Heterogeneous fenton-like reaction using Fe$_{3-x}$Mn$_x$O$_4$-MKSF composite catalyst for degradation of acid orange II dye

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Abstract. The selection of a good catalyst support is crucial in contributing towards the enhancement catalytic activity of a catalyst. Therefore, in this study, the influence of montmorillonite KSF (MKSF) clay loading in relation with catalytic performance of the resultant composite catalyst has been investigated. The MKSF clay loading were varied at x = 20, 40, 60 and 80 wt%, respectively. Interestingly, Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%) has shown greater catalytic performance up to 98% of acid orange II (AOII) dye removal in comparison to the Fe$_3$O$_4$ and Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ catalysts. The AOII degradation kinetic using Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%) was fitted well with first-order reaction kinetic and the reaction rate increased in the order of Fe$_3$O$_4$>Fe$_{3-0.3}$Mn$_{0.3}$O$_4$>Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%). It also demonstrated in the work that Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%) catalyst can be reused several times without affecting its efficiency. Thus, it can be suggested that MKSF clay as catalyst support played a significant role in enhancing the overall catalytic performance of Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ catalyst during the heterogeneous Fenton-line reaction as well as the degradation kinetics of the AOII solutions.

1. Introduction
World dye production is now estimated to be 700,000 tons per year where most of the productions are focused on textile dyes while another 15% are used for other productions such as leather and paper [1]. The synthetic dyes have stable compounds and hardly be treated by conventional methods. In recent decades, advanced oxidation processes (AOPs), which involve highly reactive oxygen species like hydroxyl radical (•OH), have attracted increasing attention due to their enormous capability in the removal of recalcitrant organic pollutants. In AOPs systems, the organic pollutants can be destructed into low toxic compounds, or even mineralize into carbon dioxide and water [2,3]. Homogeneous Fenton oxidation is one of the most appealing AOPs owing to: (i) the utilization of environmental-friendly reagents (Fe$^{2+}$ and H$_2$O$_2$), (ii) its low energy consumption compared to other AOPs, (iii) its ability to
destroy various organic compounds along with an improvement of biodegradability, and (iv) the simplicity of the required equipment allowing an easy scale-up from laboratory reactor to large scale process [4–6]. However, subsequent treatments are required for catalyst separation and effluent neutralization in the homogeneous Fenton oxidation, which often generate large volumes of iron-containing sludge that are hardly disposable [5]. In order to circumvent these disadvantages and reduce costs, application of heterogeneous iron-based catalyst is a promising solution. Nevertheless, heterogeneous iron oxide Fenton catalyst may also possess lower activities in decomposing H\textsubscript{2}O\textsubscript{2} as well as poor stability due to metal leaching in oxidation conditions [7]. Therefore, several challenges existed to develop heterogeneous Fe-based composite catalyst with good performance and stability.

The substitution of transition metals such as manganese, molybdenum, chromium, cobalt, nickel, copper, vanadium and zirconium into iron oxide catalysts have been applied recently as it can promote high degradation performances by actively modify the redox properties as well as improving the catalytic stability [8–12]. Wei et al [10] found that magnetite (Fe\textsubscript{3}O\textsubscript{4}) surface increased with an increase of Mn substitution exhibited high catalytic activity on the degradation of Acid Orange II (AOII) at neutral pH. Similarly, Liang et al [13] reported remarkable effect of Mn substitution on the catalytic activity and adsorption properties of magnetite. In addition, the selection of good catalyst support was also crucial in contributing towards the enhancement catalytic activity of the iron oxides catalyst. The incorporation of iron into different supports have been studied such as zeolite, polymer and carbon but clay appeared to be an interesting alternative due to its unique structural properties which known to be metal-(especially iron)-rich materials and highly porous pillared structures [14,15]. Based on the previous work [16], montmorillonite KSF (MKSF) clay has shown superior performance on the AOII degradation compared to the other types of clay (MK10, bentonite and kaolin). However, the effect between MKSF clay with other substituted magnetite catalyst (such as Fe\textsubscript{x−y}Mn\textsubscript{y}O\textsubscript{4}) has not been addressed in the literature. Thus, the objective of this study is to investigate the effect of MKSF loading on the catalytic activity of AOII dye using Fe\textsubscript{x−y}Mn\textsubscript{y}O\textsubscript{4} catalyst in heterogeneous Fenton-like reaction. The kinetic study and reusability test of the resultant catalyst will be evaluated as well.

