Removal of methyl orange by heterogeneous fenton process using iron dispersed on alumina pillared bentonite pellet

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ABSTRACT

Introduction: Heterogeneous Fenton is one of the Advanced Oxidation Processes (AOPs) and has proven to be effective on azo dye degradation. However, a low-cost catalyst and factors affecting the processes of this system were further investigated. Methods: In this study, pellets of iron alumina pillared bentonite (PFeAPB) were prepared by dispersing iron ions on alumina pillared bentonite pellet. Catalyst activity and lifetime were investigated via efficiencies of Methyl Orange (MO) decolorization and Chemical Oxygen Demand (COD) removal, a typical dye type of textile wastewater. Characteristics of the PFeAPB catalyst were examined by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area, and X-ray fluorescence (XRF). Results: Results of batch experiments showed that specific surface area of the PFeAPB catalyst was 111.22 m²/g higher than its precursor by 2 times (57.79 m²/g). Goethite, Hematite and Maghemite phases with approximately 11.5% of iron elements containing in the catalyst were detected via XRD and XRF. Experimental conditions of pH, initial MO solution, Hydrogen Peroxide concentration, reaction time and catalyst loading were 2.0 ± 0.1, 12.7 mmol/L, 150 min and 20 g/L, respectively, to achieve 88.68 ± 5.69% of MO decolorization and 50.27 ± 6.05% of COD removal while dissolved iron in this heterogeneous Fenton process was below standard limit (2 ppm). Catalyst activity decreased by 5.22% in decolorization efficiency after the two first reusages. Conclusion: These primary results showed the potential of applying PFeAPB catalyst in heterogeneous Fenton process with low iron leaching into water.

Key words: Heterogeneous Fenton Catalyst, Alumina Pillared Bentonite, Pellet, Methyl Orange, Textile Wastewater

INTRODUCTION

Textile is a main export industry in Vietnam and its wastewater has been listed as difficult-to-degrade wastewater. Among several physical, chemical and biological processes, adsorption has been proven as a widely used, effective method to decolorize dye in textile effluent. However, pollutants in dye wastewater are adsorbed on the adsorbent and concentrated into a smaller volume but not degraded. Advanced Oxidation Processes (AOPs) have been proven worldwide as efficient methods in dye wastewater treatment due to high oxidation of active radicals and mineralization capability to persistent organic pollutants (such as azo dyes into CO₂ and H₂O). Thus, homogeneous Fenton processes are commonly applied to treat textile wastewater. However, these processes still have some disadvantages of iron treatment, sludge, and strict operation under acidic condition. Heterogeneous Fenton processes have been introduced to overcome disadvantages of homogeneous Fenton processes. These processes apply iron catalysts which are immobilized on the surface of the adsorbent and combined with hydrogen peroxide (H₂O₂) to generate hydroxyl radicals (•OH)¹,², thus possibly minimizing iron leaching into water and operating under less acidic condition, enabling the catalyst to be reused and recycled. Bentonite clay has been used as an adsorbent and has gained much attention in environmental remediation due to iron content in clay, its low cost, its abundance, and ion-exchange capability, while still having low specific surface area³,⁴. Specific surface area of bentonite clay can be increased by intercalating inorganic/organic cations into expandable clay layers (so-called cation pillared bentonite). They are fabricated by cation exchange with polyoxocations of silica-alumina layers, then calcinated³,⁵. Among several cations to be pillared into clay, polycations of aluminum are preferred due to the well-known structure, synthesis conditions and stabilities⁷. In addition, alumina pillared clays give much higher surface Lewis acidity than their precursor⁶,⁸. Hence, alumina pillared bentonite may be used as a good supporter to be impregnated with irons which are active sites of heterogenous Fenton catalysts.

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So far there are very few investigations of iron dispersed on alumina pillared bentonite used as heterogeneous Fenton catalyst for environmental remediation. Some studies focus on iron pillared bentonite as Fenton catalysts for degradation of cinnamic acid, or dyestuff with UV light assistance. However, researchers focus on powder type which cannot be used in a continuous system due to system clogging iron leaching into water of this catalyst as well as dye removal have not been investigated. Iron phases of this Fenton catalyst can leach into water possibly due to a poor supporter, especially in relatively acidic conditions. Therefore, a heterogeneous Fenton catalyst based on alumina pillared bentonite pellet was examined. The objective of this study was to investigate the reactivity of the PFeAPB catalyst during heterogeneous Fenton process for Methyl Orange (MO) removal from water.

