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PHOTOCATALYTIC DEGRADATION OF CONGO RED DYE BASED ON TITANIUM DIOXIDE USING SOLAR AND UV LAMP

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ABSTRACT

The textile industries produce large volume of wastewater and contain chemical associated with the dyeing process. Photocatalytic degradation by using TiO_2 as catalyst is proven efficient to degrade the dye. This study was designed to evaluate the effectiveness of degradation toward Congo red dye using TiO_2 as a catalyst in different treatment using solar and UV light. The result shows that the presence of catalysts and high UV radiation will enhanced the percentage degradation of dye. The percent degradation under UV lamp with absence of TiO_2 was 31.72% and with presence of TiO_2 was 66.99%. When treated under direct sunlight, with absence of TiO_2 was 8.09% and with presence of TiO_2 was 64.72%. On different pH value of the dye, the percentage degradation of the dye will decrease in both acidic and alkaline condition.

Keywords: photocatalytic degradation; Congo red dye; TiO_2; catalyst; solar; UV lamp.

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1. INTRODUCTION

In recent years, environment pollution had become crucial especially in water pollution. The pollutions of water are mainly caused by large amount of dyes which are produced from textile, cosmetics, paper, leather, food and other industries. Textile industries are one of the most common industries that consume a lot of water in their processing textile. Wastewater generated by textile industries contains the considerable amount of non-fixed dyes especially azo dyes. It is estimated that 60% of dyes used rising great environmental concern especially in water [1] According to [2], the release of dyes into the environment caused serious problems due to their toxic, mutagenic and carcinogenic characteristic of the dye.

The textile wastewater containing pollutants that been characterized as a low biodegradability compound and high in organic content [3]. Due to the organic pollutant toxicity, it takes a long period for microorganisms to degrade those compounds [4]. The potential of toxicity of certain dye in receiving water has been a considerable matter in last two decades [5]. The presence of an even small amount of dyes is clearly visible and will influence water environment. Dyes can be defined as the different type of color particle which consist of a complex unsaturated aromatic compound that has high volume in organic content, salt content and low in biodegradation. It can differ in term of their chemical composition. Congo red dye is commonly used in textile industry as an anionic dye as it has the complex structure with various diazo aromatic groups.

Azo dyes are considered as a major group of dyes produced worldwide due to the ease in its synthesis [6]. The azo compound contains at least one azo group (-N=N-). The highly substituted aromatic rings that combining with one or more azo group will characterize their chemical structure. According to [7], azo dyes are designed to endure toward sun irradiation, chemicals, water and microorganisms. The substituted ring structure makes the molecule recalcitrant and causing the conventional wastewater treatment processes does not degradable [8]. When being released into the environment, these dyes will damage the living organism by stopping the reoxygenation capacity of water and blocking sunlight. If the colour of dyes does not remove properly, the photosynthesis processes of aquatic life are affected due to low of ultraviolet light penetration [3].

In [9] reported that traditional wastewater treatment technologies were proven to be

noticeably less productive in the treatment of wastewater that containing synthetic dyes. In this study, the chemical methods are focused. The advance oxidation processes (AOPs) are the most recent method for wastewater purification. The main idea of advance oxidation processes is where the reactive radical that have a strong oxidizing ability generated into reaction by oxidation through a different mechanism [10]. This process able to decolorized reactive dyes which involve the formation of hydroxyl radicals that used to attack pollutant in wastewater [5]. According to [11], there are several types of AOPs that are famous in water treatment such as ozonolysis, AOP hot, photolysis, photocatalysis and other. In this study, the treatment method focused on photocatalysis advance oxidation process using titanium dioxide as a catalyst.

Photocatalytic degradation is one types of degradation that can be used to degrade the dyes. This photo degradation process will change the structure of the hazardous dye into the substance that is more environmentally friendly by altering it molecule using photon found in UV, infrared and other. The usage of the catalyst such as titanium dioxide (TiO_2) and zinc oxide (ZnO) in photo degradation process is considered as having the potential to degrade various environmental pollutants including the dye. Catalysts are the most safer compound, which it did not undergo any physical or chemical changes within the process. Thus, this property had made catalyst become preferable in degradation of diazo dyes. There are two types of photocatalysis which is homogeneous and heterogeneous photocatalysis. This study is focusing on heterogeneous photocatalysis. This type of photocatalysis will practically including titanium dioxide as a semiconductor. In previous studies, heterogeneous photocatalytic degradation has been proven its efficiency to remove pollutant in wastewater [12].

