Influence of Manganese Substitution on Photocatalytic Activity of Fe$_{3-x}$Mn$_x$O$_4$ Catalyst by Heterogeneous Photo Fenton-like Reaction

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Abstract. In this study, the influence of manganese substitution on the photocatalytic activity of heterogeneous Fe$_{3-x}$Mn$_x$O$_4$ catalyst were investigated. The Fe$_{3-x}$Mn$_x$O$_4$ catalysts were synthesized through co-precipitation method at varies manganese (Mn) substitution ratio ($x$) of 0, 0.1, 0.2, 0.3, 0.4 and 0.5, respectively. The photocatalytic performance of the resultant catalysts were tested in photo Fenton-like degradation of AOII dye in the presence of 22Mm H$_2$O$_2$ at initial pH of 3. Interestingly, discoloration of 95.9% AOII was achieved at optimized $x$ value of 0.3. Enhancement of nearly 98% was observed compared to pristine catalyst ($x$=0) which was able to degrade up to 48.4% only. In addition, it also demonstrated that the AOII degradation kinetic using Fe$_{3-x}$Mn$_x$O$_4$ catalyst at $x$=0.3 by photo Fenton-like reaction was fitted well with the first order reaction kinetic ($k = 0.018$ min$^{-1}$ and $R^2 = 0.9862$). Thus, it can be suggested that the substitution of Mn into the matrix of iron oxide provides a positive influence in enhancing the overall photocatalytic performance of heterogeneous Fe$_{3-x}$Mn$_x$O$_4$ catalyst during the photo Fenton-like reaction.

1. Introduction

Recently, advanced oxidation processes (AOPs) have been widely used as an efficient treatment of industrial wastewater containing pollutant that can be harmful to the environment. Hydroxyl radical act as an oxidizing agent was generated during the process to remove pollutants and also improve the biodegradability of water. Last decades, Fenton-based reactions were extensively being studied in
AOP as their ability to degrade the huge amount of contaminations and show a successful result [1]. The Fenton-like reagent is a mixture of Fe$^{3+}$ with H$_2$O$_2$ and it is an active systems for the oxidation of organic compounds. The reaction between Fe$^{3+}$ with H$_2$O$_2$ will produce the hydroperoxyl (•OOH) radicals as the oxidizing agent [2]. In order to enhance the Fenton processes, ultraviolet light (UV) is introduced to the Fenton reaction as it can decomposed the photoactive Fe(OH)$_2^+$ species while promoting the generation of radical in the reaction as oxidizing agent [3].

Heterogeneous photo-Fenton reactions had gained much attention in the degradation of organic pollutants due to their unique characteristics of complete mineralization of organic pollutant, simple separation of catalyst from wastewater and will inhibit metal ion contamination [4]. Magnetite (Fe$^3$O$_4$) can be used as heterogeneous catalyst as it containing both Fe$^{2+}$ and Fe$^{3+}$. These iron ions have structural characteristic that peculiar than others which is the inverse spinel structure with Fe$^{2+}$ in the octahedral site while Fe$^{3+}$ occupied both octahedral and tetrahedral sites [5]. The introduction of transition metal such as nickel (Ni), manganese (Mn), cobalt (Co) and also chromium (Cr) remarkably enhanced the catalytic activity of Fe$_3$O$_4$. The presence of transition metals in spinel lattice of magnetite can modify the redox properties and also influence the stability of the catalyst [6].

A few researchers have reported the degradation of organic compounds by AOPs, including Fenton reagent, electro-Fenton, and also ultrasonic irradiation [7–9]. However, detailed research and investigation on the effect of Mn substitution on the catalytic activity of Fe$_{3-x}$Mn$_x$O$_4$ by heterogeneous photo-Fenton reaction has not yet been addressed. Therefore, in this study, the influence of Mn substitution on photocatalytic activity of Fe$_{3-x}$Mn$_x$O$_4$ catalyst by heterogeneous photo Fenton-like reaction as well as the kinetic study of the resultant catalyst will be investigated.

