Treatment of methyl orange by the catalytic wet peroxide oxidation process in batch and continuous fixed bed reactors using Fe-impregnated 13X as catalyst

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ABSTRACT

Fe-impregnated 13X (Fe-13X) catalysts were prepared for catalytic wet peroxide oxidation (CWPO) of methyl orange (MO) solution in batch and continuous fixed bed reactors. A systematical study was carried out to investigate the influence of the main operating parameters on the batch reactor performance. The kinetic curves were analyzed by using a pseudo-first-order kinetic equation over the 30–70 °C temperature range. In addition, the effects of catalysts filling amount and feed flow rate on the catalytic performance of Fe-13X catalysts in a fixed bed reactor were studied. The experimental results showed that the Fe-13X catalysts achieved the highest activity (100% MO conversion and 74.5% chemical oxygen demand (COD) elimination ratio, respectively) at 25 min with trace mount of Fe leaching concentration (<2.1 mg/L) at the optimized reaction conditions (namely 1.0 g/L catalyst concentration, pH 2.0, 17.6 mM H2O2, 70 °C) in a batch reactor. Kinetic studies showed that two different reaction regions existed, and an activation energy of 51.9 kJ/mol for the second region was found. Under the optimal operating conditions found (namely, catalysts filling amount of 3.5 g, feed flow rate of 4 mL/min), the Fe-13X catalysts displayed high MO conversion (99.4%) and COD elimination ratio (77.1%) after continuously ran for 200 min in a fixed bed reactor.

Key words | batch reactor, catalytic wet peroxide oxidation, Fe-13X catalyst, fixed bed reactor, methyl orange

INTRODUCTION

Azo dyes like methyl orange (MO) and orange II (OII) are important raw materials of many industries such as textile dyeing, paper printing, leather and so on. However, these dyes are hazardous to humans and their environment because of strong color, toxicity (mutagenesis or carcinogenesis), complex structure, high chemical stability and low biodegradability characteristics (Hua et al. 2013). Therefore, the removal of these dyes from industrial wastewater is very important for environmental protection and human health, which has drawn an increasing attention. Many techniques, such as adsorption (Li et al. 2016), biological treatments (Tomei et al. 2016), membrane separation (Zhang et al. 2017) and the advance oxidation processes (AOPs) (Güyer et al. 2016) have been developed to treat the dye wastewater.

Catalytic wet peroxide oxidation (CWPO) is a simple, effective and environment-friendly advance oxidation process based on hydrogen peroxide as oxidant. In this process, hydroxyl radicals can be produced by using transition metals as catalysts in the presence of hydrogen peroxide, which has strong oxidizing abilities that the organic compounds could be degraded efficiently. In the last decades, traditional transition metals catalysts like Fe2+/ ions was widely used in CWPO process because of high efficiency in degrading pollutants at mild conditions. However, the homogeneous catalyst also has a series of disadvantages, such as catalyst recovery difficulty and the second pollution of treated solution, resulting in a more complicated and expensive subsequent treatment process (Queirós et al. 2015). To overcome these disadvantages, heterogeneous catalysts containing Fe (Neamtu et al. 2004), Cu (Mekewi et al. 2016), Zn (Hassanzadeh-Tabrizi et al. 2016) or other transition metals supported on the surface of different porous materials such as zeolite (Sashkina et al. 2016)
carbon (Ramirez et al. 2007), SiO₂ (Panda et al. 2011), Al₂O₃ (Liu & Sun 2007), montmorillonite clays (Mekewi et al. 2016) and so on, have been developed for the removal of dyes from wastewater. Of these, Fe loading zeolite or carbon is applied broadly in the CWPO of dyes due to high catalytic reactivity. The mechanism of hydrogen peroxide decomposition by Fe-based catalysts and oxidation of organic compounds can be described by the Equations (1)–(3) (Duarte et al. 2009; Herney-Ramirez et al. 2011):

\[
\begin{align*}
H_2O_2 + XFe^{3+} & \rightarrow HO_2^- + H^+ + XFe^{2+} \\
H_2O_2 + XFe^{2+} & \rightarrow HO^- + OH^- + XFe^{3+} \\
HO^- + \text{organic compounds} & \rightarrow \text{oxygen products}
\end{align*}
\]

where X represents the support like zeolite, carbon, and so on.

