Oxidative Degradation of Methyl Orange Solution by Fe-MKSF Catalyst: Identification of Radical Species

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Abstract. Iron-immobilized montmorillonite KSF (Fe-MKSF) has been recognized as promising catalyst in degrading persistence organic contaminants. However, detailed mechanistic insight during the catalysis which involving the formation and identification of radical species were remained indeterminate due to complex reaction. Inspiring by this gap, iron-immobilized clay (Fe-MKSF) was synthesized and used as heterogeneous catalyst in the oxidative degradation of methyl orange (MO) solution. Identification of radical species were determined through the inclusion of different types of radical scavenging agent during the Fenton-like reaction at optimum condition. Interestingly, dominant radical species were found to be hydroperoxyl radicals (•OOH) which subsequently followed by hydroxyl radicals (•OH) during the catalysis. Based on the percentage of MO removal, it was suggested that approximately 88% of the •OOH radicals existed at the interface of catalyst while 39% presence in bulk solution. Meanwhile, the interface •OH radicals promoted 38% of MO removal, whilst 4% by the bulk •OH radicals. Hence, these findings have conveyed novel insight on detailed radicals’ identification as well as its’ interaction during the catalysis.

1. Introduction

The mechanism behind heterogeneous Fenton process is intriguing due to unsolved, complex interaction of radical species, organic compound and the catalyst itself. In heterogeneous Fenton-like, there are two main radical species that typically discussed in literature which are hydroxyl (•OH) radicals and hydroperoxyl (•OOH) radicals. The •OH radicals are the stronger radical than the •OOH as the standard reduction potential of the former one is 2.59 V and the latter is 1.5 V [1].

With the OH and OOH high reduction potential, many organic contaminant were able to degrade at near- diffusion controlled rate [2]. The radicals weaken the structure of organic contaminant by abstracting H-atom from C-H, N-H, or O-H bonds and adding OH to unsaturated bonds like C=C or aromatics rings [3]. In general, it was reported that the dominant radical’s presence during the heterogeneous Fenton-like catalysis is *OH radical. However, the coexistence of *OOH radical was also contributing towards the enhancement of organic’s degradation during the catalysis whilst synergic effect of both radicals were confirmed [4].

Since the lifespan for these radicals are short (microseconds), the radical only can be detected indirectly at the present. The electron spin resonance spectroscopy (ESR) [5], chemiluminescence (CL) [6] or photoluminanescence (PL) fluorescent [7] are among the common methods which were used to identify the types of radical presence during catalysis. However, the utilization of these methods are either time consuming or expensive. Therefore, a direct in-situ measurement method...
which offers reasonably cost effective is desired in determining the types of radical via the utilization of specific types of radical scavenging agent during catalysis.

The reaction of \( ^\cdot \text{OH} \) radical with alcohols [8] like methanol, butanol and inorganic anions [9] like \( \text{HCO}_3^- \) are used in \( ^\cdot \text{OH} \) dominated degradation reaction. The alcohols and inorganic anions consume the \( ^\cdot \text{OH} \) very fast, thus it served well as OH scavengers in radical identification reaction. The \( ^\cdot \text{OOH} \) may be deduced by the quenching and scavenging of benzoquinone [10].

The additions of the radical scavengers were reported to reduce [8, 10] the catalytic efficiency indicating minimal radical radicals remains after the scavenging effect. This scavenging radical method may not be the most accurate one but is fairly less complicated, cost effective and tailored towards the specific types of radical which presence either on the surface of the active sites or in bulk solution during the catalysis [8].

Hence, the aims of this work is to investigate on plausible mechanistic insight of heterogeneous Fenton-like reaction by identifying the types of radical species presence through the inclusion of specific radical scavenging agent during the catalysis at optimum reaction condition.

2. Materials and Methods

2.1. Materials

All materials that were used in this study were purchased from Merck and used as received.

