J. Appl. Environ. Biol. Sci., 6(12)138-143, 2016
© 2016, TextRoad Publication
ISSN: 2090-4274
Journal of Applied Environmental and Biological Sciences
www.textroad.com

Comparative Efficiency between Immobilize Titanium Dioxide and Zinc Oxide for Photodegradation of Azo Dye

Muhammad Nasri Abdul Rahman[1], Muhammad Aizat Azahan[1], Wan Farahiyah Wan Kamarudin[2], Adida Muhammud[2]

[1]Faculty of Applied Science, Universiti Teknologi MARA, Jengka, Pahang, Malaysia
[2]Faculty of Applied Science, Universiti Teknologi MARA, Dungun, Terengganu, Malaysia

Received: August 3, 2016
Accepted: October 20, 2016

ABSTRACT

Textile industries produce a large amount of wastewater every year through dyeing and finishing process. Most of the dye are azo dye that contain azo compound that resistant to biodegradation. Catalyst such as titanium dioxide and zinc oxide are proven efficient to degrade the dye but the post treatment of catalyst are not suitable on industrial scale. Immobilization of catalyst was studied by using cement as solid support. A laboratory set-up designed to evaluate the effectiveness of immobilize catalyst on the rate of degradation of congo red dye. The experimental was about the percentage degradation of dye on different intensity of UV radiation. The reaction time was set to 30 minutes. The result shows that the presence of UV radiation helps to increase the rate of degradation of azo dye. The percent degradation below artificial UV radiation were 27% for TiO_2 and 30.80% for ZnO, while below sunlight shows degradation of 17.72% for TiO_2 and 14.77% for ZnO. Without the presence of UV radiation, the percentage degradation of dye were 17.72% for TiO_2 and 8.86% for ZnO. On increasing the initial concentration of the dye, the percentage degradation was decrease for both catalyst. Highest concentration available for congo red dye only show degradation by 18.90% for TiO_2 and 16.26% for ZnO on 10 mg/L concentration of the dye. With the degradation of the dye measured, the colour intensity of the dye also decrease.

KEYWORDS: Photodegradation, Azo Dyes, Congo Red (CR), Immobilization of Catalyst, Titanium Oxide, Zinc Oxide.

INTRODUCTION

In recent years, textile industries are among major industries in this country. Textile industries are also one of the industries that consume a lot of water in the process of textiles. Generally, in the textile wastewater contain pollutants that characterized as low biodegradability compound [1]. The water are primarily used in the dyeing and finishing process which the cloth are dyed and operates to finished products. The dye from the process are released into the sewage and mixed with other contaminants. The water that has been employed in the dyeing and finishing process are eventually ends up as wastewater that needed to be treated before final discharge.

Dye are complex unsaturated aromatic compounds fulfilling characteristics like intense colour, their solubility, substantiveness and fastness. There are several type of dye used in textile industries. The commonly used dyes in the textile industries are reactive dyes because of its color and cost efficient. Most of the dye are 50% azo dyes and most of the organic dyes in textile effluents are linked with serious environmental problem. Even though the concentration of azo dyes in the waste water are not to concentrated and can be considered as minor pollutant, it can altered the composition of water stream if the azo dyes are not carefully degrade. The reason why azo dye are very harmful because of its carcinogenic properties. Based on the chemical structure of the dye, it has at least one –N=N– bond (azo compound) which are very reactive, toxic and non-biodegradable [2].

The study shows that almost 66% of reactive dye are azo dye [3]. Azo dyes are known for their stability and color effective. The word "azo" refers to the compound that contains at least one azo group (-N=N-). About 1-20% of azo dye lost during coloring process and released as wastewater [4]. The main problem of azo dye in wastewater are they can block the sun radiation from penetrate through the water bodies besides of their toxicity. If the color of dyes not properly removed, the photosynthesis process of aquatic life are affected due to reduce of UV light penetration [1].

The presence of pollutants in the water stream especially azo dye will make the water become unsuitable for human activities. Besides of the azo dye carcinogenic properties, the discharge of azo dye can also altered the water stream color and will affect the sunlight absorption into the water bodies. This will cause the aquatic inhabitant ecosystems will be interfere. This will also affect the growth of algae, bacteria and thus make the water bodies become polluted [5].

