

DEGRADATION OF CONGO RED DYE IN AQUEOUS SOLUTION BY USING ADVANCED OXIDATION PROCESSES

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Abstract

Degradation of azo dyes by using advanced oxidation processes (AOPs) was conducted. In this approach, different AOPs, which are Fenton process and titanium dioxide (TiO₂) catalyst, were examined and compared for the degradation of an azo dye (i.e., Congo red dye). The sample was tested under UV light and the experiment was conducted for 90 min with 15 min interval. The degradation rate of dye was determined using UV-Vis spectrophotometry. The effect of several parameters on the degradation process such as the concentration of metal ions (Fe²⁺, Cu²⁺, and Mn²⁺) as the catalyst in Fenton process, the concentration of hydrogen peroxide (H₂O₂), the mass of TiO₂, and pH value of the dye solution were investigated. The initial Congo red concentration used for both techniques was 5 ppm. The results showed that the percentage degradation followed the sequence of H₂O₂/Fe²⁺/UV, H₂O₂/Cu²⁺/UV, H₂O₂/Mn²⁺/UV, and TiO₂/UV. The best operating conditions for H₂O₂/Fe²⁺/UV were pH 3, 0.2 M concentration of H₂O₂, and 0.02 M concentration of metal ion in 15 min, which achieved 99.92% degradation of dye. The Fourier transform infrared (FTIR) spectrum showed the absence of azo bond (N=N) peak after degradation process, which indicates the successful cleavage of azo bond in the chemical structure of Congo red.

Keywords: azo dye, congo red, Fenton process, titanium dioxide

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Introduction

Nowadays, textile companies hold a big role in the textile industry. The development of a new trend in fashion makes textile companies to come up with new designs of fabrics. To catch up with the demands, a lot of alternatives have been used in producing the best products. For example, various colours of dyes are used during manufacturing and processing operations, and several industries use dyes in textile, paper, plastics, and pharmaceutical products. The most commonly used dyes are azo dyes due to their radiant colour and better dyeing processing conditions (Ajmal et al., 2016).

The yearly production of dyes and pigments is more than 7×10^5 tonnes with an estimation around 5%–15% are lost in industrial effluents (Khataee and Kasiri, 2010). The presence of dyes, surfactants, electrolytes, dispersing agents, acids, and other different organics from dye materials creates some pollutants of dyeing process from textile industry wastewater (Salazar et al., 2011). Furthermore, azo dyes such as Congo red dye have disadvantages that can cause harms to humans and animals by direct inhalation and ingestion (Khaparde and Acharya, 2016). The treatment of effluents containing such compounds is important in order to minimise their effect on the environment and to decolourise water (Ashraf et al., 2014). Therefore, many researchers have made considerable efforts to discover suitable treatment technologies in eliminating impurities and pollutants in wastewater from textile industries. Oxidation methods need to be generated to remove pollutants from textile wastewater and the discharge of the pollutants to water bodies has negative consequences to the environment.

Advanced oxidation processes (AOPs) are believed to be the most effective method for the purification of water and wastewater, including removal of toxic and non-biodegradable pollutants during the last few decades (Ljubas et al., 2015). The most common AOPs include H₂O₂/UV, photocatalysis, and Fenton process. AOPs are based on hydroxyl radicals (\bullet OH) for the initiation of reactive intermediates, which are identified as the powerful and dominant oxidising species responsible for the mineralisation

of organic matters into water and carbon dioxide (Ghaly et al., 2001). Haddad et al., (2014) found that Fenton reagent is effective for the destruction of organic pollutants, as well as a promising treatment method for the degradation of dyes. Besides, AOPs using titanium dioxide (TiO_2) have been productively used to detoxify obstinate pollutants in industrial wastewater in recent years. TiO_2 has low cost, high photocatalytic activity, high photochemical reactivity, stability in aquatic systems, and low environmental toxicity (Saggiaro et al., 2011). It is believed that both methods will increase the rate of degradation of azo dyes in an aqueous solution due to increase in the generation of hydroxyl radical species, which helps the degradation of dye molecules. Thus, the objective of this study is to determine the most effective method in the degradation of Congo red dye in an aqueous solution using different AOPs.

Methods

Materials

The materials used in this study were TiO_2 (analytical reagent grade), Congo red dye (R&M Marketing, Essex, U.K.), iron(II) sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (analytical reagent grade), copper(II) sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), manganese(II) sulphate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) (analytical reagent grade), 0.1 M sulphuric acid (H_2SO_4) (98% purity), 0.1 M sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2) (35% v/v purity), and distilled water.

