Experimental Investigation on Photo Catalytic Degradation of Textile Effluent Using Hetero Catalyst

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Abstract: **In the proposed methodology, a technique for the removal of color of textile effluent which proves to be cost efficient has been uncovered. It has also been examined that the process of photo catalytic degradation was involved in the system which is under consideration. In order to perform experimental study we need a batch reactor setup installed with adequate UV light intensity of 11W. Optimization study has been performed with heterocatalysts such as Titanium dioxide (TiO2) and iron oxide (Fe2O3) which were added at a dosage concentration of 0.25, 0.5, 0.75 and 1g/ respectively. Based on the UV absorbance and COD removal efficiency, it could be noted that the maximum dye removal was attained at the catalyst concentration of 0.5g/l with Titanium dioxide as well as Iron oxide. Also, the effective contact time of catalyst could be framed as 40 minutes and 60 minutes for Titanium dioxide and iron oxide respectively. From the experimental data, it could be finalized that the maximum absorbance removal efficiency achieved was 87.85% while using TiO2 catalyst at a dosage concentration of 0.5g/l. In the same way, maximum removal efficiency with respect to the COD concentration could be achieved was 94.11% using heterocatalysts.**

***Index Terms*— Contact time, Heterocatalyst, Optimization, photo catalytic degradation, Textile effluent, UV absorbance.**

I. INTRODUCTION

With the rapid increase of population there emerge various types of pollutions. Among those one of the major environmental ailment we encounter these days is found to be Textile industry effluent and its impact on its vicinity. There are over 700000 t of approximately 10,000 types of dyes and pigments produced worldwide according to (Carneiro et al., 2007). The major issue arises when these dyes are discharged into surface waters such as streams, lakes which are the prominent sources of freshwater. These dyes when discharged without proper treatments and reactions take place between the dyes and water and its contaminants the products yielded will be carcinogenic byproducts which in turn causes severe health problems such as skin cancer to both aquatic life and humans who intake it ,in accordance with the study (U.G.Akpan et al., 2009).

Dyes also also influence the light penetration into the water which is contaminated. They make the intensity of the penetration to be lower. The only solution is degradation of these dyes .Also there are some of the conventional methods based on physical, chemical and biological processes in different perceptions such as adsorption and UV assisted catalysis (Arun et al., 2018), Bacterial monoculture according to(Ekramul et al., 2018), chemical oxidation (Fujishima et al., 1972), incineration (T.T. Zhang et al., 2011) Fenton and photo-Fenton process (Chavaco et al., 2017) and so on. They are determined to involve not only high operational and maintenance cost but also the ineffieciency in the cases of results. One of the effective and economical methods of concern is Advanced Oxidation Process (AOP), a photo catalytic oxidation with the usage of heterocatalysts which is a promising process for degradation of industrial dye effluent in accordance with (Gemima et al., 2018).The word photocatalyst is a composite word which constitutes of two parts, “photo” and “catalysis”.

Catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered or consumed at the end. The substance which increases the rate of a reaction by reducing the activation energy is known as the catalyst.

The best fit in these cases are found to be metal oxides such as TiO2, CeO2, ZnO, Fe2O3 and SnO2 for the photo catalytic oxidation. AOP produces super hydroxyl radicals *OH by producing an electron hole in the valence band. The photon passing through conduction band to valence band is known as band gap. As much as the electron hole recombination decreases degradation of industrial dye effluent increases (U.G.Akpan et al., 2009). The minimum wide band gap of (+2.8eV) should be there for effective photo catalytic process.

TiO2 catalyst is one of the successful catalysts to achieve the maximum degradation of industrial dye effluent by initiating the free radicals in the presence of UV lamp and it has a wide band gap of (+3.2eV).

TiO2 is also examined to be inexpensive, non-toxic, increases oxidation power of electrons and also effective catalyst in the presence of UV lamp (Vorontsov et al., 2004) (Heredia et al., 2001). Increasing the UV lamp intensity can immensly increase the degradation efficiency (Ranjan et al., 2016).