Corresponding Author: Muhammad Nasri Abdul Rahman, Faculty of Applied Science, Universiti Teknologi MARA, Jengka, Pahang, Malaysia, Email: mnasri@pahang.uitm.edu.my

They are several type of degradation process to degrade the azo dye. Photo degradation are one of the chemical degradation of azo dye because it used the chemical reaction to degrade the dye. Photo degradation is the method where the molecule being altered by photon that that have the same wavelength found in sunlight such as UV, infrared and others. By simple word, the photo degradation process change the structure of hazardous pollutant into more environmentally friendly substance that can be released to surrounding without any worries.

Recent years studies shows that the usage of catalyst in photo degradation process are very efficient to degrade and discolored the dye and degrade them into harmless compound such as CO_2 and H_2O [6] . Catalyst such as TiO_2 and ZnO are considered as having the ability to degrade various environmental pollutants such as dye, pesticides, and volatile organic compound (voc) in presence of UV irradiation [7]. Both of the catalyst are considered as very efficient in photo catalytic because of its abundant availability, cheap, and chemically stable. The catalyst are non-toxic, safer compounds and did not undergoes any physical and chemical changes throughout the process. This special properties make the catalyst are very favorable in the degradation of azo dyes.

This study focused on the efficiency of immobilize catalyst for photo degradation of azo dye in wastewater. Photocatalytic degradation by using semiconductors titanium dioxide (TiO_2) and zinc oxide (ZnO) on the solid support are used to degrade the azo dye. The semiconductors are immobilize on the solid support to replace the suspension form. The reason are the suspension form of semiconductors method to degrade the dye have drawback such as separation of semiconductors, reduce in penetration of UV radiation and potentially pollute the semiconductor [2]. Due to the small particle of the catalyst, the post treatment to retrieve the catalyst using microfiltration are necessary. The post treatment process are undesirable on industrial scale as it add up capital and operating cost [8].

The main objective of the study was to evaluate and to compare the efficiency of immobilize catalyst on solid support for photo degradation of azo dye using TiO_2 and ZnO. The influence of different experimental conditions which are UV light's effect in degradation of CR dye, the initial concentration of CR dye used and the colour intensities of degradation of CR dye were investigated.

MATERIALS AND METHODS

Materials

All materials in this experiment are prepared in the laboratory and the material are analytical grade. The dye used as the model for organic dye are Congo Red. The Congo Red are prepared in distilled water and used for all experiments. The instrument used in this experiment were UV-Vis spectrophotometer – UV 1800 Shimadzu.

Methods

The photodegradation of azo dye (Congo red) process operated in the absence and in the presence of UV light radiation. The degradation of azo dye was analyzed with UV-Vis spectrometer to compare the percent degradation of azo dye by both semiconductor in all the parameter set. The semiconductor was sprinkled on the fresh cement until all the surface of cement were covered by semiconductors and the cement are left to cure for seven days. The cement then dip into solution contain Congo Red dye. The initial absorption peak were recorded before the cement dip into the solution. The parameter for this experiment are the UV radiation, effect of semiconductor and the concentration of dye.

To Study Effect of Different Catalyst in the Rate of Degradation

0.5 L of 5mg/L congo red solution was poured into 1000 mL beaker. The cement containing catalyst are dipped into the solution and then exposed to the UV lamp for 30 minutes. Each five minutes interval, small amount of the sample was pipette from the beaker and analyzed with the UV-Vis spectrophotometer. The absorbance of the dye are measured and recorded. The absorbance of the dye indicates the colour intensity of the dye. All of the experiment are conducted at constant concentration that is 5 mg/L. The above steps were repeated in dark room and under sunlight.

To Study Effect of Different Initial Concentration of Dye in the Rate of Degradation

0.5 L of 2mg/L congo red solution was poured into 1000 mL beaker. The cement containing catalyst are dipped into the solution and then exposed to the UV lamp for 30 minutes. Each five minutes interval, small amount of the sample was pipette from the beaker and analyzed with the UV-Vis spectrophotometer. The absorbance of the dye are measured and recorded. The absorbance of the dye indicates the colour intensity of the dye. The above step are repeated by using different concentration of congo red dye (4mg/L, 6mg/L, 8mg/L, 10mg/L). In this step, the UV light radiation are constant.

RESULTS AND DISCUSSION

Effect of UV Light in the Degradation Rate of Congo Red Dye

The comparison of two catalyst in the degradation of congo red dye below UV lamp are shown in Figure 1. It shows that zinc oxide degrade the dye more than titanium dioxide below UV lamp. At 30 minutes reaction time, the percent degradation of congo red dye by titanium dioxide are 27%. Zinc oxide degrade the dye about 30.8%. This phenomena shows that zinc oxide degrade the dye more than titanium dioxide in the presence of UV radiation. Since the difference in the percent degradation of dye are not too big, it can be considered as both of the catalyst are able to degrade the dye effectively under UV radiation.

