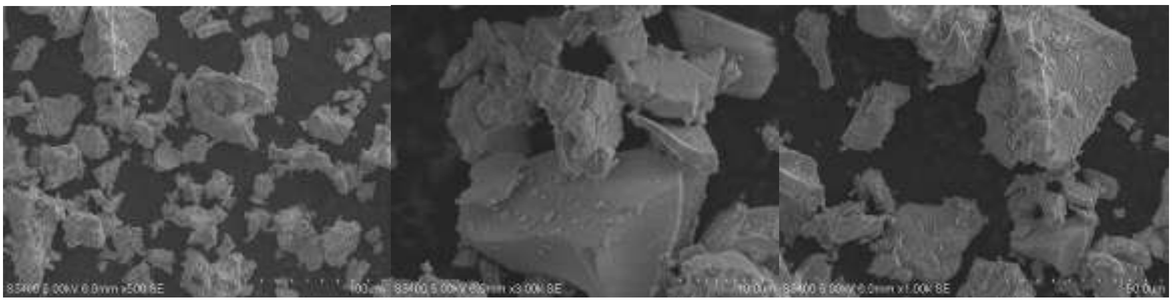

Fig 3: SEM Photograph of Al_2O_3

2.5UV-ABSORPTION SPECTROSCOPY

The optical absorption is an important tool to obtain optical energy band gap of crystalline and amorphous materials. The fundamental absorption corresponds to the electron excitation from the valence band to the

conduction band can be used to determine the nature and value of the optical band gap. The absorption spectrum reveals that the Al_2O_3 nanoparticle absorption in the visible light region with a wavelength above 400 nm.
The optical energy band gap Eg is calculated from the relation:

$$(\alpha h\upsilon) = B\,(h\upsilon - Eg)^n$$

Where, 'hυ' is the photon energy, 'B' is the constant and 'n' is the power factor and that takes 1/2, 2, 3/2 and 3 allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. The optical band gap of the Al_2O_3 nanoparticle is 2.84 eV.

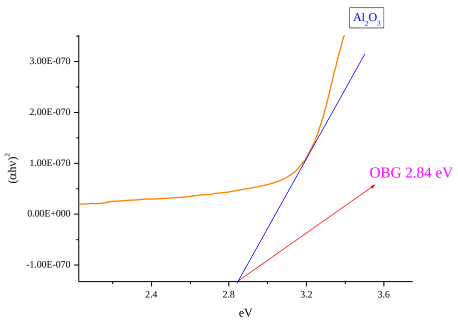

Fig 4: UV absorbance graph

III.RESULT AND DISCUSSION

3.1EXPERIMENTAL PROCEDURE

The degradation of the dye molecules was evaluated using ultraviolet and visible absorption spectroscopy. An absorbance spectrum of the dye solution was taken using UV-VIS Spectrophotometer 119 (Systronics) in the range of 200 to 800 nm. The λ_{max} of Coralene Red F3BS was found to be 510 nm. The photocatalytic reaction experiments were carried out in the presence of direct sunlight. The standard (20mg/L) dye solution was prepared by dissolving 20 mg of Coralene Red F3BS dye in 1000 ml distilled water and investigated for its decolourization by using aluminium nitrate nanoparticles as catalysts at different dosages and pH levels. The pH of the dye solution was adjusted by using dilute hydrochloric acid and sodium hydroxide. At each pH levels (ranging from 2 to 11) the reaction volume of 100 ml dye solution (of 20 mg/L concentration) was taken and catalyst dosages starting from 0.1 g to 1 g were added for the colour degradation efficiency study under direct sunlight. After the dispersion of the catalyst, the absorbance of dye solution was recorded at an interval of 30 minutes time using UV-VIS Spectrophotometer -169 (Systronics). The percentage of colour degradation was calculated by using the following formula.

$$\text{Decolriazation} = \left(\frac{A_0 - A_t}{A_0}\right) \times 100$$

Where, $\mathbf{A_0}$ is the initial absorbance of dye solution and $\mathbf{A_t}$ is absorbance at time 't'

3.2EFFECT OF CATALYST CONCENTRATION ON CORALENE RED F3BS

The effect of catalyst concentration on the photocatalytic degradation was studied over a range of the catalyst amount from 0.1 to 1g/100ml for Coralene Red F3BS. The synthesized nanoparticles have shown appreciable results. The Al_2O_3 (Acetamide) with the nano-particle size 56 nm has shown 95.70% degradation. Since, the photodegradation was most effective at 0.9g/100ml in 120 minutes for Al_2O_3 (Acetamide) nanoparticle dosages showed in (Fig. 5) (Photo 1), further experiments were continued with same dosages [13].

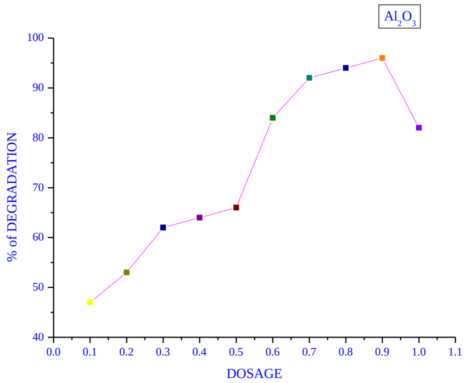

Fig. 5: Effect of catalyst concentration on Coralene Red F3BS at 120 minutes [Coralene Red F3BS =20 ppm, pH=7, Al_2O_3 (Acetamide)]

Photo 1: Effect of catalyst concentration on Coralene Red F3BS at 120 minutes [Coralene Red F3BS = 20 ppm, pH=7, Al_2O_3 (Acetamide)]

3.3MECHANISM OF THE PHOTOCATALYTIC DEGRADATION

Nanoparticles + hν → (e^-_{CB} + h^+_{VB}) (Eq. 1)

Nanoparticle molecules get excited and transfer electrons to the conduction band.