2. Material and Experimental Procedure

2.1 Chemicals

Iron (III) chloride hexahydrate (FeCl\textsubscript{3}.6H\textsubscript{2}O), manganese (II) chloride (MnCl\textsubscript{2}), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) (30% w/w), montmorillonite KSF (MKSF) and acid orange II (AOII) dye were obtained from Merck. The pH of the solution was adjusted by using dilute solutions of hydrogen chloride (HCl) and sodium hydroxide (NaOH).

2.2 Synthesis of clay supported Fe\textsubscript{x−y}Mn\textsubscript{y}O\textsubscript{4} (Fe\textsubscript{x−y}Mn\textsubscript{y}O\textsubscript{4}-MKSF) composite catalyst

Initially, Fe\textsubscript{3−y}Mn\textsubscript{y}O\textsubscript{4} was prepared by mixing of 40 mL of 0.05M FeCl\textsubscript{3}.6H\textsubscript{2}O and 18 mL of 0.05M MnCl\textsubscript{2}. The weight ratio of appropriate manganese and iron was at 0.3: 1. The mixture was heated at 90˚C using the double boiling technique while continuously stirred for 10 min. Then, 1M NaOH was added dropwise into the mixture until it reached pH 4. After that, clay at 20 wt% was added into the mixture and stirred for 15 min until well dispersed. The reason of adding clay at pH 4 is to prevent any probability of the clay stacking together which can reduce the effective surface area of the clay [17]. The NaOH was continue to be added dropwise until reached pH 10. The mixture was left for an aging process for 1 hour. Then, the formed precipitates were centrifugally separated at 400 rpm for 10 min and washed by distilled water and ethanol several times. After washing, the samples were dried in an oven at temperature 90˚C for 24 hours. The dried sample in the form of solid was further calcined in air atmosphere at 300 ˚C for 2 hours with a ramping rate of 10˚C/min. The analogous procedures were repeated to produce a different MKSF clay loading at x=40, 60 and 80 wt%, respectively.

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2.3 Catalytic performances and kinetic analysis

The catalytic performances of the resultant catalysts were performed by adding 0.01 g/L of composite catalysts (Fe$_{3-x}$Mn$_x$O$_{4-M}$) into 100 mL of 35 mg/L AOII solution at pH 3. 1M of NaOH and 1M of HCl were used for the pH adjustment. The reactions were initiated by adding 20 mM of H$_2$O$_2$ into the suspension and stirred at 210 rpm. The experiments were conducted in 3 hours and the samples were withdrawn every 15 min interval. The collected samples were filtered using 0.2 μm syringe filters and immediately analysed using a portable spectrophotometer (Hach DR 2700) at a maximum wavelength of 484 nm [18]. The experiments were run twice at the same operating conditions and the standard deviations obtained were in between 0.01 and 0.4.

It is known that dye degradation via the heterogeneous Fenton-like reaction follows two kinetic models: first-order and second-order as shown in equation (1) and (2), respectively [19].