Study of dye photodegradation

The stock solutions of Congo red (CR) of 100 ppm were prepared. The standard solutions of CR from 1 to 5 ppm were prepared by dissolving the stock solutions in distilled water. The absorption of dyes was measured using PG instruments T80+ UV-Vis spectrophotometer at the range of 350 to 650 nm. The concentration of dye was deduced from the calibration curves produced at the wavelength corresponding to the maximum absorbance (500 nm) and analysed using a UV-Vis spectrophotometer.

Photodegradation process of the blank dye solution.

This research was done in a dark reaction box (45.5 cm \times 38.5 cm \times 48 cm) with a UV lamp, and the setup is shown in Figure 1. For the blank CR solution, about 100 ml of CR solution with different concentrations was transferred into a 250 ml beaker without any metal or scavenger. The pH value of the solution was measured by using a digital pH meter calibrated with standard buffers of pH 4.0, 7.0, and 9.0 before the measurement and was adjusted with 0.1 M NaOH or H_2SO_4 . The pH for CR solution was fixed at below pH 3. Then, the sample was analysed under UV light and the process was carried out in a dark condition to avoid external light interference. The samples were taken at time intervals of 15, 30, 45, 60, 75, and 90 min.

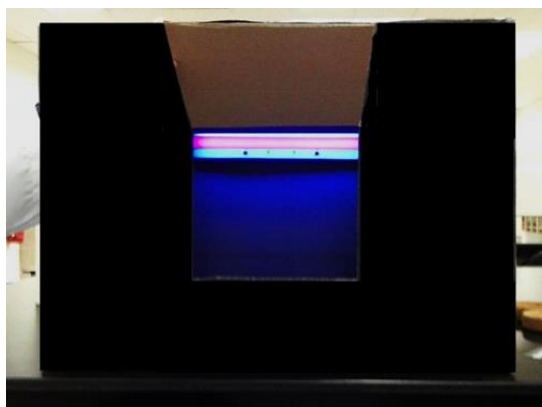


Figure 1. Dark reaction box

Photodegradation process by Fenton reagent and TiO₂ catalyst

Effect of H₂O₂ concentration. The reaction mixtures of 100 ml of dye solution (5 ppm) with H₂O₂ solution at different concentrations (0.02, 0.04, 0.06, 0.08, 0.1, 0.15, and 0.2 M) were prepared and the pH was adjusted to 3.

Effect of pH. Dye solutions (5 ppm) with different pH (3, 7, and 10) were adjusted using 0.1 M NaOH or H₂SO₄. For Fenton process, a mixture of metal ions (0.05 M) as a catalyst and 0.2 M H₂O₂ was quickly added to the solution to create solutions with 1:4 molar ratio of H₂O₂/Fe²⁺, H₂O₂/Cu²⁺, and H₂O₂/Mn²⁺. For TiO₂ catalyst, a fixed amount of TiO₂ powder (0.20 g) was added to the dye solution. A magnetic stirrer with stirring rate of 400 rpm was used continuously in the reaction for homogeneous dispersion of the catalyst all over the solution. All the collected samples were filtered using 0.45 µm Millipore membrane filter and the filtrate was subjected to analysis.

Effect of metal ions in Fenton process. The reaction mixtures of 100 ml of dye solution (5 ppm) with H₂O₂ solution (0.2 M) and metal ion solution at different concentrations (0.01, 0.013, 0.02, 0.04, and 0.05 M) were quickly added to the dye solution (5 ppm) to create H₂O₂/Fe²⁺, H₂O₂/Cu²⁺, and H₂O₂/Mn²⁺ with molar ratios of 1:4, 1:5, 1:10, 1:15, and 1:20. A magnetic stirrer with stirring rate of 400 rpm was used continuously in the reaction for homogeneous dispersion of the catalyst all over the solution. All the collected samples were filtered using 0.45 µm Millipore membrane filter and the filtrate was subjected to analysis.

Effect of TiO₂ mass. Different amounts of TiO₂ powder (0.04, 0.05, 0.08, 0.16, and 0.20 g) were added to the dye solution and tested under UV light in a dark condition. A magnetic stirrer with stirring rate of 400 rpm was used continuously in the reaction for homogeneous dispersion of the catalyst all over the solution. All the collected samples were filtered using 0.45 µm Millipore membrane filter to remove traces of powder when analysed under UV-Vis spectrophotometer.

