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Solar Light Induced Photocatalytic Degradation of Textile Disperse Dye Coralene Dark Red 2B in Effluents

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Abstract: ***Degradation of textile de coralene dark red 2B was carried out using advanced oxidation method. The whole experiment was performed under solar light irradiation intensity in range of 400-500 Lux. Results show that degradation is affected by various parameters like intensity of solar light, concentration of dye, concentration of H_2O_2, Amount of TiO_2, effect of pH exposure time. Considering all affection parameters, a protocol for degradation of coralene Dark red 2B was developed. Degraded samples were subjected to HPTLC to find out end degraded products. Results show that there is complete degradation of dye and no visible spot are obtained in the TLC plotter when scanned. This method was applied to treatment of effluent samples taken from dye industry of Ankleshwar city and promising results were obtained.***

Keywords: Coralene Dark red 2B, Solar light, HPTLC, Degradation

1. Introduction

The textile dyes are a voluminous resource of coloured organic compounds that present an increasing environmental crisis [1]. The textile industry uses approximately 21-377 m^3 of water per ton of textile produced and thus generates large quantities of wastewater from different steps of dyeing and finishing process [2]. They pose serious environmental problems because of their colour, low biochemical oxygen demand and high chemical oxygen demand. Various chemical and physical processes, such as chemical precipitation and separation, electro coagulation and elimination by adsorption on activated carbon, etc., are currently used for treating textile wastewater [3].

Disperse dyes are synthetic dyes. Disperse dye is one kind of organic substance which is free of ionizing Group. Disperse dyes are less soluble in water and used for dyeing synthetic textile materials. Disperse dyes is mainly used for dyeing polyester yarn of fabric [4].

Advanced oxidation processes (AOPs) are the group of water and wastewater treatments in which the main oxidative agent is the hydroxyl radical (HO•). This oxidant is characterized by one of the highest oxidative potentials in nature and therefore many organic compounds may be decomposed by AOPs [5].

Degradation of the dye with photocatalytic system and the effects of different parameters such as concentration of solar light coating of catalyst with cement binder and role of different commercial catalysts on the degradation efficiencies is already studied [6]. Investigations have been reported on variation of the parameters such as catalyst dosage, varying dye concentration and pH of the dye solution, H_2O_2 concentration [7].

Improving the knowledge concerning the degradation pathways may be there for helpful to optimize the process by identification of the byproducts and hence help in the determination of the metabolic degradation pathways.

HPTLC is a powerful analytical technique because of its reliability, simplicity, reproducibility and rapid measurement. Sample clean up, and its main advantage is that a large number of samples can be simultaneously analyzed. Choosing the appropriate mobile and stationary phases is the sole difficultness of the method. For a qualitative determination of a mixture of dyes, the TLC method is the best solution [8].

Here, in this paper solar assisted photo catalytic advanced oxidation method is used to degrade textile disperse dye coralene dark red 2B in effluents. Effluents were collected from shree Balaji, pvt.LTD Ankleshwar GIDC Gujarat.

These effluents are added by local industries of the area to water sources is big issue in that area.

HPTLC Method was developed to check the complete degradation and end products obtained after degradation.

2. Experimental

2.1 Chemicals

The commercially available water soluble azo dye Coralene dark red 2B (λ max-502nm) was obtained from Shree Balaji processor G.I.D.C, Ankleshwar Gujarat. The chemicals like TiO_2, H_2O_2 were obtained from Chitichem, vadodara and Samir tech-chem PVT, LTD. Vadodara, respectively.

Toluene, methanol and acetone were of analytical grade. As stationary phase Aluminum backed silica gel plate (20×10 cm) 60F254 were supplied by e Merck, USA.

2.2 Instruments

Optical density measurements of solution were studied on thermo scientific, Evolution-201 (Sr.no.-5A30253001, MA

02454) ultraviolet- visible spectrophotometer supplied by Thermo Fisher Scientific Inc, Waltham, USA.

Racer stop watch was used for measuring time and was supplied by sidhi Enterprises, New Delhi, India

For centrifugation, the centrifugation machine supplied by REMI, the Global Marketing, Nagpur, Maharashtra, India is used.

A digital µ pH meter Systronic Model 361 supplied by Systronic Pvt. Ltd Ahmadabad, India is used.