Recently, more and more papers reported about the application of Fe-based catalysts in azo dyes degradation by the CWPO process. Duarte et al. (Duarte et al. 2013a) investigated the effect of the iron salt precursor (iron acetate, iron sulphate and iron nitrate) in the preparation of Fe/activated carbon (AC) catalysts for the degradation of OII, it was found that ferrous acetate seems to be the optimal option for the precursor of Fe/AC heterogeneous catalysts. Kondru et al. (2009) studied the CWPO of Congo red at different operating parameters using Fe exchanged Y zeolite as a catalyst, and the results showed that the % removals of dye, color and chemical oxygen demand (COD) were maximum at initial pH 2 but as the iron leaching concentration was higher in acidic pH range. However, most of the researches about the CWPO processes of azo dyes were carried out in a stirred tank reactor. Batch reactor has its advantages like no backmixing and high mixing homogeneity, but the disadvantages of having no reaction time and high operating cost cannot be ignored. These shortcomings may be overcome by using a fixed bed reactor. Duarte et al. (Duarte et al. 2013b) reported the catalytic performance of Fe/AC, used for CWPO of textile effluents (Alcian Blue-tetrakis chloride, AB) in a continuous packed bed reactor and found that 93.2% of discoloration and 54.1% of total organic carbon removal was achieved under the best conditions (namely \( C_{AB,\text{feed}} = 0.01 \text{ mM}, W_{\text{cat}}/Q = 3.3 \text{ g-min/mL}, C_{H_2O_2,\text{feed}} = 30.0 \text{ mM}, \text{pH} = 2.5 \) and \( T = 50^\circ C \)). Besides, to the author’s knowledge, literature describing the CWPO of dye process in a continuous fixed bed reactor is relatively scarce.

The objective of this work is to investigate the efficiency of Fe-13X catalysts for the CWPO of MO solution in batch and fixed bed reactors. Firstly, the effects of various operating parameters like the type of catalyst, \( H_2O_2 \) concentration, catalyst concentration, reaction temperature and pH on the catalytic performance of a batch reactor are studied. Then, the catalytic efficiency of the catalysts in a fixed bed reactor at different catalysts filling amount and feed flow rate will be evaluated. Finally, the stability of the Fe-13X catalysts is measured.

**EXPERIMENTAL**

**Materials**

Commercial 13X zeolite particles (column; \( d = 1.6 \text{ mm} \)) were purchased from Shanghai Molsion Molecular Sieve Co., Ltd. Commercial AC particles (flake; \( d = 4–6 \text{ mm} \)) were purchased from Zhengzhou Yongkun Environmental Protection Technology Co., Ltd. MO and Fe(NO₃)₃·9H₂O were supplied by Shandong Xiya Chemical Industry Co., Ltd. Hydrogen peroxide (H₂O₂, 30wt% aqueous) was purchased from Xilong Chemical Co., Ltd. Nitric acid was supplied by Hengyang Xunyuan Chemical Reagent Co., Ltd. All of the chemical agents used in this research were of analytical grade.

**Preparation and characterization of Fe-13X catalysts**

Fe-13X catalysts were prepared by wetness impregnation of commercial 13X zeolite with Fe(NO₃)₃·9H₂O salt solution (Yan et al. 2014). The iron ions concentration was adjusted to get a 10% Fe (w/w) on the catalyst. After impregnation, the particles were dried overnight at 100 °C and calcined at 500 °C for 3 h in air. The same method was used to prepare Fe-impregnated AC (Fe-AC) catalysts using AC and Fe(NO₃)₃·9H₂O salt solution as raw materials.