All experiments conducted in this section were analysed under UV light and carried out in a dark condition to avoid external light interference. All the collected samples were taken at time intervals of 15, 30, 45, 60, 75, and 90 min. The concentrations at various time intervals were recorded to determine the degradation of dye. The percentage of degradation was calculated using the following equation:

$$\text{Percentage of degradation} = \frac{C_o - C_t}{C_o} \times 100\%$$

Where,

C_o = initial concentration at t = 0 minute

C_t = final concentration at reaction time, t minute

Results and Discussion

Blank experiments were conducted with various concentrations of Congo red dye prior to AOPs treatment. These experiments were conducted without the presence of catalyst in order to find a suitable concentration of Congo red dye for future studies. pH 3 was selected as the suitable pH condition due to the acidity region of the optimum range for Fenton process (Duan *et al.*, 2016).

As observed in Figure 2, dye can be degraded without catalyst at the range of 60%–77% (Li *et al.*, 2006). Therefore, the concentration of 5 ppm was chosen for degradation with Fenton process and TiO₂ catalyst due to the lowest percentage degradation shown at this concentration compared to other concentrations.

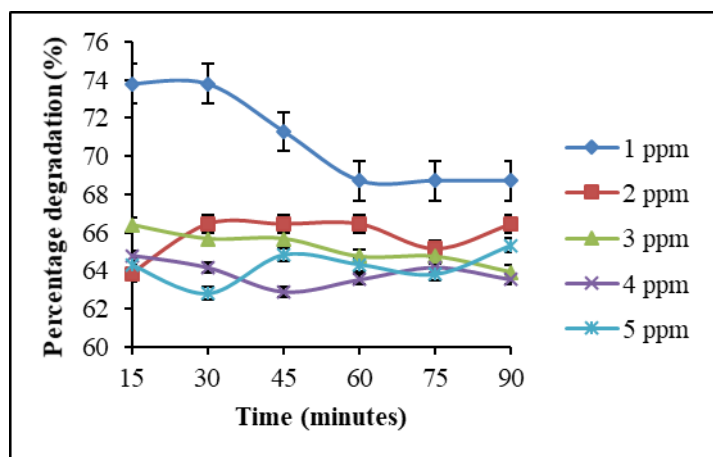


Figure 2. Graph of percentage degradation of Congo red dye versus time in blank experiment

Several parameters were studied in Fenton process, such as the effect of different concentrations of H_2O_2 , the effect of different concentrations of metal ions (Fe^{2+} , Cu^{2+} and Mn^{2+}), and the effect of different pH conditions in metal ion solutions. Meanwhile, for the photodegradation by using TiO_2 catalyst, two parameters were examined: the effect of different mass of TiO_2 and the effect of different pH conditions. The results for all parameters are shown and discussed as follows.

Effect of different concentrations of H_2O_2 . The effect of H_2O_2 concentration towards the degradation of Congo red dye was studied by varying its concentration from 0.02 to 0.2 M. The results obtained are shown in Figure 3. The concentration of dye was fixed at 5 ppm for all experiments. At 0.02 until 0.15 M of H_2O_2 concentration, the percentage degradation was slightly constant in the range of 63% to 66%. Based on the results, there were no changes in percentage degradation compared to the blank experiment for 5 ppm concentration. However, further increase of H_2O_2 concentration from 0.15 to 0.2 M increased the percentage of degradation significantly from 64.54% to 77.16% at 90 min.

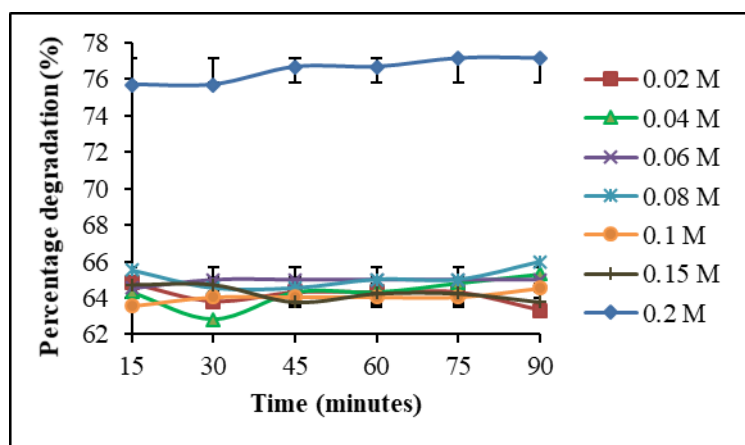


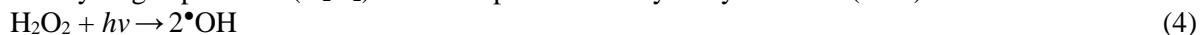
Figure 3. Graph of percentage degradation of Congo red dye versus time in different concentration of H_2O_2