Digital Lux meter Model-TES 1334 (TES-1332A) Supplied by Mumbai, Maharashtra, India is used.

HPTLC system supplied by CAMAG Switzerland equipped with Linomat v auto sampler and scanner-4 is used for degradation study.

2.3 Methods

2.3.1 Method Development

The λmax value of Coralene dark red 2B was found to be 502 nm. All experiments were carried out using the samples exposed to direct sunlight during April 2017 to June 2017. The known concentration of dye solutions were prepared by dissolving 50 mg of coralene dark red 2B in 1000 ml of double distilled water and investigated for its decolorization in the presence of TiO_2 nano particle at different catalyst dosages and pH level. Initially 100 ml of 50 mg/L dye sample were tested with different catalyst dosage (from 50 mg to 150 mg) in the presence of direct sunlight. Absorbance was recorded by thermo scientific instrument. The experiments were repeated at different pH levels (from 2 to 10) for the 100 ml of same standard dye solutions with the optimum catalyst dose.

After 120 minutes exposure to light, the samples were subjected to spectro photometric analysis and to HPTLC method to identity end degradation product.

2.3.2 Analysis of degraded End product

HPTLC method developed by using mobile phase consisting of Toluene: Methanol: Acetone (20:2:1). 5.0 µl of each sample was sprayed on the 20×10 cm plate. After drying the starting zone for 1 min, the silica gel plate was developed with each solvent according to the CAMAG method, in order to find the best eluent. Development was performed in the twin through chamber up to migration distance of measured from the lower plate edge. After drying for 10 min, the point at which the spectra recorded for various parameter, and wavelength 502 nm corresponding to the maximum absorbance, with TLC Scanner (CAMAG); evaluation was performed via peak height.

2.4 Calculations

The percentage of degradation was determined by using the following equation,

% Discoloration = $((A_0 - A_t) \div A_0) \times 100$ (1)

Where, A_0 is the initial absorbance of dye solution & At is absorbance at time interval‘t’ (30, 60, 90, 120 min).

3. Results and Discussion

3.1 Chemical structure

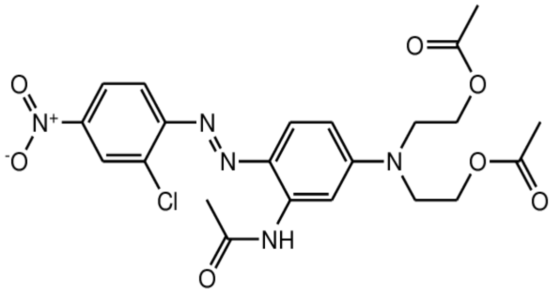

Figure 1: Chemical structure of coralene dark red 2B [Molecular formula $C_{23}H_{26}ClN_5O_7$, Molecular weight 519.93 (g/mol)]

3.2 Typical Run

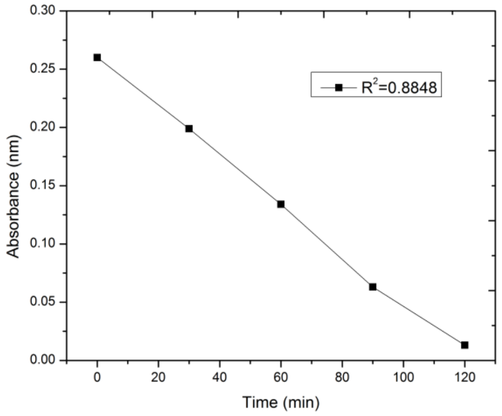

Figure 2: A typical run curve of Coralene dark Red 2B at wave length of 502nm

[Dye = 50mg/L, H_2O_2 = 2250mg/L, pH= 3.5, TiO_2 = 100mg, Light Intensity = 501×100 Lux]

The photocatalytic degradation of Coralene Dark Red 2B was observed at λ_{max}= 502 nm. The results of typical run are graphically represented in fig.2. The plot of O.D v/s exposure time was found to be a straight line. The optical density of the reaction mixture decreases with increasing time intervals showing thereby that the concentration of dye decreases with increasing time exposure.