This study focused on photocatalytic process by using TiO_2 as the catalyst with two different treatment used during this process which is under solar light and under UV lamp. The semiconductor catalyst chosen in this study is titanium dioxide (TiO_2) as it able to degrade the pollutant into the simplest compound without harming the environment. Besides, this semiconductor is affordable, easy to obtain and environmental friendly as a catalyst for the photo-oxidation of organic compounds [13]. The main objective of this study was to evaluate the efficiency of degradation of Congo red dye by using TiO_2 as a catalyst. The effect of pH

on the percentage degradation of Congo red dye were also investigated.

2. METHODOLOGY

2.1. Materials

All materials in this experiment are analytical grade and was prepared in the laboratory. The dye used representing organic dye is Congo red due its solubility in water. The Congo red was prepared in distilled water and used for all experiments. The instrument UV – spectrophotometer – UV 1800 Shimadzu and UV light instrument – UVGL – 58 handheld UV lamp was used in this experiment.

2.2. Methods

The photo degradation of Congo red dye process were operated in the presence of UV light radiation which is directly under sunlight and under UV lamp. The UV-Vis spectrometer was used to analyze the degradation of Congo red dye in all parameter set.

2.2.1. Study the Effect of Different UV Radiation in the Rate of Degradation

A 250 mL of 4 ppm Congo red solution was poured into 500 mL beaker accordingly. The initial absorption peak was recorded before the solution was exposed to UV radiation. Then, the beaker was exposed to sunlight for 30 minutes. At each five minutes interval, 30 mL of the sample was pipette from the beaker and analyzed under the UV-Vis. The absorbances of the dye are measured and recorded. The absorbances of dye indicates the color intensity of the dye. The above steps were repeated under UV lamp.

2.2.2. Study the Effect of Presence TiO_2 toward Rate of Degradation

A 250 mL of 4 ppm Congo red solution was poured into 500 mL beaker accordingly. The initial absorption peak was recorded before the solution was exposed to UV radiation. A 0.1 g of titanium dioxide was poured into the solution and been stirred for 10 minutes to make the solution homogeneous. Then, the beaker containing solution was exposed to sunlight for 30 minutes. At each five minutes interval, 30 mL of the sample was pipette from the beaker and filtered through filter paper before analyzed under the UV-Vis spectrophotometer. The above steps were repeated under UV lamp.

2.2.3. Study Effect of pH on the Rate of Degradation

A 250 mL of 4 ppm Congo red solution was poured into the 500 mL beaker accordingly. 0.1 g

of titanium dioxide was poured into the solution and been stirred for 30 minutes to make the solution homogeneous. The pH of the solution was measured using pH meter. Then, 0.1M of H_2SO_4 was added into the solution until the pH reading constantly shows under pH 4. After the pH was adjusted, the initial absorption peak was recorded before the solution was exposed to UV radiation. Then, 30 mL of the solution has been poured into 6 different 150 mL beakers and was exposed under UV lamp for 30 minutes. At each five minutes interval, one of the beakers was taken out and filtered through filter paper before analyzed under the UV-Vis spectrophotometer. The above steps were repeated for pH 6, pH 7, pH 9 and pH 11 by adding H_2SO_4 or NaOH respectively. For treatment under direct sunlight, the same step above was repeated.

3. RESULTS AND DISCUSSION

The efficiency of degradation of Congo red dye can be calculated by using the decolourization formula [14].

$$Decolorization\ (\%) = 1 - \frac{A}{A_o} \times 100$$

where A is referring to final absorption of Congo red solution at the time interval and the A_o is the initial absorption of the Congo red solution.

3.1. Effect of UV light on the degradation rate of Congo red dye

The degradation of congo red dye under sunlight radiation is slower compared to the UV radiation provided by an artificial UV lamp. Table 1 and 2 were tabulated from the absorbance of the Congo red at different places with the presence and absence of a catalyst.

Table 1. The absorbance of Congo red dye at reaction time with absence of catalyst

Reaction Time	Absorbance	
(min)	Under Sunlight	Under UV Lamp
0	0.309	0.309
5	0.306	0.225
10	0.306	0.224
15	0.305	0.224
20	0.305	0.223
25	0.302	0.220
30	0.284	0.211

Table 1 shows that the degradation of the dye under artificial UV lamp have higher efficiency compared to the degradation under direct sunlight. Table 2 also shows that the degradation of the dye under artificial UV lamp has higher efficiency compared to the degradation under direct sunlight.