The morphology of the 13X and Fe-13X catalysts was obtained by using a Germany ZEISS EVO10 scanning electron microscope (SEM). The crystallographic structures of the 13X, Fe-13X and Fe-AC catalysts were measured by X-ray diffraction (XRD) technique on a PANALYTICAL B.V. PW3040/60 X-ray diffractometer using Cu Ka irradiation at 40 kV and 40 mA and 2θ range from 5° to 60°. Fourier transform infrared spectroscopy (FTIR) of 13X and Fe-13X catalysts was analyzed in the region from 599 to 4,000 cm⁻¹ at room temperature by using an IRPrestige-21 spectrometer on KBr pellets.
Catalyst activity tests

**Batch reactor**

CWPO of MO was carried out using 0.5 L of a 50 mg/L solution, in a glass reactor equipped with a mechanical stirring and a thermal bath. After addition of H$_2$O$_2$ and stabilization of pH and temperature, absorbance of initial solution was measured followed the catalyst particles were added, this being considered as time zero (t = 0). The absorbance was measured using a V5100 visible spectrophotometer at 464 nm. The MO conversion ($X_{MO}$, %) was calculated as follows:

$$X_{MO} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\% \quad (4)$$

where $C_0$ (mg/L) is the concentration of initial MO solution and $C_t$ (mg/L) is the MO concentration at instant time t (min).

COD concentration of the samples were measured using dichromate method of national standards of People’s Republic of China (GB11914-89). And COD elimination ratio ($X_{COD}$, %) was calculated as follows:

$$X_{COD} = \left( \frac{[COD]_0 - [COD]_t}{[COD]_0} \right) \times 100\% \quad (5)$$

where $[COD]_0$ (mg/L) and $[COD]_t$ (mg/L) are the concentrations of COD at time 0 and t min.

Iron leaching concentration (mg/L) in the treated MO solution was measured by an atomic absorption spectrophotometer (TAS-990AFG).

**Fixed bed reactor**

The catalytic activity of Fe-13X catalysts was tested further by CWPO with MO solution as a model pollutant in a fixed bed reactor made of stainless tube (20 mm i.d., 80 mm length), operated at 70°C and pH 2.0 under atmospheric pressure.

The experimental device used for the oxidation of MO solution by CWPO is shown in Figure 1. To obtain a better distribution of the inlet MO solution inside the fixed bed and ensure the desired temperature, the Fe-13X catalyst particles were filled between inert glass beads (d = 2–3 mm). In the feed tank, the MO and hydrogen peroxide were mixed uniformly; following, pH were adjusted with HNO$_3$. The MO solution was transported to the fixed bed in up-flow operation with an intelligent flow-type peristaltic pump. The fixed bed reactor was heated by hot water bath to keep the desired temperature. The inlet and outlet MO concentration were determined using a V5100 visible spectrophotometer. The conversion of MO ($X_{MO}$, %) and COD elimination ratio in the effluent were calculated according to Equations (4) and (5).

**RESULT AND DISCUSSION**

**Catalysts characterization**

The morphology of 13X and Fe-13X catalysts was observed by SEM. As can be seen in Figure 2(a), the SEM image of
13X zeolite was obviously different from that of Fe-13X catalyst. For 13X zeolite, the sample particles with smooth surface and the staggered porous structure were observed. The surface of Fe-13X catalysts became rough and Fe species were well distributed on the surface of the 13X zeolite.

The crystallographic structures of the Fe-AC, 13X, fresh and used Fe-13X catalysts were measured by XRD technique.
at $2\theta$ values between 5° and 60°, as shown in Figure 2(b). For Fe-AC, peak at $2\theta \sim 26^\circ$ was a characteristic peak of AC, and that at $2\theta \sim 36^\circ$ may be the characteristic peak of iron oxide. While the XRD pattern of the Fe-13X catalyst sample was very much similar to that obtained from 13X zeolite. The possible reason is that Fe species were well-dispersed on the 13X zeolite surface and no new phase was formed in spite of high temperature calcination of 500 °C (Singh et al. 2016). Some previous works (Duarte et al. 2015a) reported that N-Fe(NO3)3 catalyst was the most well dispersed sample according to the XRD patterns of N-Fe(NO3)3, N-Ac2Fe and N-FeSO4, where the size of Fe particles was below the detection of the technique (4 nm). Whereas the intensity of Fe-13X catalyst diffraction peaks decreased compared with that of 13X zeolite, which could be attributed to the enhanced X-ray absorption coefficient of iron compounds (Rauscher et al. 1999; Yan et al. 2015). Moreover, almost no change of the reflections peaks were observed for fresh and used Fe-13X catalysts, suggesting the good stability of Fe-13X catalysts (Gao et al. 2016). The FTIR spectra of 13X and Fe-13X catalysts were shown in Figure 2(c). For 13X, the bands centered at 3,468 cm$^{-1}$ and 1,660 cm$^{-1}$ were associated to OH stretching vibration and OH bending of adsorbed waters. The peak centered at 1,429 cm$^{-1}$ was due to Si-OH groups. The band at 1,054 cm$^{-1}$ was assigned to the tetrahedral aluminosilicate framework. Changes in the FTIR spectra of Fe-13X were also discovered. Slight shifts from 1,429 cm$^{-1}$ to 1,458 cm$^{-1}$ and 669 to 684 cm$^{-1}$ occurred, suggesting that –OH of Si-OH group cross-linked with iron ion. The new band centered at 1,381 cm$^{-1}$ was assigned to Fe-OH goups (Gao et al. 2016; Garrido-Ramírez et al. 2016).