3.3 Effect of Dye concentration

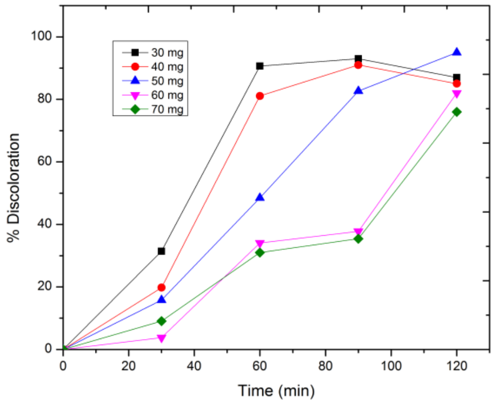

Figure 3: Effect of dye concentration of dye on the degradation of coralene dark Red 2B [Dye = 30mg/L to 70mg/L H_2O_2; 2250mg/L pH; 3.5; TiO_2 100mg; Intensity; 501×100 Lux]

Effect of variation of dye concentration was also studied by taking different concentrations of dyes, the initial concentrations of the dye from 30 to 70 mg/L in order to assess the appropriate amount of catalyst dose. This may be attributed to the fact that as the concentration of dyes was increased, more dyes molecules were available for excitation followed by inter system crossing and hence, there was an increase in the rate. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dyes further. In this case of dye 100 mg/L, 95% decolorization occurred in 120 min.

We have applied this method also for another 120 min but there is no more change in degradation rate. It was observed that increase in concentration decreased the rate of the reaction.

3.4 Effect of pH

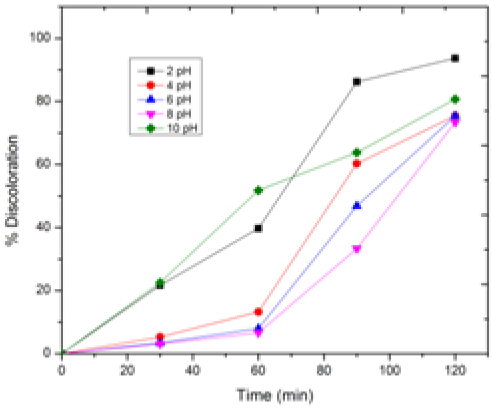

Figure 4: pH effect on degradation of Coralene dark Red 2B
[Coralene dark Red 2B; 50mg/L H_2O_2; 2250mg/L TiO_2 100mg; pH; 2 to 10 Intensity 501×100 Lux]

To investigate the effect of pH on the decolorization efficiency of Corolene Dark Red 2B experiments were carried out at various pH values, ranging from 2.0 to 10, at a constant dye concentration of 100 mg/L. The pH was maintained with help of 0.1 N (HCL) and 0.1 N (NaOH) solutions.

The decolorization efficiency of dye at different pH values was shown in fig.4. The decolorization efficiencies were 93.65% and 80.67% after 120 min of irradiation for pH 2.0 and 10.0 respectively. The pH influences the adsorption of dye molecules on the TiO_2 become surface, which is an important step in photo degradation remains positively charged in acidic medium (pH<6.8) and negatively charged in alkaline medium (pH>6.8), as shown in the following equations

$$\text{Ti - OH} + H^+ = TiOH_2^+ \tag{2}$$
$$\text{Ti - OH} + OH^- = TiO^- + H_2O \tag{3}$$

The pH changes can thus influence the adsorption of dye molecules onto the TiO_2 surface, an important step for the photo oxidation to occur. The acidic solution favors the adsorption of the dye onto photo catalyst surface; thus, the photo degradation efficiency increases.

3.5 Effect of Amount of Semiconductor

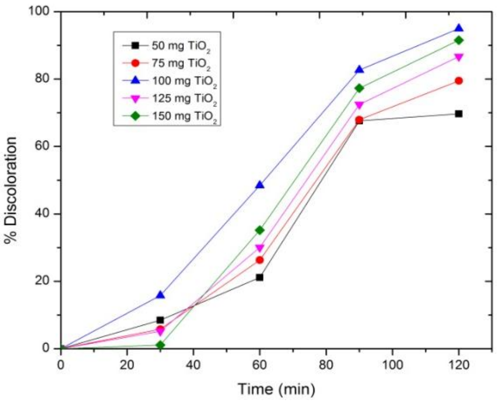

Figure 5: Effect of Amount of semiconductor of dye on the degradation of coralene dark Red 2B
[Coralene dark Red 2B; 50mg/L H_2O_2; 2250mg/L pH; 4.5 TiO_2 50mg to 125 mg; Intensity; 501×100 Lux]

The effect of TiO_2 loading on the photo degradation rate has been examined by varying its amount from 50 mg to 125 mg/100mL in the reaction solution. Rate constant values increased with the increased in catalyst loading. In Fig.5. The Discoloration value 95 % has been shown to be maximal at 100 mg/100 mL of catalyst loading.