The higher the concentration of H_2O_2 , the higher the percentage of degradation, which is caused by the increase of hydroxyl radicals produced in order to degrade the dye (Farahiyah et al., 2016). These radicals react with excess H_2O_2 (Equation 1) and the reaction competes with the destruction of dye chromophore in azo bond $\text{N}=\text{N}$, which leads to the degradation of dye solution due to its scavenging effect (Sreeja and Sosamony, 2016). Subsequently, significant changes in the percentage degradation were observed by using 0.2 M concentration of H_2O_2 and this concentration was chosen as the suitable H_2O_2 dosage for the subsequent degradation experiment (Harichandran and Prasad, 2016). The reaction between Congo red dye and H_2O_2 is shown in the following equations (1–9):

Reaction hydrogen peroxide (H₂O₂) with hydroxyl radicals (•OH):



The hydrogen peroxide (H₂O₂) itself can produce the hydroxyl radicals (•OH):



The hydroxyl radical react with dye:



The overall scheme for the reaction took place:



The peroxy radical (HO₂•) react with dye:



Effect of different pH. The effect of initial pH of solution on the degradation of Congo red dye for Fenton process and TiO₂ catalyst was studied in three pH conditions: acidic (pH 3), neutral (pH 7), and alkaline (pH 10) at 90 min. The results are shown in Figure 4.

