Wet hydrogen peroxide catalytic oxidation of malachite green over Fe₂O₃/Kaolin catalyst: optimization of reaction parameters

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ABSTRACT
This study presents an experimental investigation of wet hydrogen peroxide oxidation efficiency for the treatment of dye wastewater. In this purpose, Fe₂O₃/Kaolin catalyst was prepared by wet impregnation method and used for accelerating the degradation of malachite green under a wide range of critical metrics including processing temperature, catalyst dosage and hydrogen peroxide volume. The results indicate that satisfactory conversions of malachite green were atteint at high temperature levels and catalyst dosage. While the change in hydrogen peroxide volume has a dual effect on malachite green conversion, higher or lower values than 7ml can cause a negative impact on reaction performances. Therefore, the synergism of these optimized parameters has contributed to promising results, as suggested by a valuable improvement in catalyst activity which can promote 94.78% of malachite green removal rate.

KEYWORDS: *Dye wastewater, iron-based catalyst, parametric optimization, wet hydrogen peroxide catalytic oxidation*

I. INTRODUCTION

Recent researches in the field of wastewater treatment are mainly directed towards the development of high-efficiency processes that can guarantee a rapid degradation of hazardous components under ordinary pressure and temperature conditions and thus imposing large environmental preservation against water pollution (Huo *et al*. 2019; Zouboulis and Katsoyiannis 2018; Pizarro, Torija *et al*. 2018; Sarma and Tay 2018). In this focus, the advanced oxidation process has been emerged as a preferable and an effective technique for the treatment of any kind of recalcitrant organic molecules (Fu and Kyzas 2014). The main advantage of using this technique rather than usual methods such as flocculation, precipitation, adsorption on activated coals or membrane processes is the total degradation of pollutants to water and other mineral ions, which are friendly with the environment (Li *et al*. 2014). The destruction of organics compounds is based on the generation of strong and nonselective substances including HO• radicals from the decomposition of oxidizing agents using energetic resources such as UV rays and catalytic substances. Generally, the wet catalytic oxidation is more efficient compared to UV photolysis process, especially for rigorous treatments (Guerra-Que *et al*. 2019; Jing *et al*. 2016; Rathnayake *et al*. 2019). This technique has been successfully applied with hydrogen peroxide to eliminate many kinds of diluted dyes in aqueous solution. Also, several researches (Kim *et al*. 2005; Subramanian and Subbulekshmi 2017; He *et al*. 2019; Liou *et al*. 2010) have suggested that the use of heterogeneous catalysts instead of homogeneous catalysts for the wet hydrogen peroxide catalytic oxidation reaction (WHPCO) is highly recommended to ensure readily separation of solid-liquid mixture and thus avoiding the presence of toxic catalyst ions in the final wastewater. In this study, wet hydrogen peroxide catalytic oxidation of malachite green (MG) over iron-based catalyst was performed under a variety of reaction conditions in the objective of better understanding the effect of processing temperature, catalyst dosage and the added volume of hydrogen peroxide on process performances. This way, the optimal parameters are combined in one single reaction in order to achieve the desired degradation of MG.

II. MATERIALS AND METHODS

Catalyst preparation

The used supported catalyst in this experimental investigation were synthesized via wetness impregnation method. The main advantage of wetness impregnation compared to sec impregnation method is a thorough seep of the active phase through the support pores, in which are initially filled with solvent. The procedure of catalyst synthesis includes the following steps. An active phase was prepared in a beaker by

solving 8g of iron nitrate Fe(NO$_3$)$_3$.9H$_2$O in 1L grade of distilled water. The commercial support (Kaolin) was primarily immersed in the solvent and then added to the ferric solution. Iron nitrate precipitation was assured by adding dropwise NaOH until a precise value of pH=5 was attaint. Then, the solution was stirred by an agitator for 3 hours to ensure good impregnation of the active phase in the support pores. After that, the precipitated material was filtered and washed out by alcohol and distilled water in order to eliminate any undesirable components such as Na$^+$ ions, which can cause catalyst poisoning. Finally, the obtained precursor was dried at 80 °C for 16 h and then calcined at 400°C for 3h. The prepared catalyst is denoted as 7%wt. Fe$_2$O$_3$/Kaolin.