First-order reaction:

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

Second-order reaction:

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

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

2.4 Reusability test of catalyst

A good catalyst always fulfils the criteria of reusability. Thus, reusability study was done to test the stability of Fe$_{3-x}$Mn$_x$O$_{4-M}$ as a catalyst and to explore the possibility of recycling Fe$_{3-x}$Mn$_x$O$_{4-M}$-MKSF. Sequential decolorization experiments were performed, consisting of five cycles. Each of the cycle lasted for 180 min. The experimental conditions were set at AOII 35 mg/L, H$_2$O$_2$ 20mM, catalyst 0.1g/L and solution pH 3. In order to guarantee that the initial concentration of AOII (AOII 35 mg/L) and H$_2$O$_2$ (H$_2$O$_2$ 20 mM) were the same for all cycles, specific amounts of AOII and 20mM of H$_2$O$_2$ were added to the suspension before initiating the second, third, fourth and fifth cycles. The dose of AOII added was determined by the measured concentration of the remaining AOII after the previous run. The experimental and analytical methods for five cycles were the same as for the oxidation reaction and analysis mentioned above.

3. Result and Discussion

3.1 Catalytic performance and kinetic analysis

Figure 1 illustrates the removal efficiency of AOII using Fe$_{3-x}$Mn$_x$O$_{4-M}$-MKSF at various MKSF loading (0, 20, 40, 60 and 80 wt%) for both catalytic and adsorption tests. From the catalytic test, the highest AOII removal was achieved at the composite composition of 40 wt% MKSF loading compared to other loading. The presence of MKSF led to the increased in catalytic activity by 72% compared to the pristine catalyst (x=0). In fact, at the same MKSF loading (40 wt%), catalysis was found to be the predominance process instead of adsorption with a marginal difference of AOII removal performance (±65%). Moreover, it was reported that MKSF clay exhibits highly porous pillared structures and consists of iron-rich materials [20]. The naturally presence of iron in MKSF clay promoted to the decomposition of H$_2$O$_2$ in producing reactive radicals [16]. Therefore, it can be observed that the AOII degradation was significantly enhanced in the presence of MKSF clay and H$_2$O$_2$ due to the high formation of reactive radicals during the heterogeneous Fenton-like reaction [21,22].
Figure 1. AOII removal by adsorption and catalytic Fenton-like reaction using Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ catalyst at varies MKSF loading (wt%).

The catalytic properties of Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%) catalyst was further evaluated by time-dependent profiling for the oxidative degradation of AOII solutions within 180 min. The degradation profiling of Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%), Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ and Fe$_3$O$_4$ were tested in the heterogeneous Fenton-like reaction as showed in Figure 2. For Fe$_3$O$_4$ catalyst, the reaction was obviously took placed at the earlier 30 min but then no further degradation of AOII dye revealed for the next 150 min. Similar pattern was also found from our previous work [16] which indicated that the iron oxide catalyst has already saturated and deactivated at the earlier reaction time. However, such deactivation issue was outwitted once the Fe$_3$O$_4$ catalysts were being substituted with manganese (Fe$_{3-0.3}$Mn$_{0.3}$O$_4$) and immobilized onto and/or within the MKSF clay (Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%)) by having 95.9% and 98% AOII removal in 180 min of reaction, respectively. These results can explain the synergistic effect between the incorporated iron and manganese species of the heterogeneous catalyst as well as the unique chemical properties of MKSF clay as the catalyst support [21].