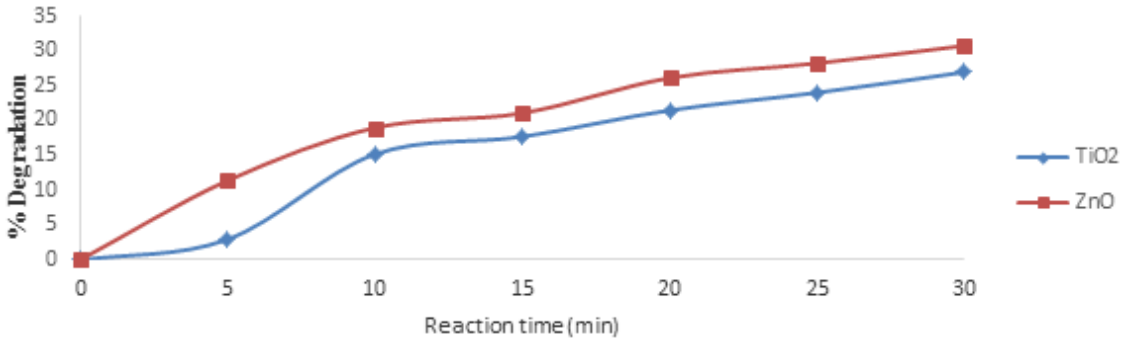

Figure 1: The comparison of two catalyst on percent degradation of congo red dye at below UV lamp

For the degradation of dye under sunlight radiation, the comparison of percent degradation of dye are shown in Figure 2.

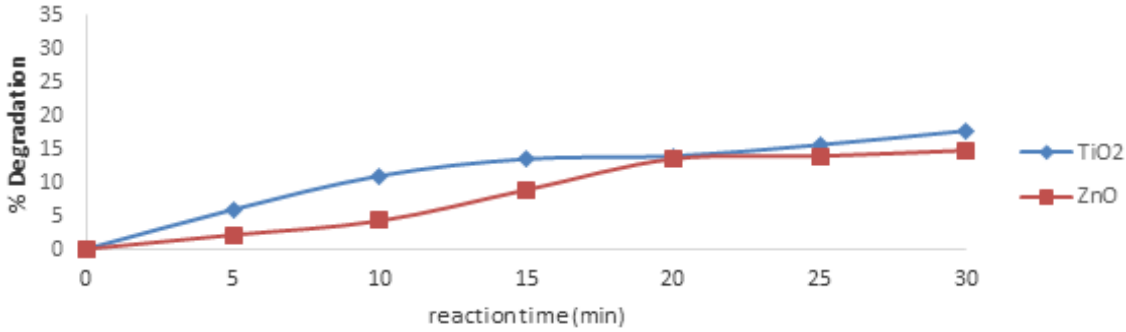

Figure 2: The comparison of two catalyst on percent degradation of congo red dye at below sunlight radiation

Figure 2 shows that the percent degradation of azo dye by both catalyst below sunlight. Based on the graph, the percent degradation of congo red dye are much higher with titanium dioxide (17.72%) at 30 minutes reaction time compared to the percent degradation of congo red dye by zinc oxide (14.77%).

For the degradation of dye in the dark room, the comparison of percent degradation of dye are shown in Figure 3.The percent degradation of azo dye by both catalyst are calculated. Similar to Figure 2, the percent degradation of congo red dye are much higher with titanium dioxide (17.72%) at 30 minutes reaction time compared to the percent degradation of congo red dye by zinc oxide (8.86%).