Table 2. The absorbance of Congo red dye at reaction time with presence of catalyst

Reaction Time	Absorbance	
(min)	Under Sunlight	Under UV Lamp
0	0.309	0.309
5	0.132	0.124
10	0.120	0.117
15	0.120	0.117
20	0.118	0.116
25	0.114	0.110
30	0.109	0.102

The color intensity of the Congo red dye is decreasing after being treated with the titanium dioxide. The comparison of two different light sources in the degradation of Congo red dye without the presence of a catalyst are shown in Fig. 1.

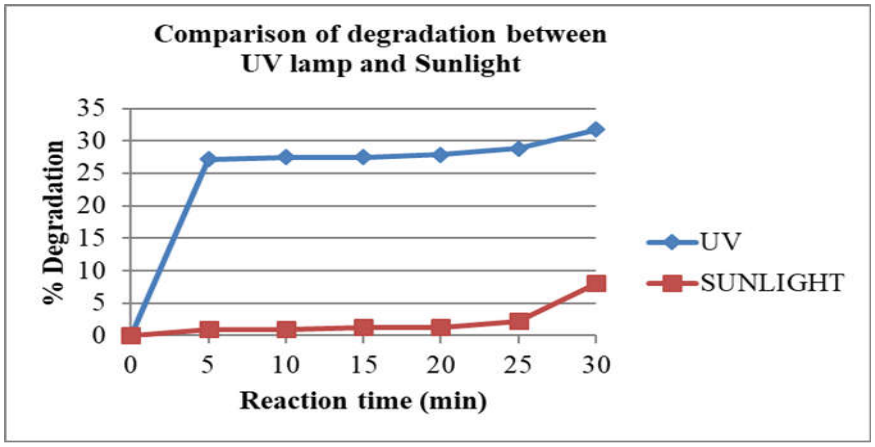

Fig.1. The comparison of degradation between UV lamp and sunlight

Fig. 1 shows that the artificial UV lamp had degraded the dye more than natural UV source which is sunlight. At 30 minutes reaction time, the percent degradation of Congo red dye treated with artificial UV lamp is 31.72%. When treated with natural sources of UV, the dyes only degrade about 8.09%. Since the differences in the percent degradation of dye are too big, it can be considered that artificial UV lamp can enhance the degradation processes as it has higher intensity of UV light. From the observation of the color intensity of the Congo red dye, all the dyes show decreasing in intensity after treated with the catalyst. The azo compound (-N=N-) plays crucial roles in making the dye colored. Thus, the colour intensity decreases due to degradation process of the compound [15].

3.2. Effect of Presence TiO_2 toward Rate of Degradation

The comparison of presence catalyst in the degradation of Congo red dye under sunlight is shown in Fig. 2.

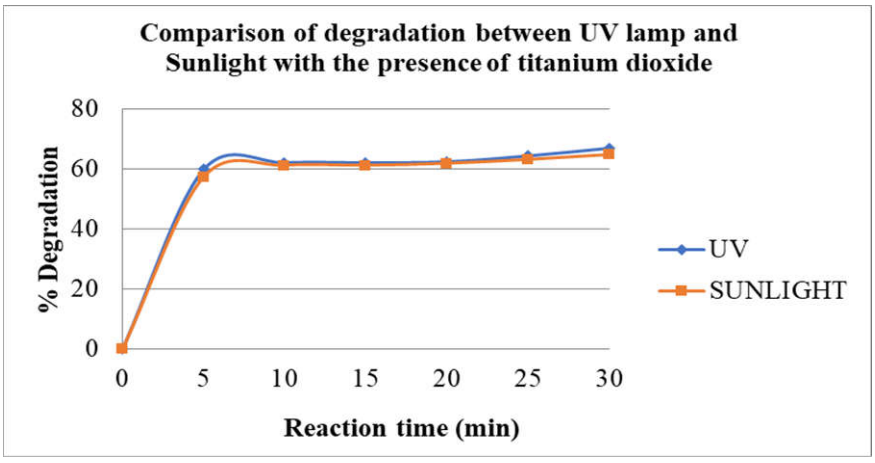

Fig.2. The comparison of percentage degradation between UV lamp and sunlight with presence of catalyst

Based on Fig. 2, the percentage degradation with the presence of the catalyst using artificial UV lamp is nearly similar with the sunlight radiation. At 30 minutes reaction time, the percent degradation of Congo red dye with the presence of titanium dioxide treated under artificial UV lamp is 66.99%. When treated with the presence of a catalyst under sunlight, the dyes degrade about 64.72%. These show that when using catalysts in photo degradation process, it will increase the percent of degradation either treating under UV lamp or under direct sunlight radiation. However, treating under artificial UV lamp radiation will give more percentage in degradation. The comparison of presence and absence of catalyst on percent degradation of Congo red dye under sunlight are shown in Fig. 3.