**MATERIALS-METHODS**

**Materials**

A commercial clay product, bentonite powder, was purchased from a local company in Vietnam (Minh Ha Bentonite Mineral Joint Stock Company, Phan Thiet Province, Viet Nam); iron catalyst was prepared from a local company in Vietnam (Minh Ha Bentonite Mineral Joint Stock Company, Phan Thiet Province, Viet Nam); iron catalyst was prepared from ferric nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O); alumina pillared in clay was prepared from aluminum nitrate nonahydrate (Al(NO$_3$)$_3$·9H$_2$O); sodium hydroxide was purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA), hydrogen peroxide (>30 wt.%) and hydrochloric acid (37%) were purchased from Fisher Scientific (UK).

**Catalyst preparation**

Inorganic pillaring technique has been reported previously and was adapted as follows: the bentonite powder was sieved with 2 mm to remove all big contaminants, then added into Al$^{3+}$ solution to become alum-bentonite slurry. The slurry was stirred vigorously in 1 hour and left to age for 24 hours under ambient conditions. The alum-bentonite after aging was centrifuged and compacted into pellet shape ($3 \text{ mm of diameter, } 2-3 \text{ cm of length}$). This pellet was dried at 105$^\circ$C for 12 hours and calcinated at 600$^\circ$C to form the so-called pellet of alumina pillared bentonite (PAPB). Fe(NO$_3$)$_3$·9H$_2$O 1M with 10% of HNO$_3$ solution was impregnated on the surface of PAPB for 4 hours and dried at 105$^\circ$C for 15 hours, and finally baked at 350$^\circ$C for 4 hours. The final product after iron impregnation was referred to as the pellet of iron alumina pillared bentonite (PFeAPB) (Figure 1).

**Experimental procedure**

The Fenton reactor was a 250 mL beaker filled with 100 mL of MO solution and placed in a magnetic stirring machine. The initial pH, H$_2$O$_2$ concentration, MO concentration and catalyst loading were as follows: 3.0±0.1, 12.7 mmol/L, 100 ppm and 20 g/L, respectively; the reaction mixture was constantly stirred at 200 rpm for 120 min. Samples of the reaction mixture were taken with syringe at selected time intervals and then increased to pH~10 with NaOH 2N, and finally filtered through a 0.45 mm membrane for analysis. Each experiment was repeated 3 times. The mean value and standard deviation (± SD) of three replicated results in each experiment were calculated and presented. The used PFeAPB catalyst was washed with distilled water and dried at 105$^\circ$C in an oven for 5 h. These regenerated pellets were used to investigate catalyst reusability and stability.

**Analytical methods**

The UV-VIS spectra of MO were recorded from 200 to 700 nm using a UV-VIS spectrophotometer with a spectrophotometric quartz cell and its concentration was measured at the maximum wavelength. Chemical Oxygen Demand (COD) and total ferrous ions were determined by dichromate and 1,10-phenanthroline methods, respectively, according to the Standard Methods for the examination of water and wastewater. Degradation of MO was investigated via MO decolorization (MO removal) and COD removal efficiency:

$$MO(\%) = \frac{C_0 - C_t}{C_0} \times 100$$

Where $C_0$ (ppm) is the MO initial concentration and initial COD, and $C_t$ (ppm) is the MO concentration and COD at time of withdrawal. The catalysts were characterized by X-ray diffraction spectroscopy (XRD), X-ray fluorescence (XRF) and nitrogen adsorption/desorption isotherm by Brunauer–Emmett–Teller (BET) surface area.