Another catalyst under consideration Iron Oxide (Fe2O3) was used in this proposed system to examine the efficiency of degradation. Iron Oxide is proven to be economical and used for additive material to cement for plastering works. It also shows efficiency while used as a catalyst for degradation of dye in the photocatalysis process. Degradation of Reactive Red4 with the catalyst Fe2O3 shows 52% efficiency in photo catalytic degradation process (Janan et al., 2016).

The available methods of installing reactors are batch type reactors and fluidized bed reactors. The fixed bed or batch type reactor set up is better than that of fluidized bed reactor and in many researches fixed bed reactors are used both in lab scale and industrial scale (Dong et al., 2011).

The advantage of fixed bed reactor is the complete utilization of the catalyst and intensity of UV lamps and degradation of the dye more efficiently. On the other hand fluidized bed reactor needs some tasks to set up such as coating or making the different form of immobilized catalyst for efficient use (Kim et al., 2002). Another disadvantage of fluidized bed reactor is their energy consuming and requirement of special equipment and costly methods but fixed bed reactor consumes less cost, energy and equipments in comparison with fluidized bed reactors. (Neyens et al., 2003).

In this experiment, TiO2 and Fe2O3 were used as catalysts in its powder form. The TiO2 in the powder form can degrade color efficiently up to 96% (Abbas et al., 2007). In most of the studies commercial dyes were used as a model pollutants (Carneiro et al., 2004).

The operating parameters for the treatment of dye effluent are pH, catalyst dosage, temperature, intensity of lamp, concentration of dye and contact time. The effects of those operating parameters were studied by many researchers for finding the optimization range (Chen et al., 2007). In most of the cases, degradation efficiencies were identified using initial and final absorbance and applying it to the empirical formula (Wasi Z khan et al., 2016).

II. MATERIALS AND METHODS

In the current methodology, photo catalytic degradation was carried out using two different catalysts namely TiO2 and Fe2O3.

Titanium dioxide (TiO2) was purchased from super scientific suppliers, Tamilnadu, India and Ferrous Oxide (Fe2O3)-red color purchased from modern lab, Tamilnadu,India, are deployed in this proposed methodology.

Four numbers of UVC lamps with intensity of each 11watts were purchased from starlite company inc. India for enhancing the degradation process. In addition to this, rate of degradation was magnified by adapting aerator [HN108] in the system.

Experimental investigation was carried out using a textile effluent from a textile industry, which was located in a nearby region in India.

The textile effluent collected was characterized and listed below:

Test	Result	Units
pH	9.3	-
TDS	12500	mg/L
Turbidity	913	NTU
Conductivity	140	µs/mm
BOD	480	mg/L
COD	1700	mg/L

Table 1

III. REACTOR SETUP

In the proposed work, the batch type reactor was designed and fabricated consist of UV lamps, aerator and power supply. The reactor was surrounded by four number of UVC lamps (11W) at a distance of 5cm from the reactor. The catalysts TiO2 and Fe2O3 were used to enhance the process of degradation when in contact with the radiation of UV lamps. Aerator was used for the supply of oxygen.The optimization was done by varying catalyst dosage and contact time. COD and absorbance was found according to the optimization and degradation efficiency was determined.

The dimension of the reactor was [30cmx30cmx35cm]. A schematic diagram of the reactor setup was shown in fig1.