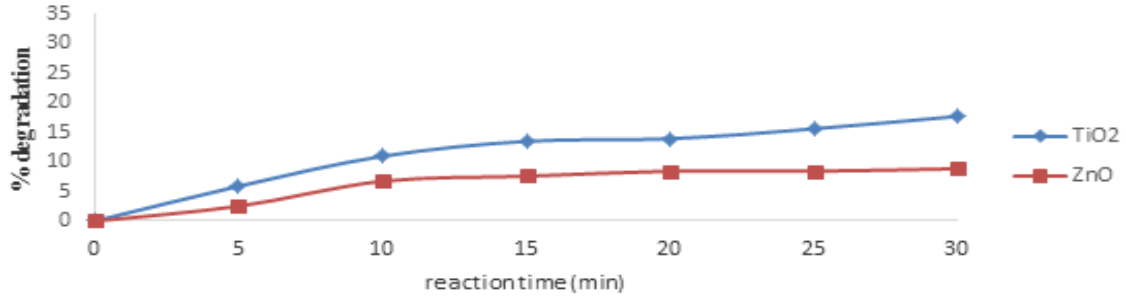

Figure 3: The comparison of two catalyst on percent degradation of congo red dye at the dark room

The degradation of congo red dye are caused by the effect of catalyst (titanium dioxide and zinc oxide). When the catalyst is irradiated with photon that have same or higher energy than the catalyst band gap, the surface of the catalyst will create the electron-hole pairs [1]. The electron holes at the surface of the catalyst then react with water in aqueous solution to form hydroxide radical. The hydroxyl radical (OH^*) are known as the most oxidizing compound in this experiment. Besides the production of the hydroxide radical, the surface of the catalyst also produce the superoxide anion radical (O_2^{*-}) when the electron at the surface of the catalyst are trapped and removed by reaction with the absorbed oxygen in the aqueous media. The reaction of catalyst are as follow:

$$\text{Catalyst } (TiO_2 \text{ or } ZnO) + h\nu \rightarrow h^+_{VB} + eC{-}B$$
$$h^+_{vb} + H_2O \rightarrow OH^* + H^+$$
$$h^+_{vb} + OH^- \rightarrow OH^*$$
$$e^-_{CB} + O_2 \rightarrow O_2^{*-}$$

Based on the equation above, the energy from light radiation are important in the degradation process of the dye. The energy are needed in the production of hydroxyl radical and superoxide anion radical. The hydroxyl radical and superoxide anion are non-selective oxidizing compound. It will degrade the all contaminant including organic substance into harmless compound such as H_2O and CO_2[9].

$$R_1\text{-}N{=}N\text{-}R_2 + OH^* \rightarrow \text{degradation products}$$

Based on the data obtained from the percent degradation of congo red dye, the highest percentage of degradation are under the artificial UV radiation followed by degradation under sunlight radiation then lastly degradation of dye in the dark room. This is because, the higher the intensity of the light radiation, the higher the rate of degradation of the azo dye [10] . The reason why degradation of congo red dye still occurred in the dark room even though there are absence of light radiation because of the energy absorbed on the surface of the catalyst. The energy being absorbed and stored on the surface of the catalyst when the curing process of the cement are done. The energy stored then create the electron holes and pair but in the small amount to trigger the production of hydroxyl radical and superoxide anion. There are also the possibilities that the light passes through the dark room to initiates the photocatalytic process. Based on the graph, the degradation of azo dye with Zinc oxide catalyst in the dark room are the smallest compared to titanium dioxide. This phenomena shows that zinc oxide needed the light radiation to activate the photocatalysis process.

Effect of Different Initial Concentration in the Degradation Rate of Congo Red Dye

From the absorbance measured, the percentage degradation of congo red dye can be calculated by using the percent decolourization formula. The percent degradation of the dye on different concentration are shown in Figure 4 for titanium dioxide and Figure 5 for zinc oxide.

Based on the Figure 4, the highest percentage of degradation of congo red dye are with 4 mg/L concentration. The lowest percentage of degradation of congo red dye are with 10 mg/L concentration. Based on the calculation, the percent degradation at highest degradation (4 mg/L) concentration are 34.42% degradation. The percent degradation at lowest (10 mg/L) concentration are 18.90%. The differences between the highest and lowest percent degradation are 15.52%. This phenomena shows that the degradation of congo red dye are higher in lower concentration [9]. This due to the at the higher concentration of congo red dye, the colour solution become less transparent to UV radiation and the dye molecule may absorb the energy from the UV radiation. So, the lesser photon reach the surface of the catalyst. When this phenomena occurs, only a small amount of the surface catalyst can produce the electron hole pairs and reducing the production of radicals thus will lower the rate of degradation of congo red dye.

