Degradation of Acid Orange II by Heterogeneous Fenton-like Reaction Using Clay Supported $Fe_{3-x}Mo_xO_4$ Composite Catalyst

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Abstract

In this study, investigations on four different types of clays as catalyst support and the influence of its loading in relation with catalytic performance of the resultant composite catalysts are performed. The inherent catalytic activity of MKSF, MK10, bentonite and kaolin as catalyst supports have been tested in the oxidative degradation of AOII as the model pollutant. The highest AOII degradation was exhibited by MKSF that followed by bentonite, kaolin and MK10. Therefore, MKSF has been chosen as the catalyst support to immobilize the active sites of $Fe_{3-0.4}Mo_{0.4}O_4$ catalyst. The MKSF loading were varied at x = 0, 20, 40, 60 and 80 wt%, respectively. Interestingly, $Fe_{3-0.4}Mo_{0.4}O_4$-MKSF(80wt%) has shown superior catalytic performance up to 98.8% of AOII removal in comparison to the Fe_3O_4 and $Fe_{3-0.4}Mo_{0.4}O_4$ catalysts. Meanwhile, the second-order reaction kinetic model well described AOII degradation and its rate increased in the order of $Fe_3O_4 > Fe_{3-0.4}Mo_{0.4}O_4 > Fe_{3-0.4}Mo_{0.4}O_4$-MKSF(80wt%). Hence, these findings prove that having MKSF clays as catalyst support provides a positive influence in enhancing the overall catalytic performance of $Fe_{3-0.4}Mo_{0.4}O_4$ catalyst during the Fenton-like reaction as well as the degradation kinetics of the AOII solutions.

Keywords: Composite, *Fenton-like*, MKSF Clay, $Fe_{3-x}Mo_xO_4$, Acid Orange II

1. Introduction

Advanced oxidation processes (AOPs) have been widely used as an efficient treatment of industrial wastewater containing pollutant that can be harmful to the environment. Among the AOPs, Fenton reaction which comprises of a reaction between the hydrogen peroxide and iron ions/salts generates hydroxyl radicals (·OH) with powerful oxidizing capacity that able to decompose many organic pollutants [1][2]. However, the homogeneous Fenton process possessed several drawbacks: (i) iron ions need to be removed from the system at the end of the reaction, which contributes to high cost, reagents and time; (ii) it is limited by a narrow pH range (pH 2–3); and (iii) iron ions cannot be regenerated due to the complexation with some iron complexing reagents, such as phosphate anions and some intermediate oxidation products [3]. Due to disadvantages of homogeneous Fenton reaction, the heterogeneous Fenton reaction had gained deliberation acceptance because of their highly efficient activity, wide pH application and durability [4]. Nevertheless, heterogeneous iron oxide Fenton catalyst usually have lower activities in decomposing H_2O_2 than their homogeneous counterparts do and some of them have poor stability due to metal leaching in oxidation conditions [5]. Therefore, the development

of the Fe-based composite catalysts with good performance and stability remains a challenge.

Substitution of transition metal into iron oxides has been known as an effective approach in improving the catalytic activity of iron oxides in the Fenton-like reaction for degrading organic pollutants [6]. The substitution of transition metal such as molybdenum, manganese, cobalt, chromium, nickel, copper, vanadium, zirconium into the iron oxide catalysts have been applied as it actively modify the redox properties as well as influencing their resultant catalytic stability in promoting high degradation performances [2][3][6], [7][8][9][10]. Lu et al. [10] found that iron molybdate ($Fe_2(MoO_4)_3$) exhibited high catalytic activity, excellent stability, and good reusability on the degradation of rhodamine B. Tian et al. [11] reported that Mo-containing system has low point of zero changes (PZC) values and thus, Mo- and Fe-containing compounds are possible to be used as solid acid Fenton-like catalysts. The low PZC value is important as it possesses an acidic condition on Fenton-like reaction. In addition, $Mo(O_2)_4$ was claimed to be reacted with H_2O_2 to form molybdenum (Mo) complex, which known as a strong oxidant to oxidize the organic pollutants [12].

Instead of substitution method, a good selection of catalyst support also plays an important role in the enhancement of the

catalytic activity of iron oxides performances as well. The incorporation of irons into different supports have been studied such as zeolites [13][14], silica [15][16] and activated carbon [17]; whilst clays are also appearing as an attractive alternative [18][19][20]. The use of clays as catalyst support was governed by their high specific surface areas, cheap, abundant and low iron-leaching rate. Moreover, the immobilization of iron oxide on clays plausible to improve the dispersion of the iron oxide throughout the clay matrix which able to circumvent the iron oxide aggregation as well as agglomeration issues [19]. Therefore, the objectives of this study were to investigate the inherent catalytic activity of four clays (MKSF, MK10, bentonite and kaolin) to be used as an auspicious catalyst support and also the effect of the clay loading on the catalytic activity of Acid Orange II (AOII) dye degradation in heterogeneous Fenton-like reaction. The kinetic study of the resultant catalysts will be evaluated as well.