Photo catalytic degradation efficiency increased with an increase in catalysts mass. This behavior might be due to an increase in the amount of active site on surface of TiO_2 particles. After the optimum amount of TiO_2, the activity of photocatalytic decolorization decreased with increase of catalyst concentration. Because higher loading of catalyst also causes increase in turbidity of the solution which reduced the light penetration in photoactive volume. Hence photoactive volume shrinks and aggregations of TiO_2 particle causing decrease in the number of surface active sites.

3.6 Effect of Variation in H_2O_2 concentration

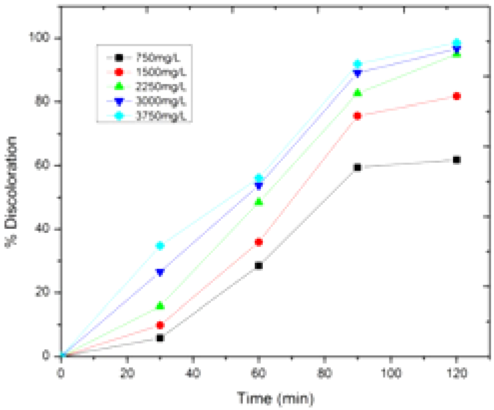

Figure 6: Effect of hydrogen peroxide on degradation of Coralene dark Red 2B
[Coralene dark Red 2B; 50mg/L H_2O_2; 750 mg/L to 3750mg/L pH; 3.5 TiO_2 100 mg; Intensity; 501×100 Lux]

The experiment of varying concentration of H_2O_2 values was conducted to study the effect of H_2O_2 concentration on degradation dye. The percentage degradation efficiency by variation in hydrogen peroxide concentration is shown in

Fig.-6. The range of H_2O_2 concentration was studied in a range of from observed 750 mg/L to 3750mg/L. The higher percentage of degradation was at 3750 mg/L, which is 98.61% as the lowest percentage was 750 mg/L. As expected, the higher the value of concentration H_2O_2, the higher percentage of degradation occur because the higher concentration of H_2O_2, the more hydroxyl radicals produce which degrade more dye molecule. The results indicate that the rate of the reaction increasing with the increasing in the oxidant concentration.

It is known that the addition of H_2O_2 was to increase the rate of dye to degrade by the formation of hydroxyl radical that react with the dye molecule compound. H_2O_2 play an important role in degradation process as the hydroxyl radical $OH^{\cdot}$ Because the radical will attacked the positive ions and the decolorization of dye occur. As the more hydroxyl will attack the positive ions, the degradation process becomes better and faster.

3.7 HPTLC Spectra of Coralene Dark red 2B

Table 1: Effluent used

Component	Dye λ_{max}	Effluent O.D
Sample-1	502.24 nm	0.298
Sample-2	470.97 nm	0.332
Sample-3	428.12 nm	0.387
Sample-4	541.65 nm	0.223
Sample-5	530.80 nm	0.538
Sample-6	504.92 nm	0.512

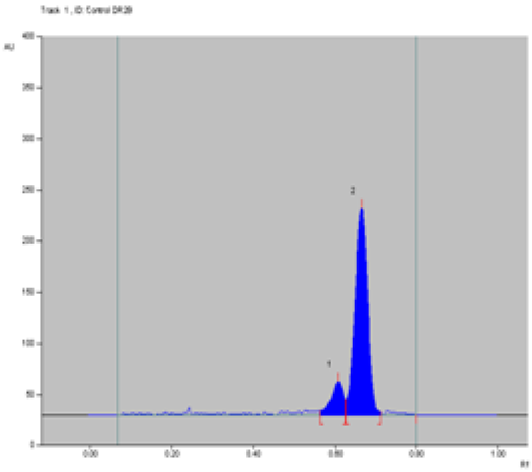

Figure 7: HPTLC chromatogram for standard undegraded dye
[Coralene dark Red 2B; 50mg/L H_2O_2; 2250mg/L pH; 3.5; TiO_2 100mg; Intensity; 501×100 Lux]

