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COMPARISON STUDY OF CONGO RED DYE DEGRADATION PROCESS USING FENTON'S REAGENT AND TiO$_2$

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ABSTRACT

Wastewater treatment is one of the major problems faced by textile manufacturers as they produce large volumes of wastewater. The main pollution in textile wastewater come from dyeing and finishing process. The effluent that comes from textile industries not only causes coloration of water, but also give potential to human health hazard and a threat to aquatic life. The main objective of the study was to evaluate and to compare the efficiency of degradation of Congo Red (CR) dye using Fenton reagent and TiO$_2$. The study also comprises the influence of different experimental conditions which are the concentration of CR dye used, the concentration of FeSO$_4$ as catalyst in Fenton reagent, the concentration of hydrogen peroxides (H$_2$O$_2$), the mass of TiO$_2$ and the value of the pH of the experimental solutions in CR dye degradation. The results indicated that the photo-degradation efficiency of the CR solution of dye was more effective when it is being treated by Fenton reagent than the TiO$_2$. For photo-Fenton reagent, the result showed that the operated condition for Fenton reagent was pH under 3 (pH < 3). As for the concentration of FeSO$_4$ as catalyst, the optimum concentration was at 4×10^{-5} M and the maximum removal of the CR dye for H$_2$O$_2$ concentration was at 2.9×10^{-2} M with the initial dye and pH value. As for the TiO$_2$, the result showed less efficiency of degradation occurred compared with the Fenton reagent in this experimental value. The higher percentage removal of dye CR was at 0.4g of TiO$_2$ dose and at the pH 7 in this heterogeneous process. Additionally, the Fenton reagent was the efficient method for pollutant removal due to the addition of the catalyst FeSO$_4$ where the Fe^{3+} ion will undergo reduction under the ultraviolet (UV) light and through the photolysis of the H$_2$O$_2$ itself.

Keywords: fenton's reagent, AZO dyes, congo red (CR), titanium oxide, advanced oxidation processes.

1. INTRODUCTION

The environmental pollution has nowadays become crucial and major factors, especially the water pollution. The most contributors in water pollution include textile industries instead of oil and gases, factories and any other industries. Wastewater from textile industries produces sludge which is difficult to dispose of water polluted [13]. It is difficult to treat wastewater from textile industries because of its contain. Also, it is estimated that 60% of dyes used rising great environmental concern especially in water [6]. Textile industry wastewater releases a very problematic effluent to aquatic life and human where the effluent contains a variety of dyes and other toxic contaminants [5]. The effluent that come from textile industries not only causes coloration of water, but also give potential to human health hazard and a threat to aquatic life [3]. Because of that, the wastewater of textile industries is rated as the most polluting of all industrial sectors [4].

As world moving forward, the use of natural resources as dye nowadays is not reliable. The scientist already found about synthetic dyes to change with natural resources which is cheaper, brighter, more colorfast and also easy to apply to fabric. Synthetic dyes that used in fabric nowadays are very problematic to human and environment. It causes environment pollutant, especially in water pollutant because of their colors, chemical compound and their effluent. It is already known that the effluent that produce from textile industries may affect to the human such as mutagenic problem [15]. Dyes are not only dangerous due to its colors, but because of their breakdown compound are toxic [13]. The removal of dye color has been concern matter due to its visibility in recipient water, which not only because of their potential toxicity [2].

The chemical reaction that occurs in wastewater produce toxic metabolizes which make it toxicity. The impact was adverse effect to animal and also human [1]. It is also raises several concerns because its high level of coloration and high organic compound which not easily eliminated by conventional treatment [7]. It causes the mutagenic action to human and aquatic life because of the effluent associated with the types of dyes used [15]. Thus, the waste water that contributes to water pollutant mostly come from textile industries [7].