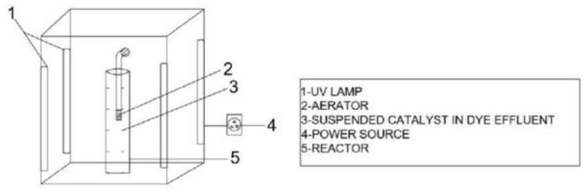

Figure 1

Titanium dioxide (TiO2) when added to the reactor, the super hydroxyl radicals will be formed that is the electron will move from valence band to the conduction band. The hydroxyl radical was produced during the reaction is as follows:

$$TiO_2 + h\upsilon \longrightarrow h^+ + e^- \qquad (1)$$

$$OH^- + h^+ \longrightarrow OH^* \qquad (2)$$

$$e^- + O_2 \longrightarrow O_2^- \qquad (3)$$

$$OH^* + O_2^- \longrightarrow \text{Degradation} \qquad (4)$$

Similarly for iron oxide the degradation starts to occur after the formation of super hydroxyl radicals. The reaction is follows:

$$Fe_2O_3 + h\upsilon \rightarrow h^+ + e^- \quad (5)$$

$$OH^- + h^+ \rightarrow OH^* \quad (6)$$

$$e^- + O_2 \rightarrow O_2^- \quad (7)$$

$$OH^* + O_2^- \rightarrow \text{Degradation} \quad (8)$$

In most of the studies degradation efficiencies were identified using initial and final absorbance by applying it to the empirical formula (Wasi Z khan et al., 2016).

In this study the degradation efficiency is calculated using,

%D = [(A0 – At)/ A0] x 100

Where,

%D = percentage of dye removal
A0 = Absorbance of initial dye
At = Absorbance of dye with respect to time

IV. RESULTS AND DISCUSSION

4.1 Removal of color using TiO2

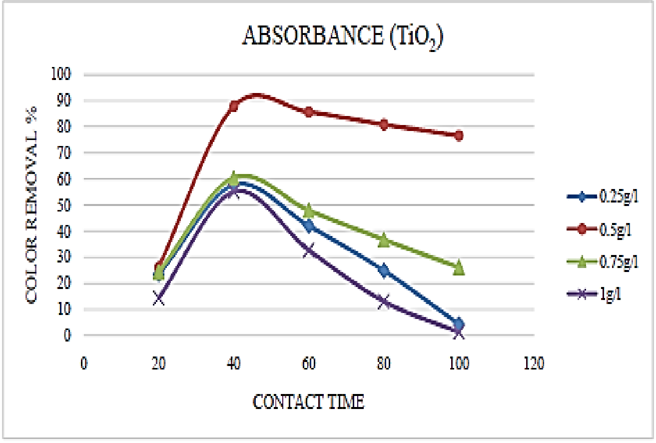

Figure 2

Batch study is carried out with the industrial effluent using UV radiation and catalyst dosage. The concentration of catalyst 1 (TiO2) is varied in the range of 0.25g/l, 0.5g/l, 0.75g/l and 1g/l. At every catalyst dosage, absorbance is observed at a time interval of 20 minutes till 100 minutes. Figure 2 shows the COD removal efficiency for different catalyst at different contact time.

The degradation of dye increases upto its optimum catalyst dosage and decreases after reaching the optimum dosage (S. Chakrabarti et al., 2004).

From the experimental data, it is observed that the removal efficiency was very low at the time duration of 20minutes.This may be due to the fact that the catalyst dosage requires more time to deteriorate the dye components. Less contact time before reaching the optimum contact time show lower degradation efficiency due to the catalyst needs some time to achieve the state of activation (Falah H.Hussain et al., 2014). After 40 minutes of contact time, the removal efficiency was peaked due to the effect of catalyst at its optimum point. Proceeding the process for 60, 80 and 100 minutes the color removal efficiency was gradually decreasing as the time is increasing.

The percentage efficiency difference from optimum dosages 0.25g/l to 0.5g/l, 0.5g/l to 0.75g/l and 0.75g/l to 1g/l at optimum time 40 minutes are 52.58%, 31.21% and 8.75%. At 0.25g/l to 0.5g/l the efficiency will be more because that is the maximum possible optimum dosage. After that the efficiency will decrease because increase in catalyst dosage after optimum point the excess catalyst prevent illumination. This may also result in agglomeration of catalyst particles (M.Huang et al., 2008).