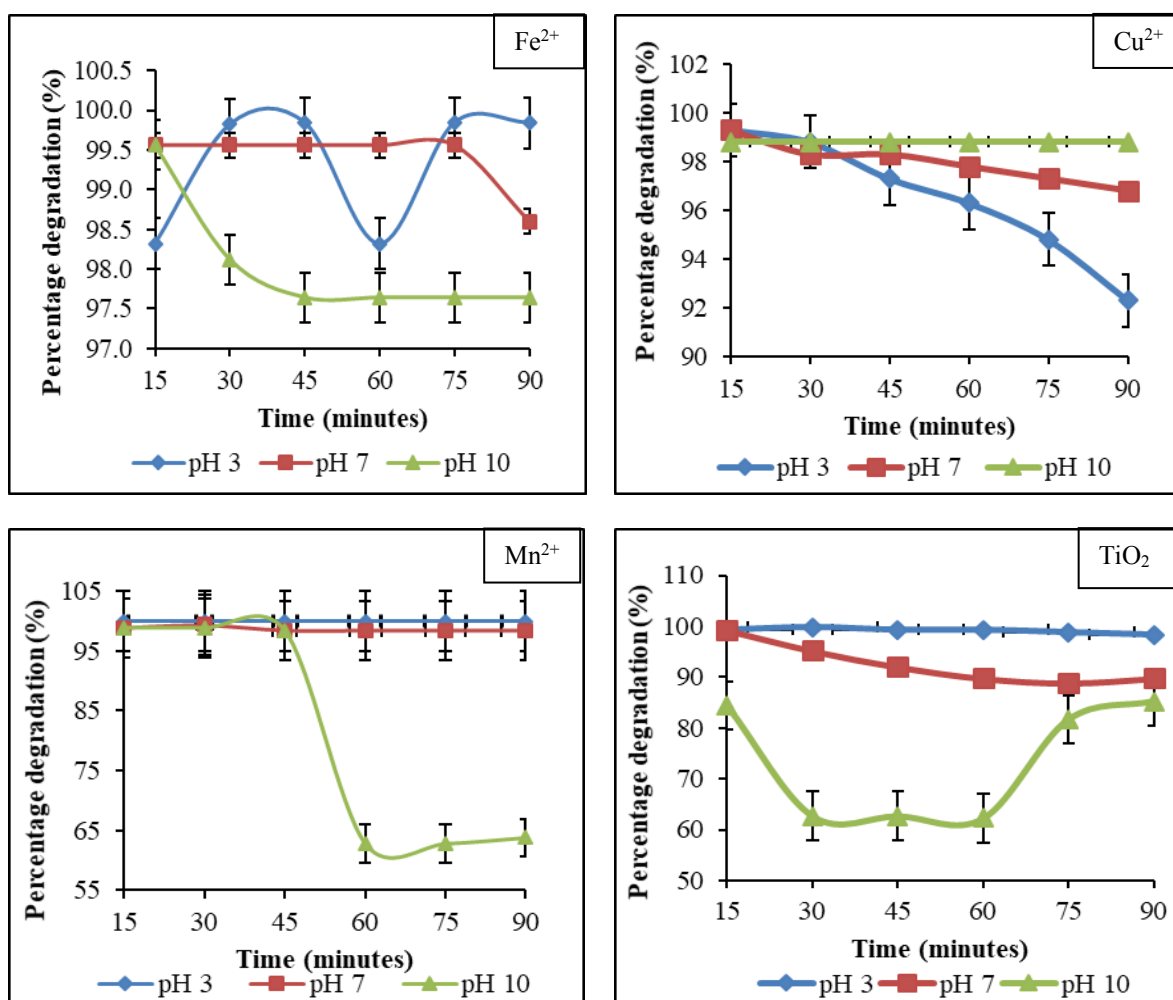


Figure 4. Percentage degradation of Congo red dye versus time in different pH for Fe²⁺, Cu²⁺, Mn²⁺ and TiO₂.

From Figure 4, it can be confirmed that the Fenton reaction in acidic pH is more effective and better compared to neutral and alkaline pH after 30 min for Fe^{2+} metal ion (Mansoorian et al., 2014). This is due to the formation of ferrous or ferric hydroxide complexes, which leads to the deactivation of ferrous catalyst and generation of a small amount of hydroxyl radicals (Youssef et al., 2016). The equations (10-11) occur in low pH:



For Cu^{2+} metal ion, the lowest percentage of degradation of dye was observed at pH 10 (i.e., 98.82%), whereas the highest percentage of degradation of dye was recorded at pH 3 (i.e., 99.32%) within 15 min of reaction. This is due to the formation of maximum amount of hydroxyl radicals to oxidise organic compounds of dye in the first 15 min. However, up to 30 min, the degradation efficiency decreased for pH 3 and pH 7 due to the formation of cuprous hydroxide complexes, which led to the deactivation of cuprous catalyst, and a small amount of hydroxyl radicals was generated (Youssef *et al.*, 2016). Even though the degradation of dye was constant at 98.82% throughout the reaction time at pH 10, it was principally due to the formation of a stable substance, which is copper ion with H_2O_2 that led to the deactivation of the catalyst; subsequently, the reduced number of active sites for H_2O_2 resulted in the constant removal efficiency throughout the reaction time (Mansoorian *et al.*, 2014). Thus, the best degradation efficiency was obtained at pH 3 for the first 15 min compared to pH 7 and pH 10.

Meanwhile, for Mn^{2+} metal ion, the solutions in the basic condition showed that the percentage of degradation was higher only for 45 min with the percentage of degradation of nearly 100%, but it started to decrease from 60 min up to 90 min with the percentage of degradation in the range of 60%–70%, and at 75 min, the percentage of degradation was 62.32%. Basically, the above situations occurred due to several reasons. First, when the pH increases, which is in acidic medium, there might be precipitation or flocculation of Mn^{2+} that affects the deactivation of Mn^{2+} , resulting in the lowest percentage of degradation. On the other hand, more hydroxyl radicals are generated from the lowest pH until the neutral pH. Thus, it increases the percentage of degradation (Wang et al., 2016).

The percentages of degradation of Congo red dye for TiO_2 catalyst were 98.32% at pH 3, 89.74% at pH 7, and 85.24% at pH 10 at 90 min. It can be obviously seen that at pH 3, the highest percentage of degradation was obtained. The surface of TiO_2 is positively charged, which can be accelerated in acidic condition due to the combination of H^+ ions, thus facilitating the separation of electron hole pair (Fujishima, 2013). This is due to the catalytic behaviour of TiO_2 surface charge density and the zero-point charge of TiO_2 that varies within the range of 6–7 (Fujishima, 2013). Besides, lower degradation rate was obtained under alkaline condition due to the abundance of hydroxyls and hydroxyl radicals (Farahiyah et al., 2016). This result shows a similarity with previous research that the degradation of dye decreased above pH 7 (Saggiaro et al., 2011).

Effect of metal ions used in Fenton process. Three different metal ions (Fe^{2+} , Cu^{2+} , and Mn^{2+}) with different concentrations were examined. The percentage of degradation of dye by Fenton oxidation process was observed through the effect of different ratios of H_2O_2 and metal ions ($\text{H}_2\text{O}_2/\text{M}^+$). The results for each metal ion are illustrated in Figure 5.