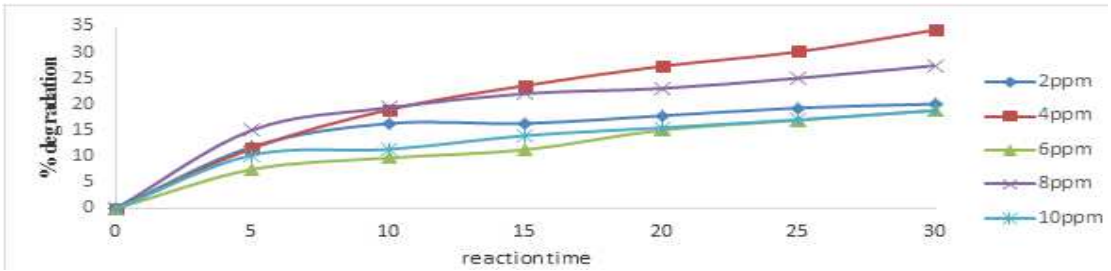

Figure 4: The percent degradation of the dye on different initial concentration of congo red dye treated with titanium dioxide

The Figure 5 show the percent degradation of congo red dye in various concentration by treating with zinc oxide catalyst. the highest percentage of degradation of congo red dye are with 8 mg/L concentration. The lowest percentage of degradation of congo red dye are with 10 mg/L concentration. Based on the calculation, the percent degradation at highest degradation (8 mg/L) concentration are 30.00% degradation. The percent degradation at lowest (10 mg/L) concentration are 16.26%. The differences between the highest and lowest percent degradation are 13.74%. Similar to the effect of initial concentration by titanium dioxide, the degradation of congo red dye by catalyst zinc oxide also exhibit lower degradation on higher concentration. This is because at the higher concentration, lesser energy from light source reached the surface of the catalyst. This will result the lower radical produce to degrade the dye.

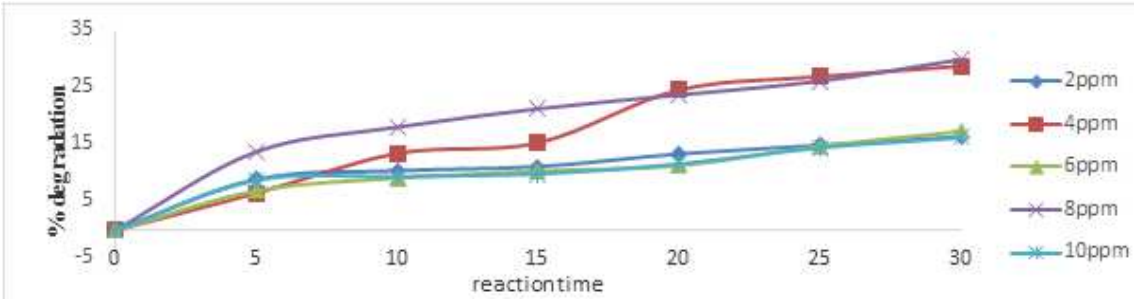

Figure 5: The percent degradation of the dye on different initial concentration of congo red dye treated with zinc oxide

Effect of Photodegradation on the Colour Intensities of Congo Red Dye

In the textile wastewater, the most challenging part are to remove the colour of the wastewater from textile effluent. Most of the colour resulting pollutant are very hard to degrade by biological treatment as the pollutant are resistant to biodegradation [11]. The colour intensity comes from the nature of the chromophore and auxochrome present in the molecule of the dye [12]. The azo compound (-N=N-) also contributed in the intensity of the dye. In this experiment, the colour observed to be decrease gradually in intensity as the reaction take place.

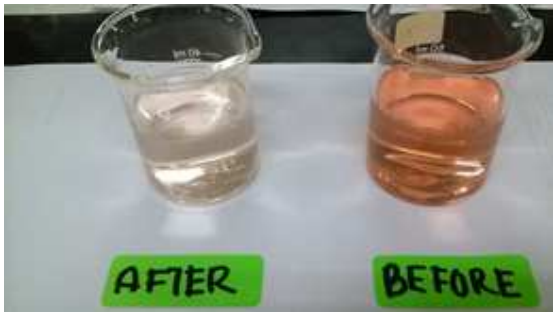

Figure 6: The colour intensity of congo red dye before and after treatment

Figure 6 shows that the colour intensity of the dye before and after the treatment with catalyst. From the figure, it displays that the compound that contributed to the intensity of the colour have been degraded. As the colour of the dye have been decline, it shows that the hydroxyl radical and superoxide anion radical have thrived in the degradation of the azo compound since the radical are non-selective oxidizing and reducing compound. The radicals will degrade all the organic compound including the azo compound itself. Subsequently the colour intensity of the dye are decreasing, it can be assume that the immobilize catalyst can degrade the dye in presence or absence of UV light radiation.