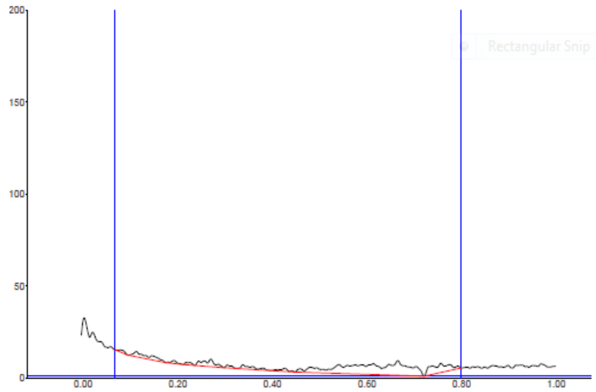

Figure 8: HPTLC chromatogram for degraded typical run

HPTLC chromatogram of undegraded and degraded dye are given in fig.7 and fig. 8, Using 50mg/L concentration of dye solution, TiO_2 as catalyst and H_2O_2. In fig.7 peak 2 is for undegraded dye at Rf value 0.71.

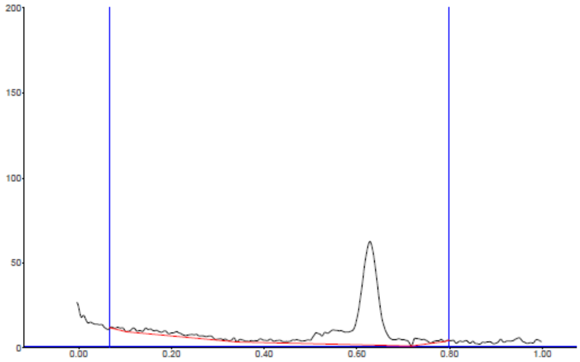

Figure 9: HPTLC chromatogram for undegraded at pH-6
[Coralene dark Red 2B; 50mg/L H_2O_2; 2250mg/L TiO_2 100mg; pH; 2 to 10 Intensity 501×100 Lux]

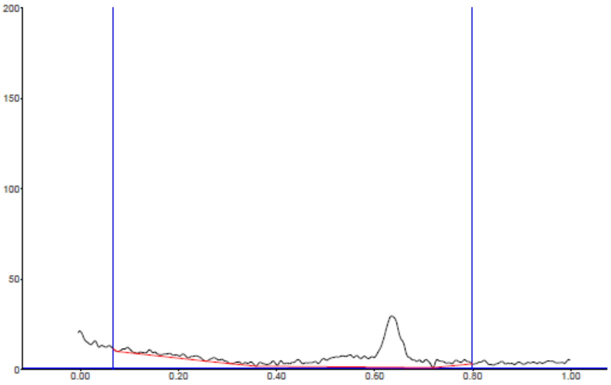

Figure 10: HPTLC chromatogram for undegraded at pH-8

Fig.9 and Fig.10 shows the chromatogram of undegraded dye effluents at pH-6 and pH-8 respectively. These spectra show the heighted peaks, it indicates that it does not give total degradation of dye.

HPTLC Analysis of degraded Coralene Dark red 2B

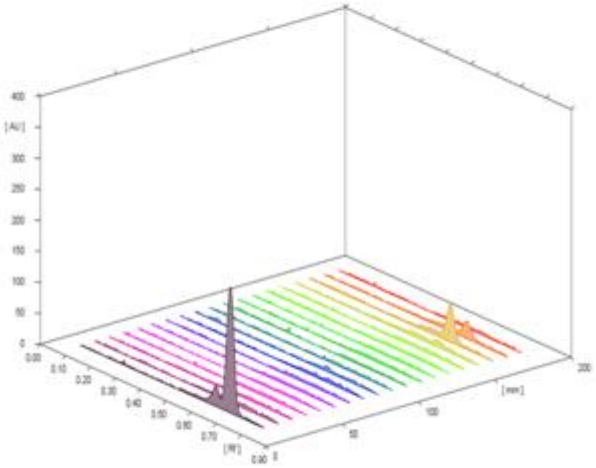

Figure 11: HPTLC Analysis of degraded Coralene Dark red 2B

Fig. 11 shows the analysis of Degraded for all studied parameters applied for the degradation of dye. From this 3D spectra we can say that dye was degraded 95% in all parameters but