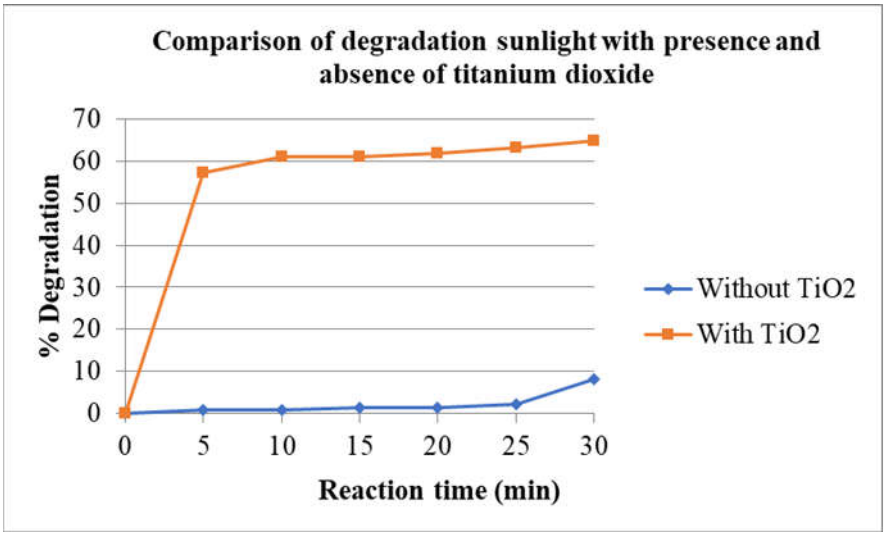

Fig.3. The comparison of presence and absence of catalyst on percent degradation of Congo red dye under sunlight

Fig. 3 shows that with the presence of titanium dioxide as catalyst degrade the dye more than the absence of catalyst when treated under sunlight. At 30 minutes reaction time, the percent degradation of Congo red dye with the presence of titanium dioxide is 64.72%. When treated with the absence of catalyst, the dyes only degrade about 8.07%. These occurrences show that the dyes degrade more with the presence of catalyst under UV radiation. Since the different in percent degradation of dyes are too big, it can be considered that catalysts are important to enhance the degradation processes.

The degradation of dye occurs due to the effect of catalyst which is titanium dioxide. The wavelength and intensity of the UV light irradiation source affect the degradation of dye in aqueous solution using titanium dioxide catalyst powder in the photocatalytic process [16].

According to [3], when the catalyst is irradiated by photon that have the same energy or higher energy than catalyst band gap, the surface of the catalyst will produce electron-hole pairs. These electron holes will react with electron donor in aqueous solution forming powerful oxidizing free radical such as hydroxyl radical. The hydroxyl radical (OH•) will oxidize the organics on the surface. In addition, during the production of hydroxyl radical, the surface of catalyst also produce the superoxide anion radical (O_2^-•). This reaction will happen when the electron at the surface of catalyst are trapped and removed by reaction with the absorbed oxygen in aqueous media. The reactions of catalyst are as follows.

$$\text{Catalyst } (TiO_2) + hv \rightarrow h^+_{VB} + e^-_{CB}$$

$$h^+_{VB} + H_2O \rightarrow OH^- + H^+$$

$$h^+_{VB} + OH^- \rightarrow OH\bullet$$

$$e^-_{CB} + O_2 \rightarrow O_2^-\bullet$$

$$OH\bullet + R_1\text{-}N{=}N\text{-}R_2 \rightarrow \text{degradation process}$$

Relating to the equation, the energy from light radiation is important in degradation process of the dye. The energy is needed to produce the hydroxyl radical and superoxide anion radical. It will degrade all contaminant including organic substance into the non-harm compounds such as H_2O and CO_2 [17].

Based on data obtained from the percentage degradation of Congo red dye, the higher percentage of degradation are under artificial UV radiation compared to the direct sunlight radiation. This is because the artificial UV irradiation is more reproducible than sunlight and this can bring higher efficiency in the degradation of dye [18]. In [19] reported that the energy of UV irradiation is largely comparing to the band gap energy of titanium dioxide. In sunlight, only 5% of total radiation possesses the optimum energy for the band gap excitation of electron.