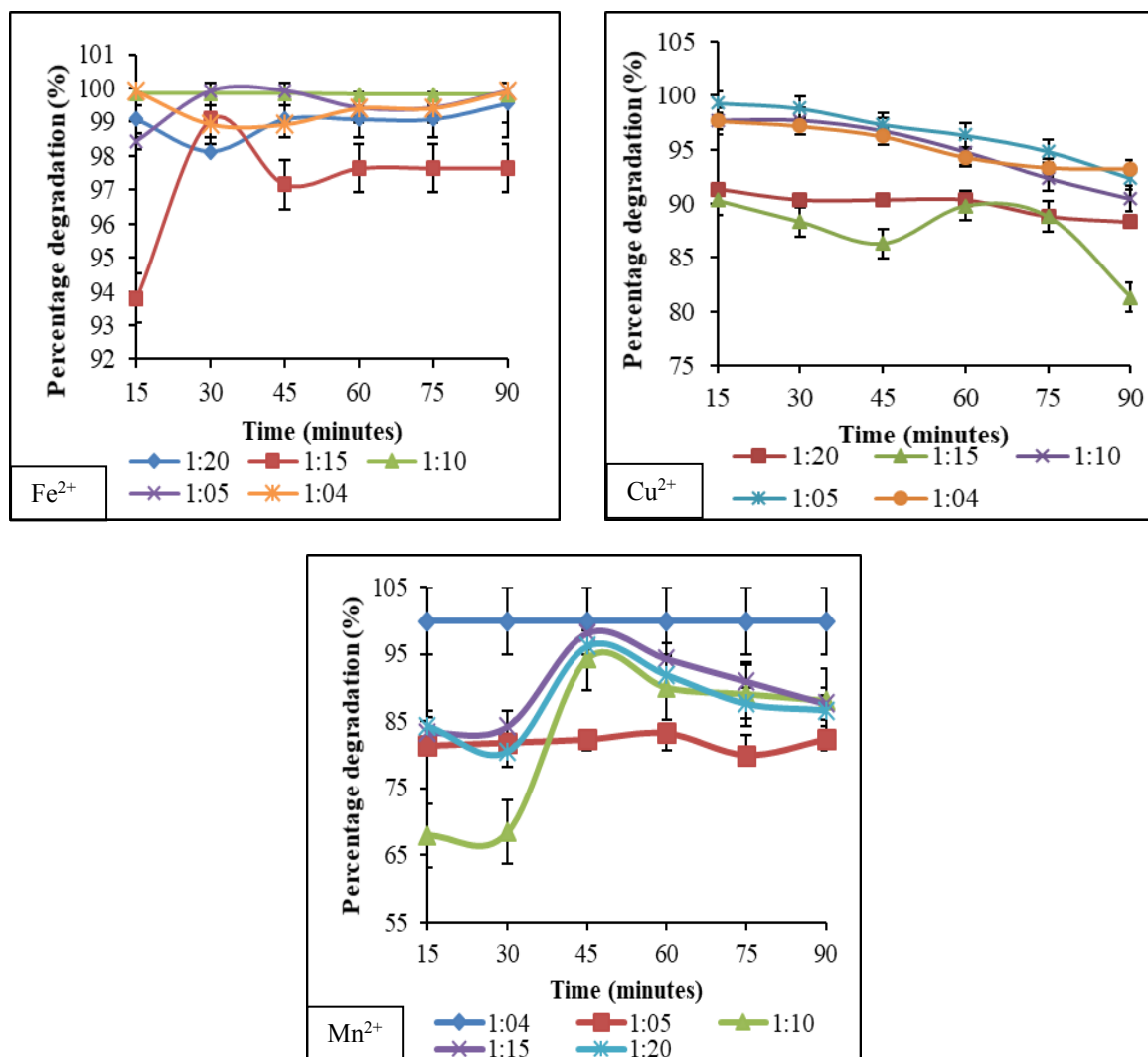


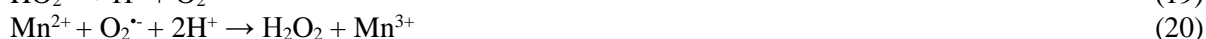
Figure 5. Percentage degradation of Congo red dye versus time in different concentration of Fe²⁺, Cu²⁺ and Mn²⁺ metal ions

Fe²⁺ metal ions showed the highest degradation at molar ratios of 1:10 and 1:04 for H₂O₂/Fe²⁺ at 15 min with 99.92% degradation. This proves that the presence of Fe²⁺ ions even at lower concentration (0.02 M) plays an important role as a catalyst to contribute to a higher production of hydroxyl radicals by the decomposition of H₂O₂ (Hashemian *et al.*, 2013). This is due to the first stage of Fenton process that generates hydroxyl radicals with the presence of Fe²⁺ ions as a catalyst, according to the following reactions (12–13) (Farahiyah *et al.*, 2016). The generation of hydroxyl radicals breaks down the azo bond in dye solution through the decolourisation of dyes.