3.8 Mechanism proposed for Degradation

On the basis of experimental observations, the following mechanism has been proposed for the photocatalytic degradation of coralene dark red 2B.

$$TiO_2 \rightarrow h^+ + e^- \tag{4}$$

$$O_2 + e^- \rightarrow O_2^- \tag{5}$$

$$O_2 + e^- + H_2O \rightarrow OH^\cdot_{aq} + H_{aq}^+ \tag{6}$$

$$h^+ + H_2O \rightarrow OH^\cdot_{aq} + H_{aq}^+ \tag{7}$$

$$h^+ + dye \rightarrow products \tag{8}$$

$$OH^\cdot_{aq} \rightarrow products \tag{9}$$

$$O_2^- + dye \rightarrow products \tag{10}$$

$$TiO_2 \rightarrow TiO_2\ (e^-_{CB} + h^+_{VB}) \tag{11}$$

$$h^+ + H_2O \rightarrow HO^\cdot + H^+ \tag{12}$$

$$h^+ + HO \rightarrow HO^\cdot \tag{13}$$

$$HO^\cdot + H_2O \rightarrow H_2O_2 + O^\cdot \tag{14}$$

$$HO^\cdot_{(aq)} + HO^\cdot_{(aq)} \rightarrow H_2O_{2(aq)} \tag{15}$$

4. Conclusion

The photocatalytic degradation of a typical run coralene dark red 2B was examined using TiO_2 catalyst under direct solar light. The results show that the maximum of 95% (50 mg/L) and 98% (3750mg/L) degradation efficiency was achieved in 120 min. Further it was also noticed that the extent of degradation was found to depend on concentration of the TiO_2, pH of the dye solutions, H_2O_2 concentration and the dye concentration.

A new HPTLC method has been developed for the identification and quantification of coralene dark red 2B degradation products. Low cost, faster speed, and satisfactory precision and accuracy are the main features of this method. In HPTLC Analysis of degraded Coralene Dark red 2B spectra of all dye parameters were maximum 95 % decolorization achieved in 120 min. pH-6 and pH-8 dye solution were difficult to degradation direct sun light.

Since the degradation was achieved in presence of direct sun light, the present protocol can be adapted to the large scale industrial decoloration processes and may reduce the water pollution to a certain extent.

The results indicated that during the photocatalytic degradation coralene dark red 2B and textile wastewater, the decolorization rate was faster than the degradation rate.

References

[1] B. Neppolian, H.C. Choi, S. Sakthivel, Banumathi Arabindoo, V. Murugesan, “Solar/UV-induced photocatalytic degradation of three commercial textile dyes,” Journal of Hazardous Materials, B89, pp. 303 317, 2002.

[2] S. Kalra, S. Mohan, A. Sinha and G. Singh, “Advanced Oxidation Processes for Treatment of Textile and Dye Wastewater: A Review,” 2nd International Conference on Environmental Science and Development IPCBEE, IACSIT Press, Singapore, 4, pp. 271-275, 2011.

[3] S. Ong, O. Min, L. Ho, Y. Wong and F. Ridwan, “Solar photocatalytic degradation of azo dye Reactive Black 5 in aqueous suspension of TiO_2,” Journal of Water Reuse and Desalination, 01.4, pp. 202-207, 2011.

[4] Textile Fashion study Textile engineering & Fashion design Blog, http://textilefashionstudy.com/.

[5] H. Djelal, C. Cornee, R. Tartivel, O. Lavaste and A. Abdeltif, “The use of HPTLC and Direct Analysis in Real Time-Of-Flight Mass Spectrometry (DART-TOFMS) for rapid analysis of degradation by oxidation and sonication of an azo dye,” journal of Arabian chemistry, 10, pp. S1619-S1628, 2017.

[6] M. srivastava, Fundamentals and theory of HPTLC-Based separation, University of Illinois, Chicago, Wisconsin and Maryland, USA, 2011.

[7] S. Saleh, “HPLC Determination of Four Textile Dyes and Studying Their Degradation Using Spectrophotometric Technique,” An-Najah National University Faculty of Graduate Studies, (thesis) 2005.