Figure 2. Degradation profile of AOII on Fe$_3$O$_4$, Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ and Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%) in catalytic test. Experimental conditions: AOII 35 mg/L, H$_2$O$_2$ 20mM, catalyst 0.1g/L and pH 3.
Kinetic models were performed to analyse the AOII degradation behaviour generated by Fe$_3$O$_4$, Fe$_{3-0.3}$Mn$_{0.3}$O$_4$ and Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%) catalysts. In determining the kinetic reactions, 5 ml of AOII sample was withdrawn at every 15 minute interval time for the first hour. Next, followed by 30 minute interval time for the second hour and 1 hour interval time for the following hour. Both kinetic model constants and linear regression coefficients are presented in Table 1. As seen in Table 1, Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%) showed better linear regression coefficients as compared to Fe$_3$O$_4$ and Fe$_{3-0.3}$Mn$_{0.3}$O$_4$. It also revealed that the AOII degradation kinetic using Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%) catalyst 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 in the order of Fe$_3$O$_4$>Fe$_{3-0.3}$Mn$_{0.3}$O$_4$> Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%) indicates that the reaction rate is increased as the catalyst been substituted with manganese and immobilized onto MKSF clay. Similar pattern was observed by our previous work using different transition metal substitution (Fe$_{3-0.4}$Mo$_{0.4}$O$_4$ catalyst) immobilize onto MKSF clay [16]. Hence, these findings further strengthen the significant role of MKSF clay as a catalyst support which able to enhance the catalytic activity of resultant catalyst in degrading the AOII solution by sustaining its catalytic activity throughout the heterogeneous catalysis.

| Catalysts                      | First-order kinetic  | Second-order kinetic  |
|--------------------------------|----------------------|-----------------------|
|                                | $k_1$ | $R^2$ | $k_1$ | $R^2$ |
| Fe$_3$O$_4$                    | 0.0031 | 0.838 | 0.0001 | 0.841 |
| Fe$_{3-0.3}$Mn$_{0.3}$O$_4$     | 0.0043 | 0.633 | 0.0002 | 0.556 |
| Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF (40wt%) | 0.0100 | 0.881 | 0.0060 | 0.822 |

Figure 3. Reusability test of Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF(40wt%) catalyst. Experimental conditions: AO7 35 mg/L, H$_2$O$_2$ 20mM, catalyst 0.1g/L and pH 3.

3.2 Reusability test of catalyst

A catalyst is recognized as good catalyst if the catalyst can be reused multiple times by maintaining its efficiency. In fact, it is also known to be one of important factors from industrial perspective. Therefore, the reusability potential of Fe$_{3-0.3}$Mn$_{0.3}$O$_4$-MKSF (40wt%) was evaluated by the catalytic performance through five sequential cycles. As shown in Figure 3, after the first cycle, the removal efficiency of AOII was 98% and no significant changes was observed at the end of the second cycle. However, in the third and fourth cycle, percentage removal was slightly reduced to 96% and 95%, respectively. Nevertheless,
the removal efficiency reached as much as 94% after the fifth cycle which is only 1% of reduction compared to the previous cycle. The small reduction of catalytic activity may occurred due to leaching of small amount of metal ions from the catalyst [24]. But, it still shows that Fe$_3$O$_4$-MKSF (40wt%) catalyst can be re-used efficiently in practical applications. The used of MKSF clay as catalyst support has improved the stability of the Fe$_3$O$_4$-MKSF catalyst as well as its catalytic performance.

4. Conclusion

Fe$_3$O$_4$-MKSF(40wt%) catalyst has successfully degraded 98% of AOII solution. The presence of MKSF clay and H$_2$O$_2$ led to the improvement of catalytic activity due to the high formation of reactive radicals during the heterogeneous Fenton-like reaction. The Fe$_3$O$_4$-MKSF(40wt%) catalyst followed the first-order kinetic model which suggests that the reaction depends on the AOII concentration only and known as unmolecular reaction. The reaction kinetic constants for both models are increased in the order of Fe$_2$O$_3$Fe$_3$O$_4$Fe$_3$O$_4$Fe$_3$O$_4$-MKSF(40wt%) indicates that the reaction rate is increased as the catalyst been substituted with manganese and immobilized onto MKSF clay. Moreover, the Fe$_3$O$_4$-MKSF(40wt%) can be reused several times, for the first cycle 98% removal occurred and up to 94% removal was observed at the end of fifth cycle. Thus, it can be suggested that MKSF clay as catalyst support played a significant role in enhancing the overall catalytic performance of Fe$_3$O$_4$-MKSF catalyst during the heterogeneous Fenton-line reaction as well as the degradation kinetics of the AOII solutions.

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