The conventional processes such as coagulation, flocculation and biological methods adopted for decoloration of effluent containing reactive dyes are no longer able to achieve adequate removal of the color. From all the treatments available, advanced oxidation process such as oxidation using Fenton's reagent has proved to effectively decolorizes almost all dyes [12] as well as for the destruction of a large number of hazardous and organic pollutants [9]. When conventional water treatment processes are incompetent remove persistent pollutants, advanced oxidation processes (AOPs) are a promising option to remove the pollutant from the contaminated water. AOPs are based on the initiation of a

very reactive species such as hydroxyl radicals that can oxidize an extensive range of dyes [10].

This study focused on chemical advanced oxidation processes using Fenton's reagent and TiO_2 in the photo degradation process of Congo red (CR) under ultraviolet (UV) light. Fenton reagent is widely used as an oxidizing agent in degradation process as it is the strongest oxidizing agent [5]. Several ways of degradation process using Fenton reagent that mostly done with dye. It is proven that Fenton process of treatment is the best way and more efficient in degradation process of organic pollutant of dyes in wastewater [2]. The reaction of Fenton process from Fenton reagent are they are oxidative degraded by hydroxyl radicals generate from H_2O_2 with the presence of Fe^{2+} [8]. TiO_2 is plentiful, inexpensive, powerful and environmental friendly as a catalyst for the photo-oxidation of organic compounds [4]. It is also stated that TiO_2 is considered an increasingly attractive approach for degradation process of organic dye [1]. TiO_2 is as predominant factors that influence decolorization and mineralization of organic compound by UV/TiO_2 process [2].

The main objective of the study was to evaluate and to compare the efficiency of degradation of CR dye using Fenton reagent and TiO_2. The influence of different experimental conditions which are the concentration of CR dye used, the concentration of photo catalysts (Fenton reagent and titanium dioxide), the concentration of hydrogen peroxides (H_2O_2) and the value of the pH of the experimental solutions in CR dye degradation were investigated.

2.   MATERIALS AND METHODS

Materials

All materials in the experiment were prepared in the laboratory and of analytical grade. The model dye of CR was purchased from its manufacturing company (SIGMA Chemical). The stock solution of the dye was prepared in deionized water and be used throughout the experiment. The instruments used in the experiment were UV-Vis spectrophotometer (UV 1800 Shimadzu) and UV light instrument (UVGL-58 handheld UV lamp).

Methods

The degradation process methodology was followed according to [11], where the sample used is CR which has 65% purity. The other chemical used is TiO_2 that used in TiO_2 degradation experiment which has 79.90 g/mol MW. H_2O_2 was used in a Fenton reagent experiment which has 35% purity and $FeSO_4$ as the catalyst to enhance the Fenton reaction process.

To Study Photo-Degradation Process by TiO_2

Before the experiment was started, several concentrations of CR were prepared from 1000 ppm stock solution of CR. The standard of CR sample from 1 ppm to 5 ppm was analyzed under UV-Vis spectrometer with 497 nm wavelength. From the result of standardization, 5 ppm

of CR was chosen in the degradation experiment with TiO_2 and Fenton reagent. For TiO_2 experiment, about 100 mL of the CR solution was transferred into 250 mL beaker without any scavengers or any metal. Then, the sample was analyzed by using UV light and dark condition. The irradiation time was 2 hours and was recorded in a certain time interval within 2 hours which are 30, 60, 90 and 120 minutes. The sample was filtered through filter paper before analyzing under a UV lamp to avoid any TiO_2 powder inside the crucible when analyzed under UV-Vis spectrometer. The sample was analyzed under UV-Vis spectrophotometer with 497 nm wavelength. The rate of decreased of color with time was continuously monitored. The TiO_2 photo-degradation experiment was conducted in different parameters which are samples with different TiO_2 mass, samples with TiO_2 but different in pH value and samples with different concentration with TiO_2.

To study photo-degradation process by Fenton reagent

As for Fenton reagent experiment, about 100 mL of 5 ppm dye solution was poured into 250 mL beaker. The pH of the dye solution was controlled by adjusting the pH with 0.05 M of HCl and 0.05 M of NaOH to make sure that the pH of the CR solution was under pH 3.5. After the pH of CR was adjusted, quickly added $FeSO_4$ solution and H_2O_2 with the amount of $FeSO_4$ and H_2O_2 was 1:5 in ratio. The sample was analyzed under UV-Vis spectrophotometer with 497 nm wavelength with time interval. The rate of color decreased was monitored. The step of the degradation process was conducted in different parameters which are different concentration of samples with $FeSO_4$ and H_2O_2, samples with different value of pH with $FeSO_4$ and H_2O_2, samples with variation of $FeSO_4$ concentration and samples with a variation of H_2O_2 concentration.