MO oxidation over Fe-13X catalysts in a batch reactor

Comparison of catalytic effect

To understand the MO removal process and determine the effect of catalytic and adsorption, 13X, Fe-13X and Fe-AC were tested as catalysts with H$_2$O$_2$ oxidant. In additional, 13X and Fe-13X were determine as adsorbents without H$_2$O$_2$ oxidant. Figure 3(a) shows that the adsorption efficiency using Fe-13X and 13X adsorbent had achieved 42.6% and 40.8% removal after 240 min. The adsorption capacity of Fe-13X was higher than that of 13X zeolite. The use of the 13X with H$_2$O$_2$ as oxidant achieved 49.2% removal after 180 min. This was much less than that using Fe-13X catalyst in the presence of H$_2$O$_2$ achieved 98.9% MO removal. This is due to the existence of iron ion which can transform hydrogen peroxide into HO- species. However, the use of Fe-AC catalyst with H$_2$O$_2$ oxidant
achieved only 57.9% removal. It is noteworthy that the Fe-13X catalyst was more active compared with the Fe-AC one at the same experimental conditions. This should be attributed to the better dispersion of iron species into the external surface provided by 13X support as shown in Figure 2(b). Similar results about the importance of the Fe dispersion into the surface of composites were reported by Ramirez et al. (2007).

**Effect of the H₂O₂ concentration**

The dependence of the reaction rate on the initial concentration of H₂O₂ was investigated by varying its concentration between 4.4 and 35.3 mM, while keeping the other operational parameters constant (namely pH 2.0, 1.0 g/L Fe-13X catalyst), and the results are shown in Figure 3(b).

As expected, increasing H₂O₂ concentration from 4.4 to 17.6 mM increased reaction rate at the beginning of the reaction, and MO conversion after a period of 180 min was 95.8%, 98.3% and 98.9% for H₂O₂ concentration of 4.4, 8.8 and 17.6 mM, respectively, which could be attributed to the reason that more HO· species were formed. However, higher H₂O₂ concentration was not beneficial either and reaction rate dropped down for further increasing H₂O₂ concentration from 17.6 to 35.3 mM. The possible reason is that hydroperoxyl radicals (HO₂⁻) was formed for an excessive H₂O₂ concentration as shown in the following equation.

\[
\text{H}_2\text{O}_2 + \text{HO} \rightarrow \text{HO}_2 + \text{H}_2\text{O} \quad (6)
\]

The oxidation potential of HO₂⁻ is much lower than that of HO and would not be helpful to the oxidation degradation of MO. Therefore, 17.6 mM H₂O₂ was suitable dosage for efficient oxidation of MO.

**Effect of the catalyst concentration**

To obtain an optimal catalyst concentration with maximum catalytic activity and minimum cost, experiments were carried out with different amount of Fe-13X catalysts while other operation parameters were kept as constant (namely, 30 °C, 17.6 mM H₂O₂, pH 2.0). The effect of the catalyst concentration (0.4–1.2 g/L) on MO conversion is shown in Figure 3(c).

As shown in Figure 3(c), after 180 min of reaction, MO conversion increased from 74.4% up to 98.9% when the catalyst concentration was raised from 0.4 g/L to 1.0 g/L. However, MO conversion was kept basically the same for further increase in catalyst concentration (1.2 g/L). Therefore, catalyst concentration of 1.0 g/L was kept as the optimum value. Lower catalyst concentration (<1.0 g/L) may generate insufficient HO· species, and higher catalyst concentration (1.2 g/L) is not conductive to the production of HO· species at a certain H₂O₂ concentration.