2.2. Preparation of iron-immobilize MKSF (Fe-MKSF) catalyst

The iron-immobilized MKSF (Fe-MKSF) composites catalyst were synthesized from a reaction solution consisting of iron precursor and dispersion of MKSF clay as describe elsewhere [11]. \( \text{Na}_2\text{CO}_3 \) was added slowly to vigorously stirred 0.2 M of \( \text{FeCl}_2\cdot4\text{H}_2\text{O} \) solution at a molar ratio of 1:1 for \( \text{[Na}^+]/\text{[Fe}^{2+}] \). The solution was continuously stirred for 3 h. Then, the MKSF was added to the mixture and stirred for another 3 h. The ratio of iron precursor to MKSF was set at 20 mmol of Fe/g of clay. After that, the mixture was aged at 100°C for 48 h in an autoclave reactor. The resulting precipitants were centrifugally recovered and washed several times with deionized water and dried at 60°C overnight. The dried samples were calcined in air at 350°C for 20 h at ramping rate of 10°C/min.

2.3. Identification of radical species

Four types of chemicals were used as radical scavenging agents during the catalysis were shown in Table 1. The scavengers were added 30 min prior to the addition of \( \text{H}_2\text{O}_2 \). The concentrations of scavengers were fixed at 6 mM. The catalysis procedure was performed at optimized conditions of pH 2.8, catalyst dosage of 0.8 g/L, concentration of oxidant of 15 mM and initial methyl orange (MO) concentration of 25 mg/L. The changes in MO’s colour were observed during 180 mins of reaction. The samples were periodically withdrawn, filtered and analyzed using UV-Visible Spectrophotometer (Lamda 25, Perkin Elmer) at \( \lambda_{\text{max}} = 464 \text{ nm} \).

### Table 1. List of radical scavengers.

| Chemicals          | Type of quenching radicals                  | Ref |
|--------------------|---------------------------------------------|-----|
| Potassium iodide   | \( ^\cdot \text{OH} \) radicals on surface of catalyst | [8] |
| T-butanol          | \( ^\cdot \text{OH} \) radicals on bulk solution | [8] |
| Sodium azide       | \( ^\cdot \text{OOH} \) radicals on surface of catalyst | [5,12] |
| P-benzoquinone     | \( ^\cdot \text{OOH} \) radicals on bulk solution | [5,12] |

2.4. Characterization of catalyst

X-ray diffraction analysis (XRD Bruker D8 Advance) for determination of catalyst’s phase. CuKα was used as source of radiation (\( \lambda = 1.54\text{Å} \)). The diffractometer operated at 40 kV and 40 mA and scan range of 20 from 10° to 80°. The concentration of iron leached was analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS NexION ® 300).
3. Results and discussions

Figure 1 shows the MO removal after quenching with scavenging agents. The sodium azide, p-benzoquinone, potassium iodide and t-butanol were added into the reaction mixture to selectively quenched surface-hydroperoxyl radical (\( \cdot \text{OOH}_\text{s} \)), bulk-hydroperoxyl radical (\( \cdot \text{OOH}_\text{b} \)), surface-hydroxyl radical (\( \cdot \text{OH}_\text{s} \)) and bulk-hydroxyl radical (\( \cdot \text{OH}_\text{b} \)), respectively.

Interestingly, the dominant radical species were found to be hydroperoxyl (\( \cdot \text{OOH} \)) radicals and subsequently followed by hydroxyl radicals (\( \cdot \text{OH} \)). Based on the MO percentage removal, it was suggested that approximately 88% of the \( \cdot \text{OOH} \) radicals existed at the interface of the catalyst while 39% presence in the bulk solution. On the other hand, only 38% of MO removal was promoted by \( \cdot \text{OH} \) at the interface and 4% removal at the bulk solution. It is contradict from the previous work [13] that reported the dominant radical detected Fenton reaction was \( \cdot \text{OH} \) radicals.

![Figure 1. The influence of radical’s scavengers on the removal of MO in heterogeneous Fenton –like reaction.](image)

On possible explanation is that the iron species that bind to the MKSF is mainly governed by Fe\(^{3+}\) ions instead of iron Fe\(^{2+}\) ions. The different oxidation number of iron species may lead to different reaction initiation of Fenton reaction. For heterogeneous Fenton-like reaction using Fe-MKSF catalyst, the reaction started with the activation of H\(_2\text{O}_2\) by Fe\(^{3+}\) and producing \( \cdot \text{OOH}_\text{s} \) radicals and Fe\(^{2+}\) as shown in the Eqn 1. The slower rate of reaction of Eqn 2 results in slower production of Fe\(^{2+}\), hence only capable to generate reserved quantity \( \cdot \text{OH}_\text{s} \) radicals.