Characterization techniques

Analyzing the physical proprieties of the prepared material is required for better understanding the influence of synthesis parameters on the activity of catalyst. The catalyst composition was characterized using Fourier-transform infrared spectroscopy (FTIR). The measurements were carried out using SHIMADZU spectrometer at spectral range of 1200 to 400 cm^{-1}. Samples were prepared by mixing 1 mg of catalyst with 100 mg of KBr and then compressed into small pellets. Data collection and transformation to readable spectrums was held by a computer program associated to the spectrometer.

The crystallinity of the structure was analyzed using X-ray Diffractometer (XRD). The prepared samples were deposit on a wet slide glass and then placed on specimen holder to be exposed to a monochromatic and parallel Cu/K$_\alpha$ radiation (λ = 1,54 Å) over the 2θ range of 10 to 90°. The identification of the existed phases in the catalyst structure was done using X'Pert Highscore software and international ASTM standards.

WHPCO reaction test

The degradation of malachite green was examined in simple laboratory installation consists of beaker (1000mL) for carrying reaction mixture and magnetic agitator. A solution of malachite green with concentration of 20mg/L was prepared and added to hydrogen peroxide (30%). The catalytic oxidation of MG was carried out by adding a specific amount of the elaborated catalyst. The reaction was lasted for 150 minutes under a continuous stirring and samples were taken regularly after each 15 minutes. The concentration of MG was measured using UV-vis spectrometer (OPTIZEN 3220UV) at an absorbance band of 617 nm.

The conversion of MG was calculated using the following equation:

$$Conversion\ (\%) = \left(\frac{C_0 - C}{C_0}\right) \times 100 \tag{1}$$

Where C_0 is the initial concentration of MG and C is MG concentration at time t.

The experimental data of MG degradation was fitted by applying a pseudo-first-order kinetic model for the evolution of reaction rate (Eq.2).

$$\mathrm{Ln}\frac{C_0}{C} = kt \tag{2}$$

Where k is the reaction rate constant.

III.   RESULTS AND DISCUSSION

Characterization of the prepared catalyst

The results of infrared analyze for the prepared catalyst are shown in Figure 1. As can be seen, two main intense peaks that correspond to absorption bands at 541cm^{-1} and 470cm^{-1} can be attributed to stretching vibrations of Fe-O bonds (Abdulah *et al*. 2015; Apte *et al*. 2007). The spectrum also contains a two bands with vibration frequencies of 1620cm^{-1} and 3200-3800cm^{-1} correspond to bending vibrational modes and stretching vibrational modes, respectively, for hydrogen bond (O-H) of adsorbed water (Benomara *et al*. 2019; Lu *et al*. 2015). The presence of bands that correspond to sodium hydroxide molecules is not defined. Accordingly, initial catalyst deactivation was avoided through the absence of undesirable components.

Figure 2 illustrates the results of X-ray diffraction analyze for the prepared catalysts. Preliminary examination of this diffractograms reveals the presence of diffraction peaks at 2θ of 20.86°, 26.64°, 36.54°, 39.46°, 40.30°, 42.45°, 45.79°, 50.13°, 54.87°, 68.14° 35.13°, and 84.37° correspond to kaolin structure (SiO$_2$ and Al$_2$O$_3$ phases) and 24.12°, 33.11°, 54°, 63.50°, 75.40° attributed to the active phase (Fe$_2$O$_3$) [14]. Regarding peaks intensity, it can be deduced that the prepared catalyst has a remarkable degree of crystallinity.
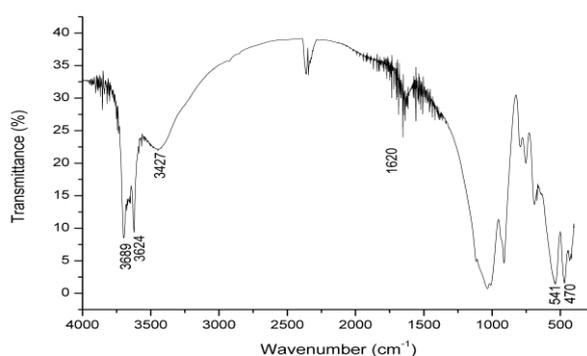
Figure 1 FTIR spectra for Fe_2O_3/Kaolin catalyst
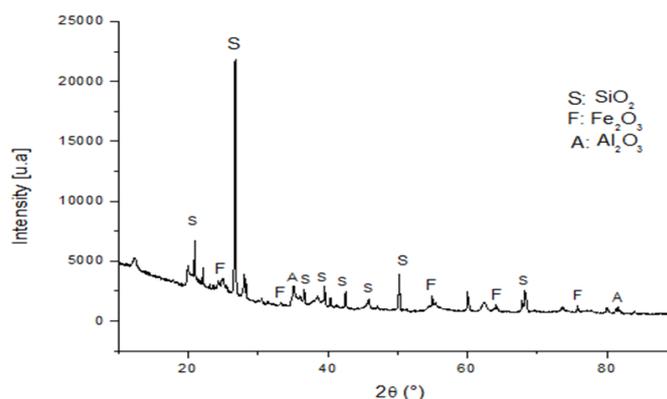
Figure 2 XRD spectrum for Fe_2O_3/Kaolin catalyst