3.   RESULTS AND DISCUSSION

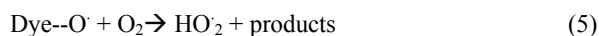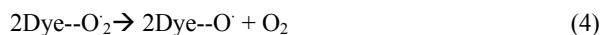**Congo red degradation under Fenton reagent**

The experiment of CR under Fenton reagent was carried out with the presence of UV light, H_2O_2 and $FeSO_4$. The decolorization of dye occurred when it was analyzed under the UV light and the presence of the H_2O_2 in the production of the hydroxyl radical to react with the dye molecule. The H_2O_2 alone can produce hydroxyl radicals as shown below:

$$H_2O_2 + hv \rightarrow 2O\,H^. \tag{1}$$

The hydroxyl radical can react with dye as shown:

$$^.OH + dye \rightarrow ^.Dye + H_2O \tag{2}$$

Another reaction took place in the overall scheme

$$^.Dye + O_2 \rightarrow Dye\text{--}O^._2 \tag{3}$$

$$2Dye\text{--}O^._2 \rightarrow 2Dye\text{--}O^. + O_2 \tag{4}$$

$$Dye\text{--}O^. + O_2 \rightarrow HO^._2 + products \tag{5}$$

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Peroxy radical can react with dyes as follows:

$$HO_2^. + Dye \rightarrow {}^.Dye + H_2O_2 \qquad (6)$$

It is known that Fenton reaction is one of the most effective methods of degradation process. The organic pollutant is oxidatively degraded by hydroxyl radicals which generated from the H_2O_2 in the presence of the Fe^{2+} as the catalyst

$$Fe^{2+} + H_2O_2 \rightarrow OH^. + OH^- \qquad (7)$$

Rapid reaction occurs between ferrous ion and hydrogen peroxide as shown in Eqn. (1) when the ferrous salt is used and hydroxyl radical is produced. Eqn. (2) showed the rapid reaction between ferrous ion and hydrogen peroxide

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^- + H^+ \qquad (8)$$
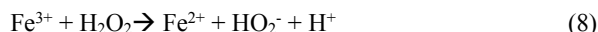
But, the efficiency of the Fenton reagent depends on the concentration of Fe^{2+} and H_2O_2, and the pH value [8]. The degradation efficiency was calculated by using the following formula:

Degradation Efficiency (%) = $[(C_0 - C_t) / C_0]$ x 100   (9)

Effect of variation in pH by Fenton Reagent
The percentage degradation efficiency of CR dye in variation of pH by Fenton reagent is shown in Figure-1.
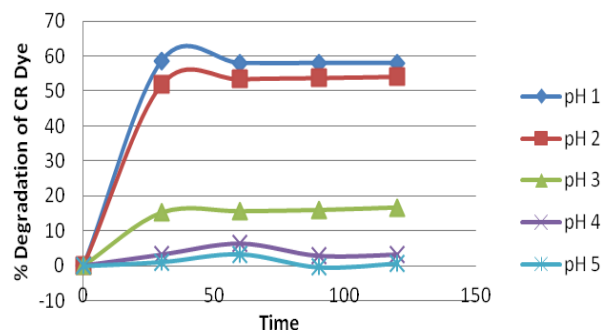

Figure-1. Effect of variation in pH by Fenton reagent.