[8] S. Gupta, D. Soni, R. Meta, S. Benjamin, “Use of Barium Chromate in PhotocatalyticDegradation of Eosin Yellow,” Journal of Chemical Science Trasactions, 4(3), pp. 851-857, 2015.

[9] P. Panjabi, R. Ameta, A. Kumar and M. Jain, “Visible Light Induced Photocatalytic Degradation Of Some Xanthene Dyes Using Immobilized Anthracene,” Journal of Chemical Society of Ethiopia, 22(3), pp. 361-368, 2008.

[10] P. Malik and S. Saha, “Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst,” Journal of Separation and Purification Technology, 31, pp. 241- 250, 2003.

[11] S. Speers, B. Little and M. Roy, “Separation of acid, basic and dispersed dyes by a single gradient elution reversed-phase high-performance liquid chromatography system,” Journal of Chromatography, A 674, pp. 263-270, 1994.

[12] S. Al-Shamli, “Photocatalytic Degradation of Methylene Blue in the Presence of TiO2 Catalyst Assisted Solar Radiation,” Journal of Australian Basic and Applied Sciences, 7(4), pp. 172-176, 2013.

[13] D. Gumus and F. akbal, “Photocatalytic Degradation of Textile Dye and Wastewater,” Journal of Water Air Soil Pollut, 216,pp. 117–124, 2011.

[14] S. kansal, N. Kaur and S. Singh, “Photocatalytic Degradation of Two Commercial Reactive Dyes in Aqueous Phase Using Nanophotocatalysts,” Journal of Nanoscale Res Lett, 4, pp. 709-716, 2009.

[15] U. Akpan and B. Hammed, “Parameters affecting the photocatalytic degradation of dyes using TiO2-based photocatalysts: A review,” Journal of Hazardous Materials, 70, pp. 520–529, 2009.

[16] O. Panwar, A. Kumar, M. Paliwal, R. Ameta and S. Ameta, “Use of Zirconium Phosphate as Photocatalyst in Photobleaching of Some Dyes.” Journal of Bulletin of the Catalysis Society of India, 7, pp. 105-110, 2008.

[17] L. Petrick, T. Wilson and W. Fawcett, “High-Performance Liquid Chromatography– Ultraviolet–Visible Spectroscopy–Electrospray Ionization Mass Spectrometry Method for Acrylic and Polyester Forensic Fiber Dye Analysis,” Journal of Forensic Sci, 51 (4), pp. 771-779, 2006.

[18] B. Pare, D. Raghuvanshi, R. Dixita And D. Swami, “Decolorization And Mineralization Of Hazardous Brilliant Cresyl Blue Dye Utilizing Visible Light And Tio2 As Photocatalyst,” Journal of International Chemical Science, 11(4), pp. 1876-1890, 2013.

[19] R. Patel, M. Patel, K. Bhatt and B. Patel, “Development and Validation of HPTLC Method for Estimation of Carbamazepine in Formulations and Its In Vitro Release Study,” journal of International Chromatography Research, pp. 1-8, 2011.

[20] Y. Kambalagere, B. Channappa, K. Mahadevan, M. Narayanappa, “Decolorization of synthetic Coralene Violet 3R and Disperse Blue 2BL azo dyes using photoactive Calcium Aluminate nanoparticle in presence of sunlight,” Journal of International Advances in Chemical Engg., & Biological Sciences, 3 (1), pp. 108-112 , 2016.

[21] S. Andleeb, N. Atiq, A. Parmar, G. Robson, S. Ahmed, “An HPLC method development for the assessment of degradation products of anthraquinone dye,” Journal of Environ Monit Assess, 176, pp. 597-604, 2011.

[22] W. Kamarudin, M. Rahman, Z. Irwan and A. Donak, “Comparison Study Of Congo Red Dye Degradation Process Using Fenton’s Reagent And Tio2” Journal Of Engineering and Applied Sciences ARPN, 11, pp. 6176-6181, 2016.

[23] A. Baffoun, A. Ghali and I. Hachani, “Decolorization Kinetics of Acid Azo Dye And Basic Thiazine Dye In Aqueous Solution By Uv/H_2O_2 And Uv/Fenton: Effects Of Operational Parameters,” Journal of Autex Research, 17(1), pp. 85-94, 2017.