4.2 Removal of COD using TiO2

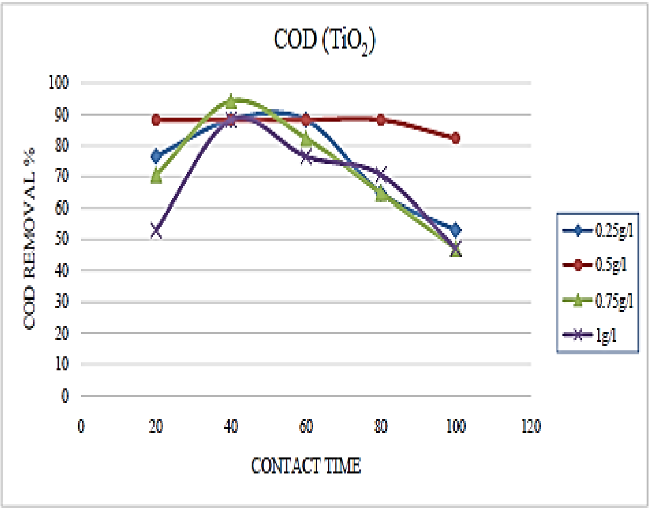

Figure 3

In this study the Chemical Oxygen Demand (COD) was observed for different catalyst at different irradiation time. After the dosage is added to the reactor the contact time was varied at a rate of 20, 40, 60, 80 and 100 minutes. Figure 3 shows the COD removal efficiency for different catalyst at different contact time.

The optimum degradation was identified in the catalyst dosage of 0.5g/l. In that the maximum deterioration was found to be 88.23% which is stable at 20, 40, 60 and 80 minutes. At 100 minutes the degradation efficiency was lowered which is 82.35% which is because the increase of COD in reactor after the optimum efficiency point. At the dosage of 0.25g/l the maximum COD removal was found to be 88.23% at contact time of 40 and 60 minutes. At 0.75g/l catalyst dosage the maximum removal efficiency was found to be 94.11% at 40 minutes which shows more removal percentage than optimum degradation point. At the catalyst dosage of 1g/l the maximum COD removal efficiency was found to be 88.23% at 40 minutes.

4.3 Removal of color using Fe2O3

The concentration of catalyst 2 (Fe2O3) is varied in the range of 0.25g/l, 0.5g/l, 0.75g/l and 1g/l. At every catalyst dosage, absorbance is observed at a time interval of 20 minutes till 100 minutes. From the experimental data, it is observed that the degradation efficiency varies according to the change in catalyst dosage and contact time. Figure 4 shows the color removal efficiency for different catalyst at different contact time.

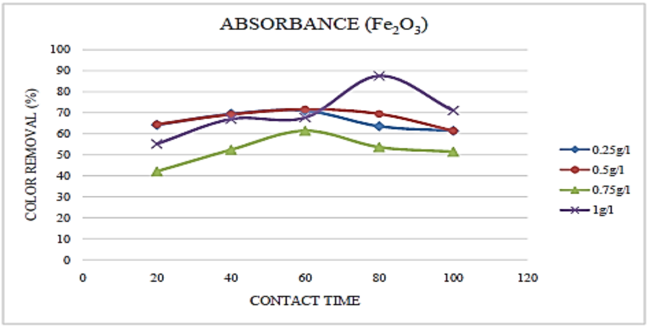

Figure 4

After the dosage is added to the reactor the contact time is varied as 20min, 40min, 60min, 80min and 100min. In this study the absorbance is noted for each sample collected at time intervals for set of catalyst dosages. From the above graph it is identified that the removal efficiency was very low at 20minutes.That is because the concentration of dye will be more initially and catalyst dosage need more time to show its efficiency so the dye is not deteriorated. Then the removal efficiency increase and decrease gradually at 40, 60, 80 and 100 minutes. The optimum deterioration was identified at 60 minutes.