Parametric study

This investigation is based on changing only one parameter at an extended range of study, while other parameters were remain constant. Such analyze will conduct to a deep survey of each parameter effect on the reaction performances and then optimal metrics were combined together in order to reach the desired conversion of malachite green.

Effect of catalyst dosage

The added amount of catalyst to the reaction process has a significant influence on the reaction rates. Actually, increasing catalyst amount can result in large surface area of active sites. For better understanding his impact on the catalyst activity, the evolution of MG conversion along the reaction time was performed under different catalyst dosage 0.2g/L, 0.5g/L and 0.8g/L (Figure 3). The obtained results from this investigation indicates that the degradation of MG has been enhanced by increasing the catalyst dosage. It is obvious that using 0.8g/L of catalyst dosage has led to preferable and satisfactory results, which can be reflected to the strong decline in MG concentration along the reaction time. The conversion has tends to reach maximum value of 93.28% after 150 minutes. This can be due to the large contact area between the catalyst particles and the dye molecules. Also, it is relevant from the kinetic investigation (Figure 4) that better results was reported for the reaction rate at highest catalyst dosage, as suggested by an increase in the reaction rate constant from 0.0042 to $0.0121 min^{-1}$ by raising the catalyst dosage from 0.2 to 0.8g/L.
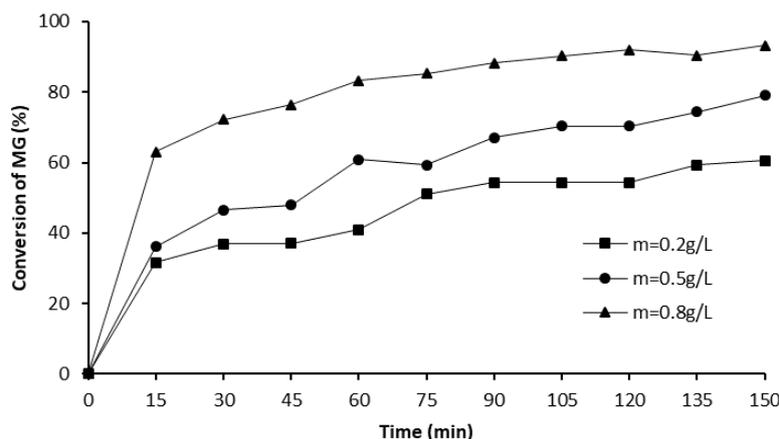
Figure 3 Effect of catalyst dosage on the conversion of MG
Conditions: T=21°C and V(H$_2$O$_2$)=10mL
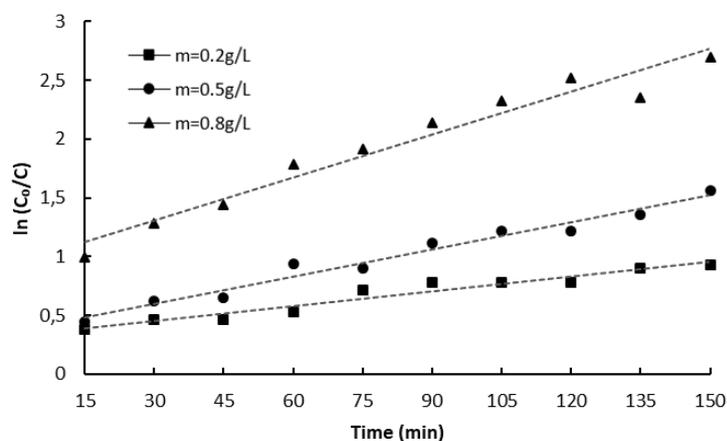
Figure 4 First-order kinetic plots for WHPCO of MG under different catalyst dosages