3.3. Effect of pH on the Rate of Degradation

The pH is considered as important role in reaction mechanism which contributes to dye degradation process. The percentage degradation of Congo red by different pH value under UV light are shown in Fig. 4.

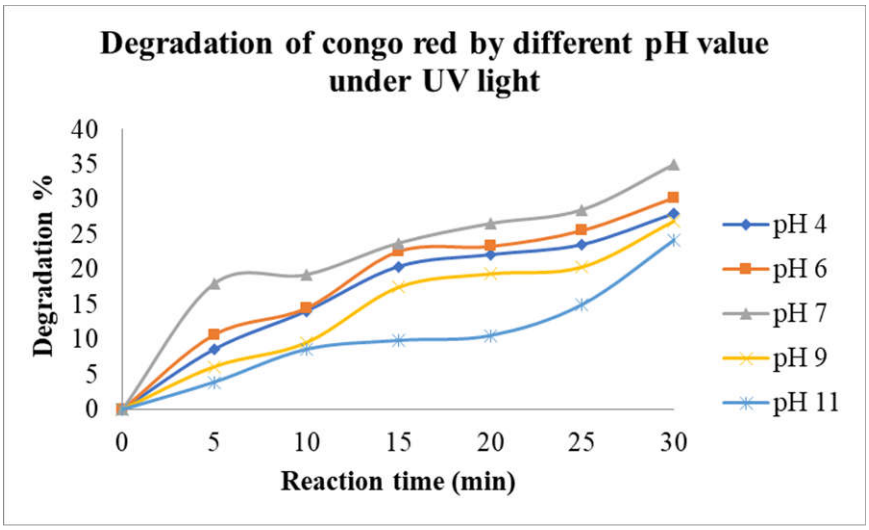

Fig.4. Degradation of Congo red by different pH value under UV light

Based on Fig. 4, at earlier reaction for 5 minutes, pH 7 shows the highest percentage of degradation followed by pH 6, pH 4, pH 9 and pH 11. The values of percent degradation are 18.00%, 10.70%, 8.62%, 6.14% and 3.93% correspondingly. At the end of reaction time, the same patterns of percentage degradation are showed. The highest percentage degradation is pH 7 followed by pH 6, pH 4, pH 9 and pH 11. The values of dye degradation are 35.02%, 30.30%, 28.03%, 26.96% and 24.24% correspondingly. From the result, the difference in pH of the Congo red dye affects to the percent of degradation either it will increase or decrease the degradation process. It also can be concluded that the most efficient degradation of Congo red dye using titanium dioxide is at pH 7, which is neutral condition. The percentage degradation of Congo red by different pH value under sunlight are shown in Fig. 5.

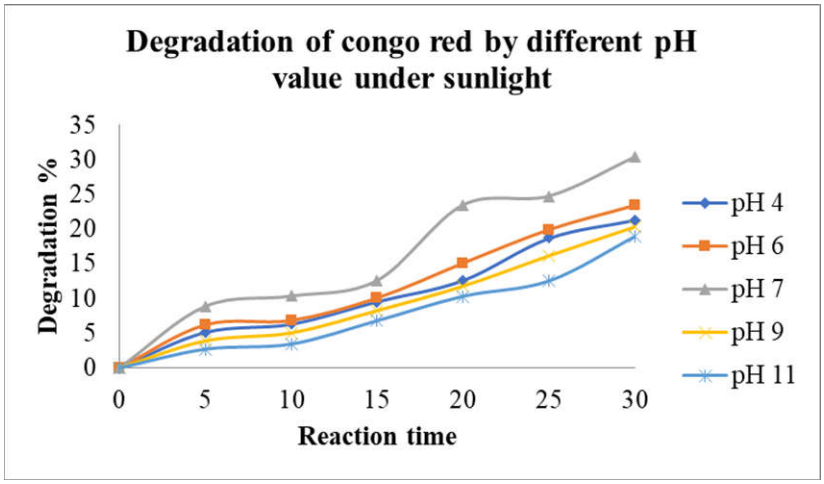

Fig.5. Degradation of Congo red by different pH value under sunlight

Based on Fig. 5, at 5 minutes reaction time, pH 7 also shows the highest percentage of

degradation which is 8.87%. Then, the percentage degradation decrease by pH 6, pH 4, pH 9 and pH 11. The values of percent degradation are 6.20%, 5.12%, 3.91% and 2.70% correspondingly. At 30 minutes of reaction time, the highest percentage degradation is pH 7 which is 30.38%. Then, the percentage degradation patterns are decreased by pH 6, pH 4, pH 9 and pH 11. The values of dye degradation are 23.40%, 21.33%, 20.39% and 18.92% correspondingly. Thus, the percent of degradation will be affected by the acidity of the Congo red dye give either it will increase or decrease the degradation process. As a conclusion, the most efficient degradation of Congo red dye using titanium dioxide is at pH 7 which is neutral condition either treated under UV lamp or direct sunlight.