2. Material and Experimental Procedure

2.1. Synthesis of clay supported $Fe_{3-x}Mo_xO_4$ ($Fe_{3-x}Mo_xO_4$-MKSF) composite catalyst

Initially, $Fe_{3-0.4}Mo_{0.4}O_4$ was prepared by mixing of 10 mL of 0.05 mol/L $(NH_4)_6Mo_7O_{24}.4H_2O$ and 40 mL of 0.05 mol/L $FeCl_3.6H_2O$. The weight ratio of appropriate molybdenum and iron was at 0.4: 1. The mixture was heated at 90℃ 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 of the clay [21]. The NaOH was continued to be added dropwise until reaching 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℃ 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.

2.2 Catalytic performances

The catalytic performances of the resultant catalysts were performed by adding 0.01 g/L of clay or composite catalysts ($Fe_{3-0.4}Mo_{0.4}O_4$-MKSF) into 100 mL of 35 mg/L AOII solution at pH 3. 1 M of NaOH and 1 M of HCl were used for the pH adjustment. The reactions were initiated by adding 20 mM of H_2O_2 into the suspension and stirred at 210 rpm. The samples were withdrawn at 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 [22].

3. Result and Discussion

Fig. 1 shows the degradation profile of AOII using four different types of clay; MKSF, MK10, bentonite and kaolin in the oxidative degradation of AOII solution. The actual degradation performance of all the clays were determined with the presence of H_2O_2 concentration of 20 mM. From the catalytic test, MKSF clay showed superior performance of 98.8% AOII removal. This observation portrayed the unique characteristics of MKSF clay as promising catalyst support which can be ascribed by its physico-chemical properties that was known to be metal-(especially iron)-rich materials [22] and highly porous pillared structures [23]. The naturally presence of iron in MKSF clay led to the decomposition

of oxidant (H_2O_2) in producing reactive radicals during the heterogeneous Fenton-like catalysis. On the other hand, MK10, kaolin and bentonite clay displayed very low dye removal which was at 0.6%, 4.7% and 28.7%, respectively. The oxidation reaction may be inhibited due to the presence of originally inactive Fe species like Hematite phase (α-Fe_2O_3) as reported elsewhere [24][25]. Therefore, due to the excellent AOII degradation performance using MKSF clay, it has been chosen as the catalyst support to immobilize the active sites for $Fe_{3-0.4}Mo_{0.4}O_4$ catalyst in this study.

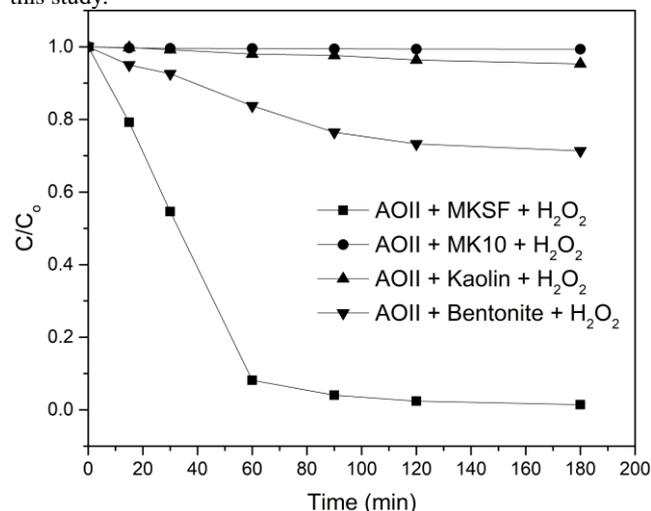**Fig. 1**: Degradation profile of AOII on MKSF, MK10, Kaolin and Bentonite in catalytic test