According to the Figure-1, the sample that has the value of pH 1 has the higher percentage of degradation. It was followed by sample that has a value of pH 2, which has the second highest percentage of degradation. The CR dye started to degrade as soon as the pH was adjusted by the 0.05 HCl acids this may due to more hydrogen ion acts as $^.OH$. As the percentage of the photo catalytic bleaching process increases with an increase of pH, but has an adverse effect on increasing pH. The data on the percentage also shown that percentage of degradation, which started to decrease up from pH 3 to pH 5. The degradation efficiency dropped at high pH values may due to the precipitation of $Fe(OH)_3$. On this form, the iron is decomposed H_2O_2 into oxygen and water and the oxidation rate decreased consequently because of less hydroxyl radical are available [8]. At high pH (pH > 3),

the generation of $^.OH$ getting slower due to the formation of the ferric hydroxo complexes.

Effect of Variation in CR Concentration
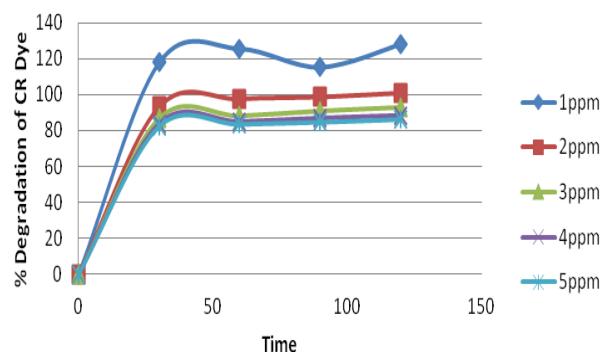The percentage degradation efficiency in variation of CR concentration is shown in Figure-2.

Figure-2. Effect of variation in CR concentration.

It was shown respectively that 5 ppm concentration has a less percentage of degradation between 1 ppm, 2 ppm, 3 ppm and 4 ppm concentration of dye with the initial concentration of $FeSO_4$ and H_2O_2 with the pH was maintained. As the 1 ppm concentration has the higher percentage which is 128.21% where the dye was perfectly decolorized because it is more than 100% degradation. However, the 5 ppm concentration has the lowest percentage which is 86.1% but has almost nearly to 100% degradation efficiency. It means that the photo-degradation of dye decrease as the increases of the concentration of dye. From the result, it can be explained that the increases of the concentration of the dyes lies in the consistency of the hydroxyl radical's concentration of dye molecules so that the rate of decolorization decreased. It also means that with constant pH, H_2O_2 and $FeSO_4$ value more hydrogen peroxide need to be consumed because of higher concentration, but the amount of hydrogen peroxide available becomes smaller as the concentration increased [8].

Effect of Variation in Concentration of $FeSO_4$
The percentage degradation efficiency of variation in concentration of $FeSO_4$ is shown in Figure-3.
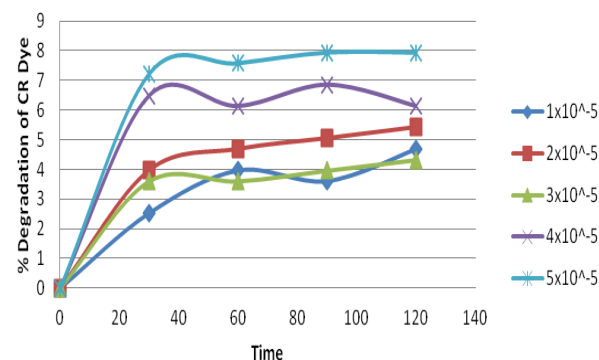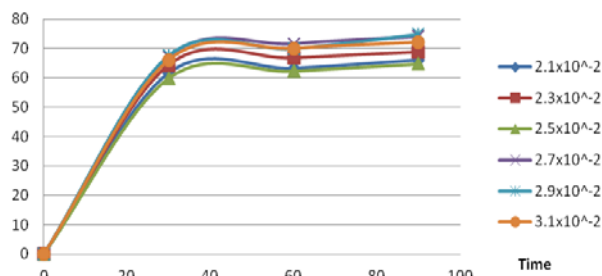
Figure-3. Effect of variation in concentration of FeSO$_4$.