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\begin{align*}
\equiv \text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \equiv \text{Fe}^{2+} + \cdot \text{OOH}_\text{s} + \text{OH}^- \\
\equiv \text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \equiv \text{Fe}^{3+} + \cdot \text{OH}_\text{s} + \text{H}^+
\end{align*}
\]

This postulation was strongly supported by the XRD results analysis. The Fe-MKSF was ascribed to the hematite phase, \( \alpha-\text{Fe}_2\text{O}_3 \), a rhombohedral iron (iii) oxides as shown in Figure 2. The crystal structure of hematite, \( \alpha-\text{Fe}_2\text{O}_3 \) (indexed to PDF-01-087-1165) was presented in the iron oxide structure with peaks at 20 = 25.12°, 33.08° and 35.63° assigned by (012), (104), and (110) crystal planes respectively. The \( \alpha-\text{Fe}_2\text{O}_3 \) spinel structures detected in the catalysts were in evident with the calcination temperature of 350°C. The phase formation as function of temperature were reported by
Farbod (2012) [14] and the iron oxide thermodynamically transform to hematite phase at temperature above 300°C [15]. Hence, the immobilized Fe$^{3+}$ ions (≡Fe$^{3+}$) in the system can be ascribed to this hematite phase.

Figure 2. XRD patterns for iron oxide and Fe-MKSF catalysts.

Figure 3. Proposed mechanism during heterogeneous Fenton-like reaction using Fe-MKSF catalyst.
The reaction initiate with the $\text{Fe}^{3+}$ ions activated by the presence of $\text{H}_2\text{O}_2$ to produced $\cdot\text{OOH}$ radicals. Figure 3 demonstrates the proposed mechanism based on the identified radicals special during the catalysis. The $\equiv\text{Fe}^{3+}$ ions was mainly presence at the interface of the catalyst rather than the $\equiv\text{Fe}^{2+}$ ions that resulted to the detection of $\cdot\text{OOH}_5$ and $\cdot\text{OH}_5$ radicals, respectively. However, a minimal amount of immobilised ions ($\equiv\text{Fe}^{3+}$ and/or $\equiv\text{Fe}^{2+}$) may also leached to bulk solution homogeneously in the form of $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ ions, which subsequently resulted to the detection of $\cdot\text{OOH}_5$ and $\cdot\text{OH}_5$ radicals. Leaching of immobilised ions ($\equiv\text{Fe}^{3+}$ and/or $\equiv\text{Fe}^{2+}$) was due to the solution acidity during catalysis.

The amount of leached iron in the solution after undergoing 180 mins of reaction was found to be 0.3 mg/L. The concentration of iron is below limit of standard effluent discharge of 2 mg/L as stated in European legislation [16]. The relatively minimal concentration of leached-out iron indicates that negligible contribution of homogeneous Fenton process in the reaction. It strongly suggests a solid deposition of iron ions ($\equiv\text{Fe}^{3+}$ and/or $\equiv\text{Fe}^{2+}$) onto the MKSF matrix and the decolourization may dominantly attributed to the heterogeneous Fenton-like reaction that take place on the surface of Fe-MKSF catalyst.

4. Conclusions
The degradation of MO was mainly contributed by the surface-hydroperoxyl radical ($\cdot\text{OOH}_5$) which subsequently facilitated by surface-hydroxyl radical ($\cdot\text{OH}_5$) as secondary radicals during the heterogeneous Fenton-like reaction using Fe-MKSF catalyst. The contribution of these radical on the degradation of MO can be represented in the sequence of $\cdot\text{OOH}_5 > \cdot\text{OH}_5 > \cdot\text{OOH}_b > \cdot\text{OH}_b$. Such findings can be attribute to hematite phase found in the Fe-MKSF catalyst. This new findings provide a novel insight in understanding the underlying MO’s degradation mechanism which directly relates towards identification as well as interaction of radical species presence during the heterogeneous Fenton-like reaction.

5. References
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