The removal efficiency of AOII using $Fe_{3-0.4}Mo_{0.4}O_4$-MKSF at varies MKSF loading (0, 10, 20, 40, 60 and 80 wt%) for both catalytic and adsorption tests are illustrated in Fig. 2. From the catalytic test, the AOII removal was significantly being oxidised at the composite' composition of 80 wt% MKSF loading compared to others loading. The presence of MKSF has improved the catalytic activity by 85% compared to the pristine $Fe_{2.6}Mo_{0.4}O_4$ catalyst (absence of MKSF). In fact, a marginal difference of AOII removal performance (±75%) was observed between the catalytic activity and adsorption capacity at the same MKSF loading (x=80wt%), which infers to the prevalence of catalysis rather than adsorption during the reaction. It can be seen that the AOII degradation was significantly enhanced in the presence of MKSF clay and H_2O_2 due to the high formation of reactive radicals during the heterogeneous Fenton-like reaction [24][25][26]. Interestingly, the oxidative degradation of AOII solution were favourable in the presence of $Fe_{3-0.4}Mo_{0.4}O_4$-MKSF composite catalysts at higher MKSF loading of more than 60 wt% instead of the low loading.

The catalytic properties of $Fe_{3-0.4}Mo_{0.4}O_4$-MKSF(80wt%) catalyst was further evaluated by time-based profiling for the oxidative degradation of AOII solution within 180 min. The degradation profiling of $Fe_{3-0.4}Mo_{0.4}O_4$-MKSF(80wt%), $Fe_{3-0.4}Mo_{0.4}O_4$ and Fe_3O_4 were tested in the heterogeneous Fenton-like reaction as illustrated in Fig. 3. For Fe_3O_4 catalyst, the reaction was clearly taking placed within the first 30 min but then no further degradation of AOII dye was observed for the next 150 min. A similar pattern of AOII degradation profile was observed for $Fe_{3-0.4}Mo_{0.4}O_4$ catalyst but with slightly higher of AOII degradation as compared to Fe_3O_4 at the end of 180 min. The results indicated that both catalysts are already saturated and deactivated after the first 30 min of reaction. However, such deactivation issue was circumvented once $Fe_{3-0.4}Mo_{0.4}O_4$ catalysts were being immobilised onto and/ or within the MKSF clay matrix by having 98.8% AOII removal in 180 min of reaction. This phenomenon can be explained due to the synergistic effect between the properties of MKSF clays as the catalyst support as well as the incorporated iron and molybdenum species of the heterogeneous catalyst [27].
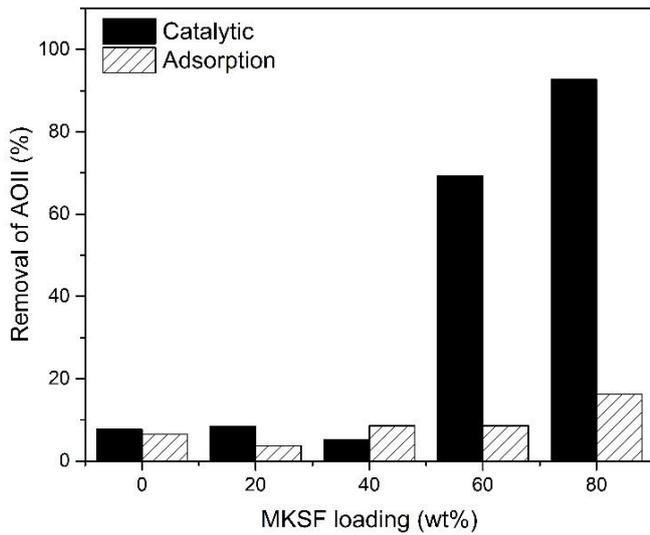
Fig. 2: AOII removal by adsorption catalytic Fenton-like reaction using $Fe_{3-0.4}Mo_{0.4}O_4$ catalyst at varies MKSF loading (wt%)
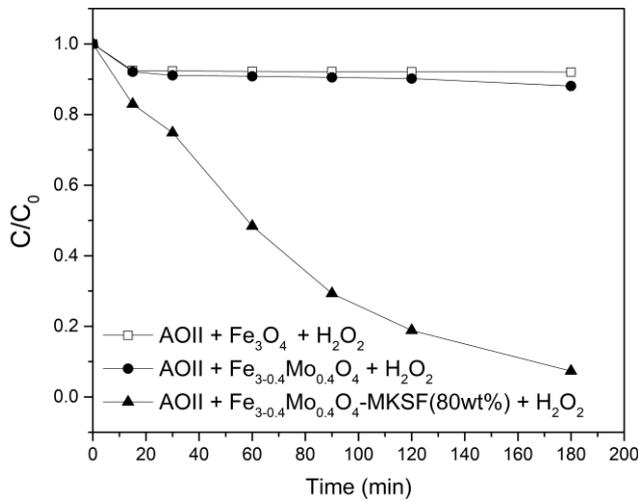

Fig. 3: Degradation profile of AOII on Fe_3O_4, $Fe_{3-0.4}Mo_{0.4}O_4$ and $Fe_{3-0.4}Mo_{0.4}O_4$-MKSF(80wt%) in catalytic test. Experimental conditions: AO7 35 mg/L, H_2O_2 20mM, catalyst 0.1g/L and pH 3.