Effect of processing temperature

The processing temperature has a great impact on catalyst activity. Accordingly, inadequate levels of temperature can cause an adverse change in the adsorption properties of reactants. This relative effect can also be noticed through the change in the reaction rate constant. In this focus, the variation of MG conversion along the reaction time has been investigated under a broad range of temperature that correspond to 21°C, 35°C and 50°C. The results of Figure 5 has shown that the increase in temperature has favored the discoloration of MG. At highest processing temperature 50°C, the conversion tends to reach valuable improvement of 91.8% after just 60 minutes. This is 21.1% and 31.24% higher than the obtained conversions for 35°C and 21°C, respectively, after 150 minutes of reaction aging. This significant increase in reaction efficiency can be related to the positive influence of temperature on the activity of catalyst. In term of kinetic constants, it is obvious from the linear presentation of reaction kinetic in Figure 6 that higher temperature levels results in higher reaction performances.
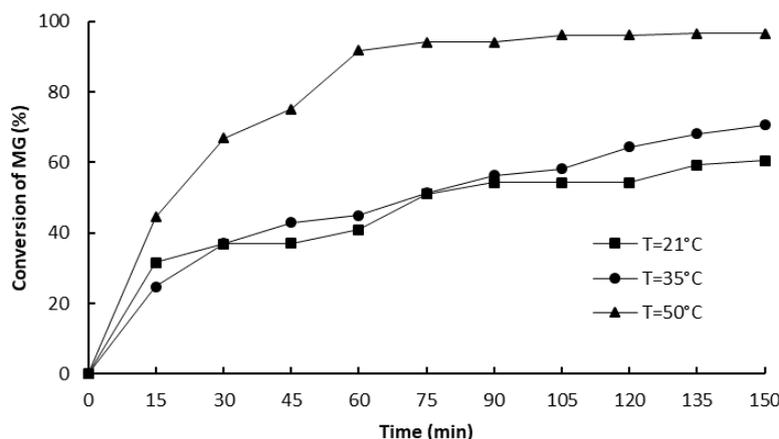
Figure 5 Effect of processing temperature on the conversion of MG
Conditions: catalyst dosage =0.2g/L and $V(H_2O_2)$=10mL
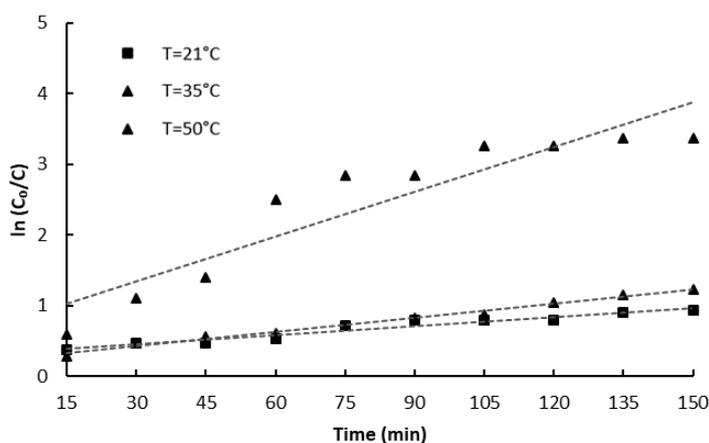
Figure 6 First-order kinetic plots for WHPCO of MG under different temperatures