The catalyst dosage 0.5g/l shows more deterioration than any other catalyst dosages. It shows maximum removal efficiency of 71.65% at 60 minutes.

4.4 Removal of COD using Fe2O3

In this study the Chemical Oxygen Demand (COD) was observed for different catalysts at different irradiation time. After the dosage is added to the reactor the contact time was varied at a rate of 20, 40, 60, 80 and 100 minutes. The catalyst is added varying as 0.25g/l, 0.5g/l, 0.75g/l and 1g/l. Figure 5 shows the COD removal efficiency for different catalyst at different contact time.

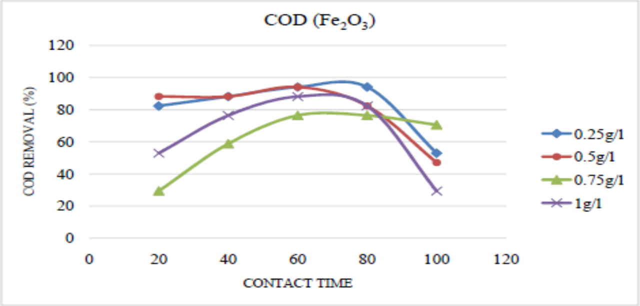

Figure 5

The optimum degradation was identified in the catalyst dosage of 0.5g/l. In that the maximum deterioration was found to be 94.11% at 60 minutes. The deterioration of 88.23% was achieved at the contact time of 20 and 40 minutes. At 80 and 100 minutes the COD removal efficiency was gradually decreasing as 82.35 and 47.05 respectively.

As the contact time increases the removal efficiency decreases up to the optimum point (M.A.Barakat., 2010).

V. CONCLUSION

This study explains in detail about the process of photo catalytic degradation process on real textile effluent using Heterocatalyst such as TiO2 and Fe2O3 with UV lamps. It is clearly seen that the COD and color were greatly reduced. Titanium dioxide shows great efficiency than Iron oxide with respect to the removal of COD as well as Color. From the performance of TiO2 and Fe2O3, TiO2 at dosage of 0.5g/L shows 87.85% color removal efficiency at 40 minutes of contact time. In addition, TiO2 shows optimum COD removal of 88.23% with the contact period of 60 minutes. This process has shown more efficiency and proven to be economical than many other processes. It could be adopted on pilot scale and large scale model for effective treatment of textile dye effluents.

REFERENCE

[1] A.Ajmal, I.Majeed, R.N.Malik, M.Iqbal, M.Arif Nadeem, I.Hussain, S.Yousuf, Zeshan, G.Mustafa, M.I.Zafar, M.Amtiaz Nadeem, “Photo catalytic degradation of textile dyes on Cu2O-CuO/TiO2 anatase powder,” Journal of Environmental Chemical Engineering, 2016.

[2] Abbas J.Attia, Salih H.Kadhim and Falah H.Hussein, “Photo catalytic degradation of textile dyeing wastewater using Titanium dioxide and Zinc oxide,” E-Journal of Chemistry, 2007.

[3] Arun kumar Dutta, Uttam kumar Ghorai,Kalyan kumar Chattopadhyay,Diptonil Banerjee, “Removal of textile dyes by carbon nanotubes:A comparison between adsorption and UV assisted photocatalysis,” Physica E:Low-dimensional systems and nanostructures, 2018.

[4] Carneiro, P.A., Pupo Nogueira, R.F., Zanoni, M.V.B., “Homogeneous photodegradation of C.I. reactive blue 4 using a photo-Fenton process under artificial and solar irradiation,” Dyes Pigments 74, 127-132, 2007.

[5]Dong, F., Wang, H., Sen, G., Wu, Z., Lee, S.C., “Enhanced visible light photo catalytic activity of novel Pt/C-doped TiO2/PtCl4 three-component nanojunction system for degradation of toluene in air,” Journal of Hazardous Materials 187, 509–516, 2011.