**Effect of the reaction temperature**

Experiments under different reaction temperatures (30–70 °C) were conducted while the other operational parameters were fixed as constant (namely pH 2.0, 1.0 g/L catalyst, 17.6 mM H₂O₂), and the results are shown in Figure 4(a). It can be seen that MO conversion increased at a faster rate when the reaction temperature increased. However, the MO conversion was finally similar for temperature from 30 to 70 °C, with almost complete conversion. This could be attributed to the fact that higher temperature only leads to a quicker productive rate of HO· species, resulting in higher MO reaction rate.

The kinetics for the degradation of MO were analyzed by using a pseudo-first-order kinetic equation, and the integrated form is expressed as:

\[
kt = \ln \frac{C_0}{C_t} = \ln \frac{1}{1 - x_{\text{MO}}} 
\]

where \(k\) is the rate constant (min⁻¹), \(t\) is the time (min), \(C_0\) and \(C_t\) are the concentrations of MO at time 0 and \(t\) min (mg/L), respectively, and \(x_{\text{MO}}\) is the conversion of MO.

Pseudo-first-order plots for the MO degradation carried out at different reaction temperatures from 30 to 70 °C are shown in Figure 4(b). As seen in this figure, each curve displayed two linear regions in the plot, but the time to achieve the second linear region decreased with increasing the reaction temperature. Gordon & Marsh (2009) also pointed out the similar results for the goethite-catalyzed reaction at different reaction temperatures. The catalytic oxidation process of MO first involves the activation of catalyst and then the oxidation of MO by HO· produced at the Fe-13X surface. This may be explained that the activation of Fe species is an endothermic reaction. For the second region of the MO degradation, rate constants (k, min⁻¹) had been calculated by a linear regression analysis (Figure 4(c)). These rate constants obtained at different reaction temperatures from 30 to 70 °C had been used to calculate activation energy by an Arrhenius equation.
plot is shown in Figure 4(d), with an activation energy of 51.9 kJ/mol.

**Effect of initial pH value**

It is well-known that the Fenton reaction occurs easily in acidic medium (in the range of pH 2–4), because this catalyst is able to facilitate the production of HO· species in this range of pH value. Thus, the experiments were carried out at pH values between 1.0 and 3.0 while other operation parameters were kept as constant (namely, 70 °C, 17.6 mM H$_2$O$_2$, 1.0 g/L catalyst). The main parameters such as the MO conversion, COD elimination ratio, and the iron leaching concentration in the treated solution were measured, and the results are displayed in Figure 5. As can be seen from Figure 5(a), the MO conversion enhanced with decreasing pH value from 3.0 to 2.0, and then approached steady state with a further decrease of pH value. The MO conversion were 99.0%, 99.2%, 100%, 98.3% and 34.1% at 25 min when pH values were 1.0, 1.5, 2.0, 2.5 and 3.0, respectively. A similar phenomenon was reported by Khataee et al. (2016) using natural pyrite as catalyst in CWPO of Reactive Orange 29. The possible reason is that suitable acidity is beneficial to acidify the medium and enhance the oxidation potential of the hydroxyl radical. It is also noteworthy that the reaction rate of MO was almost the same when the initial pH value varied in the range of 1.0–2.0. It can be found from Figure 5(b) that the COD elimination ratio increased rapidly with decreasing pH value from 3.0 to 2.0. The COD elimination ratio when the reaction reached equilibrium was 74.5% at pH 2.0. While COD elimination ratio decreased with decreasing pH value from 2.0 to 1.0. This trend is similar with Queirós et al. (2015), in a continuous stirred tank reactor and Fe/ZSM-5 as catalyst, where it was found that the decreased efficiency was observed at a very acidic pH value (1.5). This may be due to the formation of the H$_3$O$_2$ by proton solvation at very low pH value, leading to less generation of HO· (Rache et al. 2014). As shown in Figure 5(c) that the pH value may have some relationship with the iron leaching concentration in the treated solution. The lower the pH value, the higher the Fe ions loss, in agreement with other papers (Liu & Sun 2007; Queirós et al. 2015). The iron leaching concentrations were under 2.1 mg/L with pH values in the range 2.0–3.0. The maximum iron leaching concentration of 8.38 mg/L was noticed for pH 1.0. Thus, pH of 2.0 was considered as the optimal value.
Experiments under different catalysts filling amount and feed flow rate were carried out and the results are presented in Figures 6 and 7. As can be seen from Figure 6(a), MO was partly oxidized with the 13X zeolite and its highest conversion only reached 47.8% with the catalysts filling amount of 3.5 g. Although the MO conversion decreased slightly with decreasing the Fe-13X catalysts’ filling amount from 3.5 to 1.25 g, it still kept a high level of conversion above 92% when the Fe-13X catalysts filling amount reached 1.25 g. It is also noteworthy that the MO conversion remained steady (>98%) within 200 min with the catalysts filling amount of 3.5 g. Figure 6(b) shows that the COD elimination ratio increased drastically from 42.8% to 77.1% with the catalysts filling amount increased from 1.25 g to 3.5 g when the fixed bed was running continuously for 200 min. This behavior can be due to the decrease in decomposition of hydrogen peroxide into highly reactive hydroxyl radicals with decreasing catalysts’ filling amount. Insufficient HO· led to incomplete oxidation of MO. In other words, MO was decomposed to low-molecular-weight organic compounds, and was not further oxidized into carbon dioxide and water, which ultimately result in low COD elimination ratio. The iron leaching concentration increased with increasing catalysts’ filling amount (Figure 6(c)). However, the maximum leached iron concentration was under 4.5 mg/L within 200 min.