Kinetic models were employed to analyse the AOII degradation behaviour generated by Fe_3O_4, $Fe_{3-0.4}Mo_{0.4}O_4$ and $Fe_{3-0.4}Mo_{0.4}O_4$-MKSF(80wt%) catalysts. The kinetic analysis was conducted using the data within 30 min of reaction. It is known that dye degradation via the heterogeneous Fenton-like reaction follows two kinetic models: first-order and second-order. Both model equations can be derived from n^{th} order kinetics equations [28](equations (1)-(4)).

First-order reaction:

$$\frac{dC}{dt} = -kC^n \tag{1}$$

$$\ln\left(\frac{C_o}{C_t}\right) = k_1 t \tag{2}$$

Second-order reaction:

$$\frac{dC}{dt} = -k_2 C^2 \tag{3}$$

$$\frac{1}{C_t} - \frac{1}{C_o} = k_2 t \tag{4}$$

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.

Both kinetic model constants and linear regression coefficients are summarised in Table 1. As seen in Table 1, $Fe_{3-0.4}Mo_{0.4}O_4$-MKSF (80wt%) catalyst showed better linear regression coefficients as compared to Fe_3O_4 and $Fe_{3-0.4}Mo_{0.4}O_4$ catalysts. It was also demonstrated that the AOII degradation kinetic using $Fe_{3-0.4}Mo_{0.4}O_4$–MKSF(80wt%) catalyst seems to follow the second-order kinetic model which suggests that the reaction mainly occurs at the surface of the catalyst [29]. The immobilized active sites ($\equiv Fe^{3+}$, $\equiv Fe^{2+,}$ $\equiv Mo^{6+}$) [6] might be concentrated on the catalyst surface whist •OH radicals are generated locally within the catalyst surfaces' vicinity [30]. The reaction kinetic constants for both models are increased in the order of $Fe_3O_4 >$ $Fe_{3-0.4}Mo_{0.4}O_4 >$ $Fe_{3-0.4}Mo_{0.4}O_4$-MKSF(80wt%) indicates that the reaction rate is increased as the catalyst is substituted with molybdenum and immobilized onto MKSF clay. The used of MKSF as a catalyst support to immobilize $Fe_{3-0.4}Mo_{0.4}O_4$ catalyst led to enhance the catalytic activity of resultant catalyst in degrading the AOII solution by sustaining its catalytic activity throughout the heterogeneous catalysis.

Table 1: First-order and second-order kinetic model constants and linear regression coefficients

Catalysts	First-order kinetic		Second-order kinetic	
	k_1	R^2	k_2	R^2
Fe_3O_4	0.0031	0.838	0.0001	0.841
$Fe_{3-0.4}Mo_{0.4}O_4$	0.0062	0.750	0.0002	0.750
$Fe_{3-0.4}Mo_{0.4}O_4$ -MKSF (80wt%)	0.0097	0.972	0.0003	0.983

4. Conclusion

MKSF clay has shown auspicious performance as catalyst support for $Fe_{3-0.4}Mo_{0.4}O_4$ catalyst compared to MK10, bentonite and kaolin. $Fe_{3-0.4}Mo_{0.4}O_4$-MKSF(80wt%) has successfully degraded 98.8% of AOII solution. The presence of MKSF clay and H_2O_2 led to the enhancement of catalytic activity due to the high formation of •OH reactive radicals during the heterogeneous Fenton-like reaction process. The AOII degradation kinetic using $Fe_{3-0.4}Mo_{0.4}O_4$–MKSF(80wt%) catalyst followed second-order kinetic model which suggests that the reaction mainly occurs at the surface of the catalyst. The reaction kinetic constants are increased in the order of $Fe_3O_4 > Fe_{3-0.4}Mo_{0.4}O_4 > Fe_{3-0.4}Mo_{0.4}O_4$-MKSF(80wt%) for both of first and second kinetic models indicates the improvement of reaction rate as the catalyst been substituted with molybdenum and immobilized onto MKSF clay. Hence, it can be concluded that the use of MKSF clay as catalyst support provides a positive influence in enhancing the overall catalytic performance of $Fe_{3-0.4}Mo_{0.4}O_4$ catalyst during the Fenton-like reaction as well as the degradation kinetics of organic pollutants.

Acknowledgement

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