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

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

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

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

$O_2^{\bullet -}$ + Coralene Red F3BS→ Coralene Red F3BS-OO$^{\bullet}$ (Eq. 5)

Molecular oxygen, adsorbed on the surface of the photocatalysts prevents the hole-electron pair recombination process [14]. 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. 6)

Hydrogen peroxide can be generated in another path

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

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

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

$OH^{\bullet}$ / $O_2^{\bullet -}$/ Nano-particles$^{\bullet +}$ + Coralene Red F3BS → Coralene Red F3BS degradation (Eq. 9)

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

3.4EFFECT OF pH ON CORALENE RED F3BS

In order to study the effect of pH on the degradation efficiency of Al_2O_3 (Acetamide) as catalyst, the experiments were carried out at pH ranging from 2 to11. The results showed that pH significantly affected the degradation efficiency (Fig. 6) (Photo 2).

The degradation rate of Coralene Red F3BS for Al_2O_3 the degradation of the Coralene Red F3BS increased from 81.3% to 96% from pH 2 to 4 and decreased 87.5% at pH 11 in 120 minutes for 0.4g/100ml. The maximum degradation rate for the nanoparticle was achieved at pH 4 [15].

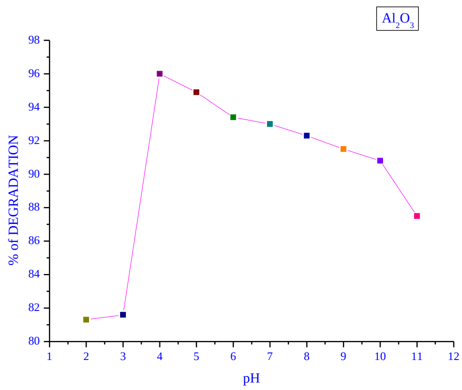

Fig. 6: Effect of pH on Coralene Red F3BS at 120 minutes [Coralene Red F3BS=20 ppm, Al_2O_3 (Acetamide)]

Photo 2: Effect of pH on Coralene Red F3BS at 120 minutes [Coralene Red F3BS=20 ppm, Al_2O_3 (Acetamide)]

3.5EFFECT OF INITIAL DYE CONCENTRATION

The experiments were conducted to study the effect of initial dye concentration by varying the Coralene Red F3BS concentration from 20 ppm to 70 ppm (Photo 3). The results obtained for Al_2O_3 (Acetamide) is 96% for

20ppm, 93% for 30ppm , 89.3% for 40ppm, 86.8% for 50ppm, 73.9% for 60ppm and 47.8% for 70ppm respectively (Fig 7). 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 [16]. 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 absorption of the catalyst particles, and consequently decrease photocatalytic reaction rate [17].

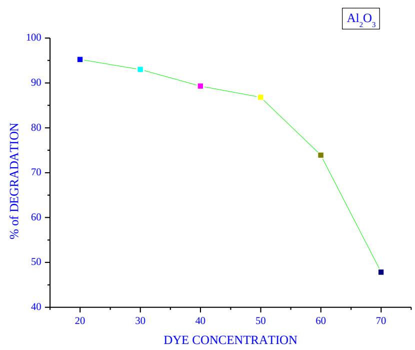

Fig 7: Effect of initial dye concentration on the photocatalytic degradation of Coralene Red F3BS [Al_2O_3 (Acetamide) g/pH=0.9/4 and Coralene Red F3BS = (20+30+40+50+60+70) ppm]

Photo 3: Effect of initial dye concentration on the photocatalytic degradation of Coralene Red F3BS [Al_2O_3 (Acetamide) g/pH=0.9/4 and Coralene Red F3BS = (20+30+40+50+60+70) ppm]

3.6EFFECT OF SUNLIGHT IRRADIATION ON CORALENE RED F3BS

The photocatalytic degradation of Coralene Red F3BS azo dye (20mg/L) under three different experimental conditions were examined, *i.e.,* through sunlight alone, dye/dark/catalyst, dye/UV/catalyst and dye/sunlight/catalyst for the catalyst. Coralene Red F3BS azo dye solution when exposed directly to the sunlight 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/sunlight/ Al_2O_3 showed 96%, dye/UV/catalyst found to be 61.76% and for dye/dark/ Al_2O_3 54.04% was recorded (Fig 8). These results clearly indicate that photodegradation occurs most efficiently in the presence of sunlight (Photo 4) [18,19].

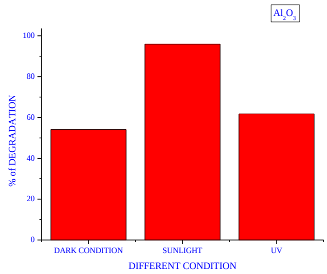

Fig. 8: Effect of sunlight irradiation with respect to Dark condition and UV condition on photocatalytic degradation of Coralene Red F3BS in 120 minutes

Photo 4: Effect of sunlight irradiation with respect to Dark condition and UV condition on photocatalytic degradation of Coralene Red F3BS in 120 minutes.

IV.CONCLUSION

The synthesized aluminium nitrate is proved to be photocatalytic and effective in degrading the Coralene Red F3BS dye in a shorter interval of time. The photocatalytic degradation of this dye Coralene Red F3BS using sunlight as a source of irradiation was studied. The proposed photocatalytic methods proved to be very effective for the degradation of dye Red F3BS. For the dye Coralene Red F3BS we have achieved 96% degradation in pH 4. With this result we can say that the application of nano sized materials is more suitable for degradation of dye effluents in laboratory conditions. This will help in the treatment of textile effluents which are causing pollution to the environment.

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