Effect of the flow rate

The effects of the residence time were investigated by varying the feed flow rate of MO solution of 4, 6 and 8 mL/min in a fixed bed reactor, respectively, while other operation parameters were maintained as constants (namely 3.5 g catalyst, 50 mg/L MO). The MO conversion and COD elimination ratio were measured and are shown in Figure 7. It can be found from Figure 7 that higher feed flow rate was not conductive to the reaction of MO and H₂O₂. The MO conversion decreased from 99.4% to 81.6% at 200 min (Figure 7(a)), and the COD elimination ratio also decreased slightly from 77.1% to 69.5% (Figure 7(b)) with the feed flow rate increasing from 4 to 8 mL/min when the fixed bed was running continuously for 200 min. At relatively higher flow rate, the residence time of the MO and H₂O₂ in the fixed bed is not enough and thus the MO
does not get sufficient time to oxidize efficiently. If the feed flow rate is low enough, it is ideal for H₂O₂ react with iron species, producing enough hydroxyl radicals for the MO oxidation. In other words, at high feed flow rate, hydroxyl radicals generated by H₂O₂ is not enough, resulting in lower oxidizing abilities.

### Stability of the catalysts

In order to investigate the stability and reusability of the Fe-13X catalysts, three runs were carried out in both batch and fixed bed reactors at the same experimental conditions. The solid catalysts were recovered, washed and dried at 100 °C after a run. It can be found from Figure 8(a) that MO conversion decreased at the initial of reaction after being used three times, but the conversion was kept the basically same after 25 min in the batch reactor. As can be seen in Figure 8(b), MO preserved high conversion rates (>90%) but decreased slightly after being used three times in 200 min in the fixed
CONCLUSION

The catalytic activities of Fe-13X catalysts in batch and fixed bed reactors were studied for the MO degradation. The catalytic performance of Fe-13X catalysts was found to perform better compared with that of the original 13X zeolite and Fe-AC catalysts. Under the optimal reaction conditions (namely, 1.0 g/L catalyst, pH 2.0, 17.6 mM H₂O₂, 70 °C), MO and COD conversion of Fe-13X achieved 100% and 74.5% at 25 min in a batch reactor, and iron leaching concentration reached very low levels (under 2.1 mg/L) in the treated solution within the time studied. Pseudo-first-order plots for the MO degradation carried out over the 30–70 °C temperature range exhibited two linear regions, and an activation energy 51.9 kJ/mol for the second region was determined. In the fixed bed reactor, the MO and COD conversion still preserved high level (99.4% and 77.1%, respectively) after continuously ran for 200 min with the catalysts filling amount of 3.5 g and feed flow rate of 4 mL/min. After three successive runs, the Fe-13X catalysts retained high catalytic efficiency.

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