Cu²⁺ ion is another metal ion that can be used in Fenton process to generate hydroxyl radicals from H₂O₂. From Figure 5, it can be observed that at 15 min for molar ratio of 1:05, the percentage of degradation of dye was higher, with 99.32% degradation. Cu²⁺ ion is from the transition metal group that holds two or more valance states suitable for oxidation reduction potential and reacts with H₂O₂ in order to generate more hydroxyl radicals. This metal ion also gives very good contribution as it catalyses H₂O₂ to generate hydroxyl radicals with oxidising ability (Xu *et al.*, 2004).

Meanwhile, Mn^{2+} ions also showed excellent percentage of degradation of dye at 15 min for molar ratio of 1:04 with 99.92% degradation. In this case, H_2O_2 acts as a benchmark for the addition of Mn^{2+} due to the hydroxyl radicals produced by H_2O_2 that attack Mn^{2+} and decolourise the dye. The equations (14–20) below are involved in generating hydroxyl radicals in the presence of $MnSO_4 \cdot H_2O$ (Khataee *et al.*, 2014):



It can be observed that the optimum concentration for Fe^{2+} and Cu^{2+} ions in the degradation of dye was lower compared to Mn^{2+} ion. This may be due to self-scavenging of hydroxyl radicals by metal ions at higher concentration and hence reduces its efficiency to degrade pollutants (Ashraf *et al.*, 2014).

Effect of different mass of TiO_2 . The photocatalytic degradation of Congo red dye influenced by TiO_2 catalyst dose was studied. The results obtained are illustrated in Figure 6. The percentage of degradation increased significantly from 89.82% to 97.86% as the mass of TiO_2 increased from 0.04 to 0.05 g. However, only a slight increase in the percentage of degradation was recorded when the mass of TiO_2 increased to 0.20 g. The results showed that 0.20 g of TiO_2 had higher percentage of degradation (i.e., 99.84%) at 15 min. This phenomenon occurs due to the increased amount of catalyst, which increases the amount of active sites on TiO_2 surface, thus the number of hydroxyl radicals and O_2 are increased (Farahiyah *et al.*, 2016). The degradation of dye for relevant reactions at the semiconductor by using TiO_2 catalyst is shown in the following equations (21–28):

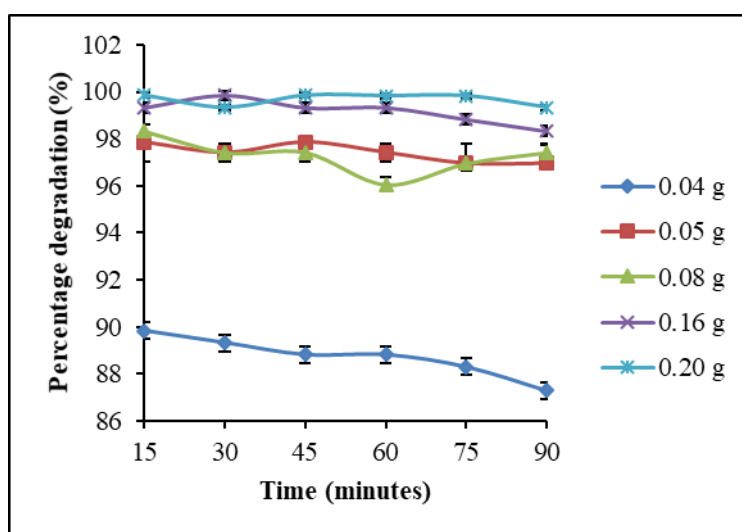


Figure 6. Percentage degradation of Congo red dye versus time in different mass of TiO_2 catalyst