[6] Fujishima, A., Honda, K., “Electrochemical photolysis of water at a semiconductor electrode,” Nature 238 (5358), 37-38, 1972.

[7] Gemima Santos Arcanjo, Ann H.Mounteer, Carlos Roberto Bellato, “Heterogeneous photocatalysis using TiO2 modified with hydrotalcite and iron oxide under UV-visible irradiation for color and toxicity reduction in secondary textile mill effluent,” Journal of Environmental management, 2018.

[8] Janan parhizkar, Mohammed Hossein Habibi, “Synthesis, characterization and photo catalytic properties of Iron oxide nanoparticles synthesized by sol-gel autocombustion with ultrasonic radiation,” Volume2, Issue 2, page166-171, 2016.

[9] J.B. Heredia, J. Torregrosa, P. Dominguez and J.A. Peres, “Oxidation of p-hydroxybenzoic acid by UV radiation and by

TiO2/UV radiation: comparison and modelling of reaction kinetic," Journal of Hazardous Materials B 83, 255–264, 2001.

[10] Kim, T.H., Park, C., Shin, E.B., Kim, S., "Decolorization of disperse and reactive dyes by continuous electrocoagulation process," Desalination 150, 165–175, 2002.

[11] L.C.Chavaco, C.A.Arcos, D.Prato-Garcia, "Decolorization of reactive dyes in solar pond reactors:Perspectives and challenges for the textile industry," Journal of Environmental management, 2017.

[12] L.-C.Chen, C.-M.Huang,F.-R.Tsai, "Characterization and photo catalytic activity of K+-doped TiO2 photo catalysts," Journal of Molecular Catalyst and Chemistry 265, 133– 140, 2007.

[13] Md.Ekramul karim, Kartik Dhar, Md.Towhid Hossain., "Decolorization of textile reactive dyes by bacterial monoculture and consortium screened from textile dyeing effluent," Journal of Genetic Engineering and Biotechnology, 2018.

[14] M. Huang, C. Xu, Z. Wu, Y. Huang, J. Lin, J. Wu, "Photo catalytic discolorization of methyl orange solution by Pt modified TiO2 loaded on natural zeolite," Dyes Pigments 77, 327– 334, 2008.

[15] Neyens, E., Baeyns, J., "A review of classic Fenton's peroxidation as an advanced oxidation treatment," Journal of Hazardous Materials 98, 33-50, 2003.

[16] P.A. Carneiro, M.E. Osugi, J.J. Sene, M.A. Anderson, M.V.B. Zanoni, "Evaluation of color removal and degradation of a reactive textile azo dye on nanoporous TiO2 thin-film electrodes," Electrochim. Acta 49, 3807–3820, 2004.

[17] Ranjan, S., Sasselov, D.D., "Influence of the UV environment on the synthesis of prebiotic molecules," Astrobiology 16 (1), 68-88, 2016.

[18] S. Chakrabarti, B.K. Dutta, "Photo catalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst," Journal of Hazardous Materials B112, 269–278, 2004.

[19] U.G.Akpan, B.H.Hameed, "Parameters affecting the photo catalytic degradation of dyes using TiO2-based photocatalysts:a review," Journal of Hazardous Materials 170, 520-529, 2009.

[20] V.A. Vorontsov and V.P. Dubovitskaya, "Selectivity of photo catalytic oxidation of gaseous ethanol over pure and modified TiO2," Journal of Catalyst., 221, 102– 109, 2004.

[21] Wasi Z Khan, Imad Najeeb, Shagufta Ishtiaque, "photo catalytic degradation of real textile wastewater using titanium dioxide, zinc oxide and Hydrogen peroxide," International Journal of Engineering and Science, Volume 5 Issue 7, pp-61-70, 2016.