In order to study the function of different concentration of Fe^{2+} on the degradation of CR by the Fenton process, a variation of the concentration of FeSO$_4$ experiment was conducted from 1 x 10^{-5} M to 5 x 10^{-5} M and the result was presented in Figure-3. The degradation efficiency of CR was increased with increasing the value of FeSO$_4$. The highest percentage efficiency was recorded at 5 x 10^{-5}M values of FeSO$_4$ after 120 minutes irradiation time as the lowest was recorded at 1 x 10^{-5} M of FeSO$_4$. Many studies have revealed that the higher used of Fe^{2+} could lead to self-scavenging of ·OH radical by Fe^{2+} and induced the decreased in degradation rate of pollutants [8].

**Effect of variation in hydrogen peroxide concentration**
The percentage degradation efficiency of variation in hydrogen peroxide concentration is shown in Figure-4.

Figure-4. Effect of variation in H$_2$O$_2$ concentration.

The experiment of varying concentration of H$_2$O$_2$ values was conducted to study the effect of H$_2$O$_2$ concentration on degradation of CR dye. The range of H$_2$O$_2$ concentration was studied in a range of from 2.1 x 10^{-2} M to 3.1 x 10^{-2} M. The higher percentage of degradation was at 3.1 x 10^{-2} M, which is 75.3% as the lowest percentage was at 2.1x 10^{-2} M. As expected, the higher the value of concentration H$_2$O$_2$, the higher percentage of degradation occur because the higher concentration of H$_2$O$_2$, the more hydroxyl radicals produce which degrade more dye molecule. It is known that the addition of H$_2$O$_2$ was to increase the rate of dye to degrade by the formation of hydroxyl radical that react with the dye molecule compound. H$_2$O$_2$ play important role in degradation process as the hydroxyl radical ·OH because the radical will attacked the Fe^{2+} and the decolorization of CR dye occur. The amount of H$_2$O$_2$ must be more than FeSO$_4$ amounts in the dye solution. As the more hydroxyl will attack the Fe^{2+}, the degradation process becomes better and faster.

Effect of variation of pH for TiO$_2$
The percentage degradation efficiency of pH for TiO$_2$ is shown in Figure-5.
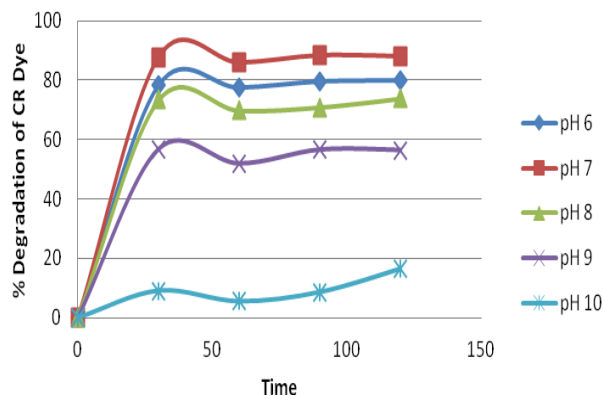
Figure-5. Effect of variation of pH for TiO$_2$.

The result shown that there is an increased of decolorization percentage of dye from pH 6 to pH 7, but has an adverse reaction on the decolorization after pH 7 as the pH increased. It is known that increasing the value pH will actively increase the number of OH$^-$ ions. Furthermore, the OH$^-$ ion generated more ·OH radicals to react with the dye molecule. It is shown that pH 7 has a high percentage value of degradation process which is 88.04%, and the lowest is at pH 10 where the value is 16.32%. It is known that, increasing degradation efficiency through pH is when the organic dye contains the negatively charged sulfonate group in structure, acidic solution favors adsorption of dye into the TiO$_2$ surface, where it is an explanation of low decolorization at pH > 8 that obtained.