According to [20], the surface charge properties of TiO_2 are found to change correspondingly with the pH value due to amphoteric behavior semi conduction of catalyst. Thus, the variation of pH value can influence the percentage degradation of Congo red dye. In acidic solutions where the pH is below than 6, the photo degradation process is delayed due to the high concentration of proton. This had caused in a lower percentage of degradation efficiency. Apart from that, in alkaline where the pH is higher than 8, there is presence of hydroxyl ions neutralizing the acidic end products that been produced by the photo degradation reaction. In alkaline solutions, a decrease of the initial rate is due to the difficulty of the dye molecules to approach the catalyst surface will result the optimum pH among those tested appears to be neutral one [13]. At high pH values, the hydroxyl radicals are rapidly scavenged and they do not have opportunity to react with the dyes [18]. The percentage degradation of Congo red dye on pH 7 treated under UV lamp and direct sunlight are shown in Fig. 6.

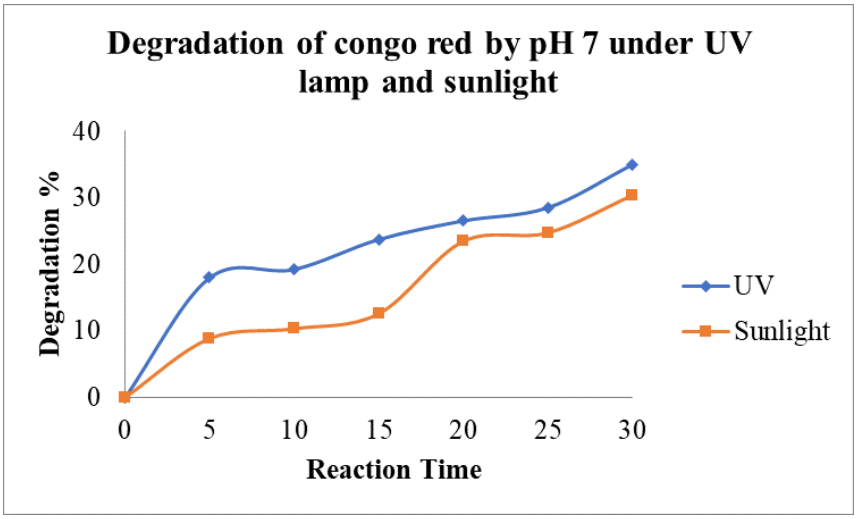

Fig.6. The percentage degradation of Congo red dye on pH 7 treated under UV lamp and direct sunlight

Based on the Fig. 6, at pH 7, the percentage degradation of Congo red dye are higher when treated with the artificial UV lamp more than natural UV source which is sunlight. At 5 minutes reaction time, the percent degradation of Congo red dye treated with artificial UV lamp is 18.00%. When treated with natural sources of UV, the dyes only degrade about 8.87%. After 30 minutes reaction time, the percent degradation of Congo red dye at pH 7 is 35.02% under UV lamp treatment. When treated with direct sunlight at pH 7, the dyes only degrade about 23.40%. These occurrences show that the dyes degrade more under artificial UV lamp compared to direct sunlight in any condition.

4. CONCLUSION

The experiment proved that the uses of titanium dioxide as a catalyst in photo degradation of Congo red dye enhanced the degradation process. Both treatments of dye between direct sunlight radiation and artificial UV lamp radiation show higher degradation percentage with slightly different in presence of catalyst. Treatment of Congo red dye with artificial UV lamp show 66.99% degradation after 30 minutes reaction time and 64.72% degradation when treated under sunlight. With the absence of catalyst, there is huge different in percentage degradation of Congo red dye after treated with both radiations. After treated under artificial UV lamp, the percentage degradation is 31.72% and when treated with natural sources of UV, the dyes only degrade about 8.09%. In acidic condition, the rate of degradation of Congo red

dye will decrease as the decrease in pH value. While in alkaline condition, the rate of degradation of Congo red dye will decrease when the pH value increase. The highest percentage degradation of Congo red dye is when the pH is in natural which is pH 7.

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