2. Methodology

2.1. Synthesis of Fe$_{3-x}$Mn$_x$O$_4$ catalyst

Fe$_{3-x}$Mn$_x$O$_4$ was prepared by mixing of 40 mL of 0.05M FeCl$_3$.6H$_2$O and 18mL of 0.05M MnCl$_2$. The mixture was heated into a beaker at 90°C using the double boiling technique while stirred continuously for 10 minutes. Then, 1M NaOH was added dropwise to the mixture until it reach pH 10. The mixture was left for aging process for 30 minutes. Then, the precipitate formed was separated by using centrifuge at 400 rpm for 10 minutes and washed by using distilled water and ethanol several times. After washing, the precipitation was dried in an oven at temperature 90°C for 24 hours. The same procedures were repeated to produce different ratio of manganese loading at x=0, 0.1, 0.2, 0.3, 0.4 and 0.5 respectively by using different volume of 0.05M MnCl$_2$ solution.

2.2. Photocatalytic performance

The photocatalytic degradation of Acid Orange II was tested using 0.1g/L dosage of Fe$_{3-x}$Mn$_x$O$_4$ catalyst at various Mn loading (x = 0, 0.1, 0.2, 0.3, 0.4, and 0.5) with 100mL of Acid Orange II solution with concentration 35 ppm at pH 3. The reaction was carried out using a photo-reactor. Four 9W UVC lamp were inserted in the center of the photo reactor as the UV light source. Then, 22Mm of H$_2$O$_2$ was added to the mixture as an oxidizing agent and the four 9 UVC lamps were turned on to initiate the degradation reaction. The concentration of Acid Orange II was analyzed at wavelength of 484nm using DR 2800 Portable Spectrophotometer. In order to compare the performance of the catalysts under UVC light irradiation, the control reaction of dark heterogeneous Fenton-like reaction was carried out in the same photo reactor under same reaction conditions but without the presence of light source.

3. Results and Discussion

3.1. Photocatalytic activity of Fe$_{3-x}$Mn$_x$O$_4$
Figure 1 shows the degradation efficiency of AOII using Fe$_{3-x}$Mn$_x$O$_4$ at x value of 0, 0.1, 0.2, 0.3, 0.4 and 0.5 in both photo Fenton-like reaction and Fenton-like reaction, respectively. The performance of Fe$_{3-x}$Mn$_x$O$_4$ catalysts in both reactions were compared to determine the effect of Mn substitution in the Fenton-like reaction with and without the aid of UV irradiation. Interestingly, discoloration of 95.9% AOII was achieved at optimized x value of 0.3 in photo Fenton-like reaction. Enhancement of nearly 98% was observed compared to pristine catalyst (x=0) which was able to degrade up to 48.4% only. The degradation process was greatly enhanced in the presence of UV irradiation due to additional source of highly oxidative •OH radicals generated in the system and its ability to influence the formation of the radicals [10]. In fact, at the same x value (x=0.3), degradation of AOII in dark Fenton-like reaction (without UV irradiation) was also found higher (62%) compared to others manganese loading. It was suggested that the substituted manganese at x=0.3 enable to accelerate the redox properties of active sites between the iron and manganese species by increasing generation of interfacial •OH radicals during catalysis [11].

![Figure 1. AOII degradation by Photo Fenton-like reaction and Fenton-like reaction (dark) using Fe$_{3-x}$Mn$_x$O$_4$ catalyst at various manganese loading (x).](image)

In addition, the presence of Mn ions in magnetite, strongly favored the H$_2$O$_2$ decomposition as as there is changes in the structure of Mn-magnetite surface [8]. The enhancement of the percent degradation was mainly caused by the increases of active site available for photo Fenton-like reaction and also due to the unique redox loop (Mn$^{2+}$/Mn$^{3+}$) that involve in single electron transfer. Hence, the Mn demonstrate a great potential of transition metal that can be substituted in Fe$_3$O$_4$ catalysts. However, at x=0.4 and 0.5, the percentage of degradation obtained were reduced to 81.0% and 34.6%, respectively. According to Wang et al. [12], high content of Mn loading has increased the turbidity of the solution, hence there were some fraction of incident rays of UV light scatter and consequently reduce the penetration of the light into the solution. With decreasing penetration depth, the photons reached the surface of catalyst decreased and the generation of •OH radicals also decreased.