Effect of different concentration of dye in TiO$_2$
The percentage degradation efficiency of CR dye in the presence of different concentration of TiO$_2$ is shown in Figure-6.
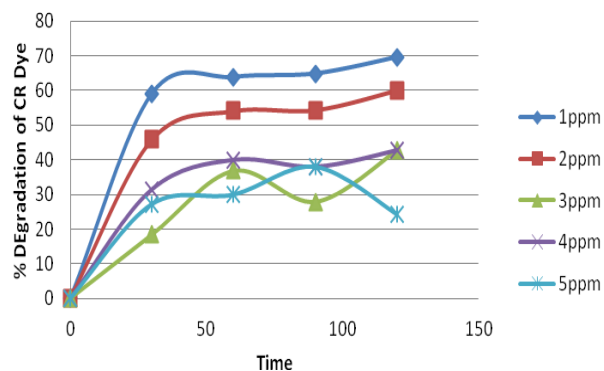
Figure-6. Effect of different concentration of dye.

It was observed from the results obtained that the percent degradation of dye decreased with the increase of concentration of CR dye. The result was obtained from this experiment with the constant amount of TiO$_2$ for each sample, also the irradiation time was the same. The higher percentage of degradation in TiO$_2$ process is at 1 ppm concentration, which has 69.58% and the lowest was at 5

ppm concentration 24.19%. The plausible explanation for this result is given by [11]. The amount of dye adsorbed on catalytic surfaces increased when initial dye concentration increased. This situation reduces the light adsorption of catalyst and lowering the activity. It is also stated that the increasing dye concentration decreasing the solution transparency. Thus, the path length of the photon that entering the dye solution also decreased [2]. The higher concentration of dye the higher unabsorbed dye in solution, thus it will lead to lesser penetration of light within solution on the surface of TiO_2.

Effect on different mass of TiO_2

The percentage degradation efficiency of CR dye in the presence of different mass of TiO_2 is shown in Figure-7.
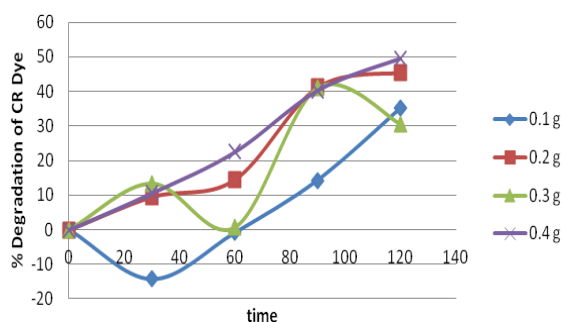

Figure-7. Effect of different mass of TiO_2.

The result obtained showed that 0.4g of TiO_2 has a high percentage of degradation which is 49.58%. It is stated that the number of active sites on TiO_2 surface increases when the amount of catalyst increase, thus increasing number of $O_2^{.-}$ and $^.OH$ radicals. The amount of catalyst increased will increase the amount of active sites on photocatalytic surface. Referring to [14], if all molecules of dyes are absorbed at the TiO_2 surface, the addition of higher quantities of TiO_2 would be no effect on further degradation efficiency. It is also stated that if the dosage of TiO_2 too high over 0.4g, there will be increases in turbidity that will reduce the light transmission through dye solution negatively influenced degradation of dye solution.

4. CONCLUSIONS

The experiment proved that the photo-degradation efficiency of CR solution of dye was more effective when it is being treated by Fenton reagent than the TiO_2. For Fenton reagent under UV light, the result showed that the operated condition for Fenton reagent was pH under 3 (pH < 3). As for the concentration of the catalyst, the optimum concentration was at 4×10^{-5} M and the maximum removal of the CR dye for H_2O_2 concentration was at 2.9×10^{-2} M with the initial dye and pH value. The Fenton reagent was expected as the most efficient method of pollutant removal due to the addition

of the catalyst $FeSO_4$ where the Fe^{3+} ion will undergo reduction under the UV light and through the photolysis of the H_2O_2 itself. As for the TiO_2, the result showed less efficiency of degradation occurred compared with the Fenton reagent is this experimental value. The higher percentage removal of dye CR was at 0.4g of TiO_2 dose and at the pH 7 in this heterogeneous process. The degradation of CR is less efficient in this TiO_2 experiment process as there is no addition of H_2O_2 in this degradation process, even though H_2O_2 itself does not enough for complete reaction degradation. The process of degradation can be faster and can achieve more percentage of removal by adding catalyst in the process.

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