FTIR spectroscopy. Congo red dye was characterised by using FTIR spectroscopy before and after degradation process. FTIR spectrum and the structure of Congo red dye before and after degradation process are shown in Figure 7. Before degradation of Congo red dye, the stretching vibration bands of C-N, sulfonic group (S=O), azo group (N=N), aromatic (C=C), and primary amine (N-H) were observed at 1123.54 cm^{-1} , 1360.77 cm^{-1} , 1500.37 cm^{-1} , 1583.66 cm^{-1} , and 3472.20 cm^{-1} , respectively (Al-Rubaie and Mhessn, 2012). Nevertheless, after oxidation treatment, the bands of Congo red dye were shifted, broadened, and reduced. Only two peaks were obtained in the spectrum. There was a broad peak of O-H stretching vibrations at 3378.5 cm^{-1} due to the presence of water and aromatic C=C stretching peak at 1623.8 cm^{-1} . From the spectrum, it is confirmed that the absence of the peak of azo bond (N=N) stretching vibration at 1500.37 cm^{-1} (Babu *et al.*, 2015) indicates the cleavage of azo bond by the degradation process in this study. Other bonds such as C-N, S=O, and N-H were also absent after degradation process. This is due to partial or complete dye molecule degradation and the products undergo oxidation reactions (Ortiz *et al.*, 2016).

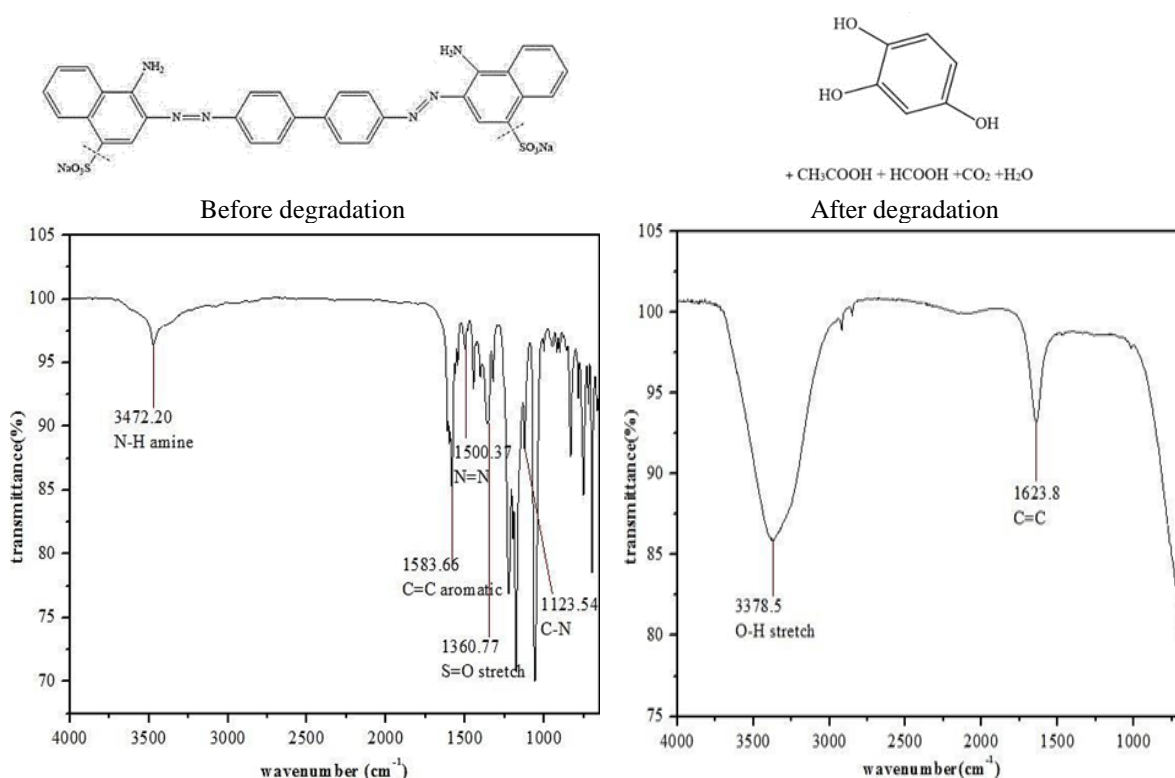


Figure 7. FTIR spectrum and structure of Congo red before and after degradation process

Conclusion

In conclusion, the highest photodegradation efficiency of Congo red dye was achieved when it was treated by Fenton process using Fe^{2+} metal ion at the optimum conditions of pH 3, 0.2 M concentration of H_2O_2 , and 0.02 M concentration of metal ion in 15 min. This technique and parameters are more effective than Fenton process using Cu^{2+} and Mn^{2+} ions, as well as TiO_2 catalyst.

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