Effect of H_2O_2 volume

Hydrogen peroxide plays a vital role in the oxidation reaction through the generation of hydroxide anions, which are responsible for colorants degradation. In most ways, the decomposition reaction of hydrogen peroxide to hydroxide is activated by an energetic source such as UV or catalytic substance. In order to investigate the effect of hydrogen peroxide concentration on wet catalytic oxidation reaction performances, the evolution of MG conversion along the reaction time was carried out under different volumes of hydrogen peroxide 4mL, 7mL and 10mL. As illustrated in Figure 7, increasing the volume from 4ml to 7ml has led to a positive effect on MG degradation by increasing the conversion from 54.96 to 69.3% after 150 minutes of reaction aging. But a persistent increase in hydrogen peroxide volume will cause a negative trend on conversion change. This can be justified by investigating the reaction rate of each solution (Figure 8). The results has indicated that optimal reaction rate constant (0,0066 min⁻¹) was obtained at H_2O_2 volume of 7mL. Hence, higher or lower injection of hydrogen peroxide will disfavor the degradation of MG.
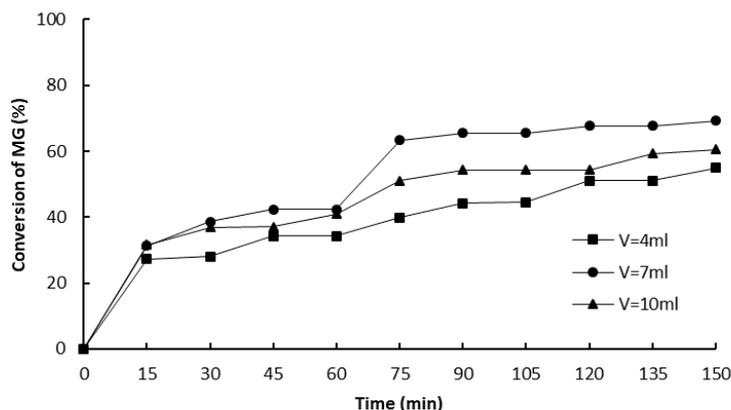
Figure 7 Effect of H_2O_2 volume on the conversion of MG
Conditions: T=21°C and catalyst dosage =0.2g
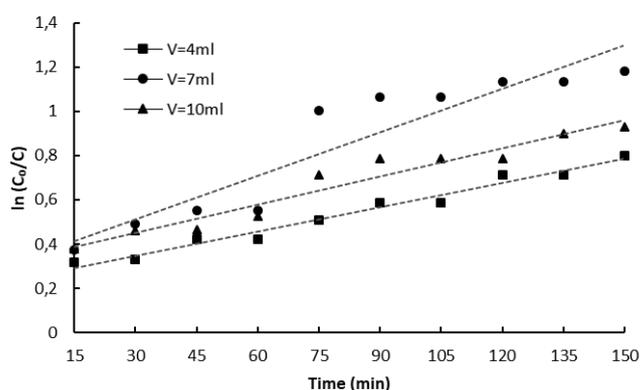
Figure 8 First-order kinetic plots for WHPCO of MG at different H_2O_2 volumes

Optimization results

The objective of parametric optimization is to maximize the conversion of MG. Accordingly, inappropriate chose of reaction conditions can cause lower tendency in dye discoloration. It can be seen from the results of Figure 9 that better conversion was obtained under optimal values of processing temperature (50°C), initial volume of H_2O_2 (7mL) and catalyst dosage (0.8g/L). The conversion has reached 94.78% after just 30 minutes of reaction aging, which is roughly three times higher than that of MG oxidation when the reaction conditions are set at standard processing temperature of 21°C, initial volume of H_2O_2 of 10mL and catalyst dosage of 0.2g/L. Indeed, a quasi-total degradation of MG was atteint for longer reaction time. These obtained results justify that the parametric optimization is required for improving the catalyst activity and thus achieving high efficiency of wet catalytic oxidation process.
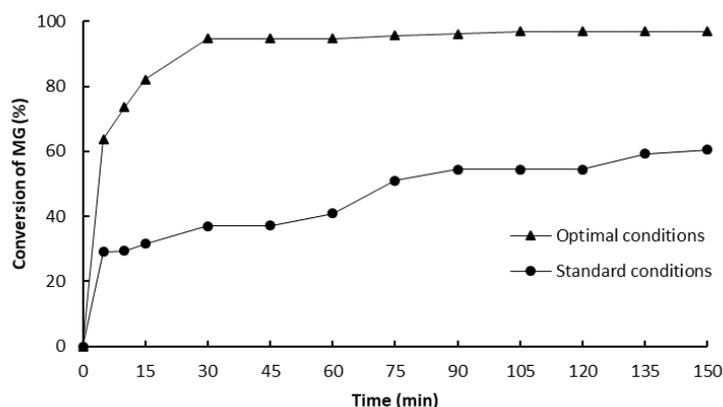
Figure 9 Evolution of MG conversion along the reaction time under optimal and standard reaction conditions

IV.   CONCLUSIONS

Wet catalytic hydrogen peroxide oxidation of MG aqueous solution over Fe_2O_3/Kaolin was performed under an extended range of processing parameters. The catalyst prepared by wet impregnation method has shown high activity towards the elimination of MG when the reaction conditions was optimized. Accordingly, the increase in catalyst dosage and processing temperature results in high process efficiency, as suggested by an increase in the reaction rate. Otherwise, adding hydrogen peroxide to the reactional solution must not exceed or be inferior to 7mL. Any change beyond this critical volume will cause a negative effect on MG degradation.

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