CONCLUSION

The experiment demonstrated that the immobilize catalyst on solid support are efficient in photodegradation process of congo red dye. All the degradation of congo red dye show decreasing in term of the absorbance and colour intensity of the dye in 30 minutes of reaction time. The experiment also demonstrate the comparison of titanium dioxide and zinc oxide catalyst in the degradation of congo red dye at the place where both of the

catalyst show higher degradation of congo red dye under artificial UV radiation compared to under sunlight and dark room. Titanium dioxide show 27% degradation after 30 minutes treatment and zinc oxide shows 30.8% degradation after 30 minutes treatment. The least percentage degradation of congo red dye for both catalyst are in the dark room where titanium dioxide only degradde the dye by 17.72% and zinc oxide only degrade the dye by8.86%. The increase of the intensity of the UV radiation will increase the percent degradation of congo red dye. On increasing the concentration of the dye will decrease the rate of degradation of congo red dye. Both of the catalyst shows lower percentage degradation on 10 mg/L (highest available) concentration of the congo red dye. The catalyst titanium dioxide degrade 18.90% of 10 mg/L congo red dye and zinc oxide degrade 16.26% of 10 mg/L congo red dye.

REFERENCES

1. Barka, N., S. Qourzal, A. Assabane, A. NounahandY. Ait-Ichou, 2010. Photocatalytic Degradation of an Azo Reactive Dye, Reactive Yellow 84, in Water Using Industrial Titanium Dioxide Coated Media. Arabian Journal of Chemistry, 3 (4): 279-283.
2. Marandi, R., M. Khosravi, M.E. Olya, B. Vahidand M. Hatami, 2011. Photocatalytic Degradation of an Azo Dye Using Immobilised Tio_2 Nanoparticles on Polyester Support: Central Composite Design Approach. Micro and Nano Letters, 6 (11): 958-963.
3. Moradi, H., S. Sharifnia and F. Rahimpour, 2015. Photocatalytic Decolorization of Reactive Yellow 84 from Aqueous Solutions Using ZnO Nanoparticles Supported on Mineral LECA. Materials Chemistry and Physics, 158: 38-44.
4. Madhavan, J., F. Grieser andM. Ashokkumar, 2011. Degradation of Orange-G by Advanced Oxidation Processes. Ultrasonic Sonochem, 17 (2): 338-343.
5. Hussein, F.H. andT.A. Abass, 2010. Photocatalytic Treatment of Textile Industrial Wastewater. International Journal Chemistry Sciences, 8(3): 1353-1364.
6. Motta, M.D., R. Pereira, M.M.AlvesandL. Pereira, 2014. UVTiO_2 Photocatalytic Reactor for Real Textile Wastewaters Treatment. Water Science and Technology, 2(3): 78-89.
7. Ong, S.T., W.S. Cheong and Y.T. Hung, 2012. Photodegradation of Commercial Dye, Methylene Blue Using Immobilize TiO_2. In the Proceedings of the 2012 Chemical, Biological and Environmental Engineering, pp. 109-113.
8. Rao, K.V.S., A. Rachel, M. SubrahmanyamandP. Baoule, 2003. Immobilization of TiO_2 on Pumice Stone for the Photocatalytic Degradation of Dyes and Dye Industry Pollutants. Applied Catalyst B: Environment, 46 (1): 77-85.
9. Alahiane, S., S. Qourzal, M. E. Ouardi, A. Abaamrane andA. Assabbane, 2014. Factors Influencing the Photocatalytic Degradation of Reactive Yellow 145 by TiO_2-Coated Non-Woven Fibre. American Journal of Analytical Chemistry, 5 (8): 445-454.
10. Divya, N., A. Bansaland A. K. Jana, 2009. Degradation of Acidic Orange G Dye Using UV-H2O2 in Batch photoreactor. International Journal of Biological and Chemical Sciences, 3 (1): 54-62.
11. Hung, C.H.andC. Yuan, 2000. Reduction of Azo Dye Via TiO_2 Photocatalysis. Journal of the Chineese Institute of Environmental Engineering, 10 (3): 209-216.
12. Kechi, A., R. B. Chavan andR. Moeckel, 2013. Dye Yield, Color Strength and Dyeing Properties of Natural Dyes Extracted from Ethiopian Dye Plants. Textile and Light Industrial Science and Technology, 2(3): 137-145.