Figure 2 shows the time-dependent degradations of AOII under different reaction conditions. Without using H$_2$O$_2$ as oxidant but under UV irradiation, the degradation of AOII was only took placed at the earlier 10 minutes but then no further degradation was shown for the next 150 min. A similar pattern of AOII degradation profile was obtained when H$_2$O$_2$ was added with the presence of UV irradiation but with slightly higher of AOII degradation at the end of 180 min. It can be observed that H$_2$O$_2$ contributed to the degradation of AOII dye. Interestingly, the degradation of AOII reached 95.9% (magenta line) when Fe$_{2.7}$Mn$_{0.3}$O$_4$, H$_2$O$_2$ and UV irradiation presence in the reaction; while the degradation efficiency of AOII was just 62% (blue line) when only Fe$_{2.7}$Mn$_{0.3}$O$_4$ and H$_2$O$_2$ existed in the solution. This indicates that UV irradiation also played an important role in accelerating the
generation of •OH radicals in the system. The •OH radicals has stronger oxidizing ability to mineralize the organic dye into small molecule [10]. The synergistic effect between the incorporation of Mn as an active sites and the iron species under UV irradiation might also be the possible reason to this phenomenon [13].

Figure. 2. Degradation profile of AOII under different reaction conditions. Experimental conditions: AOII 35 mg/L, H2O2 20mM, catalyst 0.1g/L and pH 3.

3.2. Kinetic study of Fe3-xMn0.3O4 catalysts

Kinetic models were employed to analyse the AOII degradation behaviour generated by Fe1−xMn0.3O4 catalyst in photo Fenton-like reaction and Fenton-like reaction, respectively. The kinetic analysis was conducted using the data within 30 min of reaction. In this work, two kinetic models have been used to study the degradation kinetics of AOII dye: first-order and second-order. Both model equations can be derived from nth order kinetics equations [14](equations (1)-(4)).

First-order reaction:

\[
\frac{dC}{dt} = -kC^n
\]

\[
\ln\left(\frac{C_t}{C_0}\right) = k_1 t
\]

Second-order reaction:

\[
\frac{dC}{dt} = -k_2 C^2
\]

\[
\frac{1}{C_t} - \frac{1}{C_0} = k_2 t
\]

where C_t is the AOII concentration at time t (min), C_0 is the initial concentration of AOII, and k_1 and k_2 denote the first-order and second-order reaction constants, respectively.

Both kinetic model constants and linear regression coefficients are summarised in Table 1. As seen in Table 1, Fe1−0.3Mn0.3O4 catalyst in photo Fenton-like reaction showed better linear regression
coefficients as compared to the reaction in dark Fenton. It also demonstrated that the AOII degradation kinetic using Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ catalyst in photo Fenton-like reaction followed the first-order kinetic model which suggests that the reaction depends on the AOII concentration only and known as unimolecular reaction. The reaction kinetic constants for both models are increased for Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ in photo Fenton-like reaction compared to the reaction in dark Fenton which indicates that the reaction rate is increased as the reaction been carried out under UV irradiation. The used of external source energy such as UV has accelerated higher •OH yield compared to dark Fenton process [15]. As a result, it will enhance the photocatalytic activity of AOII dye using Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ catalyst.

| Catalysts                          | First-order kinetic | Second-order kinetic |
|------------------------------------|---------------------|----------------------|
| Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ (Fenton-like reaction) | 0.0043 0.6333 | 0.0002 0.5563 |
| Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ (Photo Fenton-like reaction) | 0.0180 0.9862 | 0.0010 0.8903 |

4. Conclusions
As a conclusion, substitution of manganese into the Fe$_3$O$_4$ structure has an outstanding effect on the photocatalytic activity of AOII degradation. Fe$_{3-x}$Mn$_x$O$_4$ catalyst with x value of 0.3 has shown great photocatalytic activity with 95.9% of AOII degradation. The presence of manganese, H$_2$O$_2$ and UV irradiation led to the enhancement of photocatalytic activity due to the high formation of •OH reactive radicals during the heterogeneous photo Fenton-like reaction. The AOII degradation kinetic using Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ catalyst in photo Fenton-like reaction followed the first-order kinetic model which suggests that the reaction depends on the AOII concentration only and known as unimolecular reaction. The reaction rate is increased as the reaction been carried out under UV irradiation. Hence, such findings suggested that the substitution of manganese provide positive influence in enhancing the overall photocatalytic performance of resultant catalyst during photo Fenton-like reaction as well as the degradation kinetics of organic pollutants.

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