**RESULTS**

Active phases of Fenton catalysts were examined with XRD and XFR analysis. Figure 2 shows X-ray diffraction spectra of 5% iron dispersed on the alumina pillared bentonite catalyst; there were Goethite ($\alpha$-FeOOH), Hematite ($\alpha$-Fe$_2$O$_3$) and Maghemite ($\gamma$-Fe$_3$O$_4$) found in the PFeAPB catalyst. Element compositions of the catalyst and its precursor were obtained by XRF analysis and are shown in Table 1. Notably, Si, Al, Fe, Ca and Mn were five elements found...
in both PFeAPB catalyst and its precursor in the range of 0.09 to 51.0%. Si, Al and Fe contents in the PFeAPB catalyst accounted for 49.1%, 21.1% and 11.5% of the total content, while their presence in its catalyst precursor accounted for 51.0%, 12.2% and 6.95%, respectively.

Performance of PFeAPB catalyst in the heterogeneous Fenton system was evaluated by comparing removal efficiencies among H$_2$O$_2$, PAPB, PAPB + H$_2$O$_2$, and PFeAPB + H$_2$O$_2$ systems with time; the data are presented in Figure 3. The results showed that increasing time from 15 to 180 minutes led to enhanced decolorization efficiency of MO from 2.09 ± 0.66% to 75.23 ± 5.35%, respectively, and in a sequence of H$_2$O$_2$<PAPB<PAPB+H$_2$O$_2$<PFeAPB+H$_2$O$_2$.

Iron element was likely a main contribution to the heterogeneous Fenton processes. The effects of the iron contents impregnated in the catalyst were evaluated and recorded in Figure 4. An increase from 5 to 20% of iron impregnated in the PFeAPB catalyst enhanced MO decolorization efficiency from 68.50 ± 6.59% to 82.10 ± 7.02%, respectively. The dissolved iron started to leach into the water and its level was over the standard limit (2 ppm) when 15% of iron ions were dispersed in the catalyst.

The pH effect on leaching of iron ions and -OH production on MO decolorization was depicted in Figure 5. The results in Figure 5 indicate that the high decolorization efficiencies of MO were achieved at pH = 2 (80.32 ± 5.26%) and pH=3 (69.10 ± 4.26%). The other pH values yielded around 47.20 - 52.05% of decolorization efficiencies.

The H$_2$O$_2$ concentrations were examined in a range of 0 – 50.8 mmol/L. The results of the effect of H$_2$O$_2$ are shown in Figure 6 a, b. When H$_2$O$_2$ concentration was increased from 0 to 12.7 mmol/L, the decolorization efficiencies of MO increased to 75.69 ± 4.35%. This efficiency decreased when H$_2$O$_2$ concentration was over 12.7 mmol/L.

The effect of reaction time on MO decolorization, COD removal, and iron leaching in water are shown in Figure 7. MO decolorization and COD removal efficiencies were achieved from 60.45±6.26% to 88.68±5.69% and 30.32±3.69% to 50.27±6.05%, respectively, in the range of 15-150 min.

Reusability and stability of the PFeAPB catalyst were investigated and shown in Figure 8. The repeatability of catalyst reactivities for the first two runs was achieved below 5.22%. Decolorization efficiencies were dropped to 16.39% and 39.08% in the 3rd and 4th run of the experiments.

**DISCUSSION**

**Catalyst characterization**

Iron active phases observed at around 21.23°, 33.1° and 35.6° were Goethite (α-FeOOH), Hematite (α-Fe$_2$O$_3$) and Maghemite (γ-Fe$_3$O$_4$), respectively, with increasing intensity (Figure 2). Hematite and Maghemite phases are proposed to be the active sites of heterogeneous Fenton catalysts $^{14\text{,}15}$. The bentonite is a natural clay with 2:1 silicate layer which is featured with hydroxide aluminium phyllosilicates. Aluminum (Al) and Silicon (Si) elements are dominant in bentonite clay. Change of PFeAPB composition was indicated by successful intercalation and impregnation of aluminum and iron ions into Bentonite clay (Table 1). The specific surface area of the pillared catalysts increased dramatically, from 57.79 m$^2$/g to 111.22 m$^2$/g, compared to the precursor clay. The alumina pillared into the Bentonite layers increased the specific surface area and adsorption capabilities due to the wider basal space among the 2 silicate layers. These results support many previous observations that the specific surface area increases when the precursor clay is pillared with cation
Iron content in the PFeAPB catalyst increased from 6.95% to 11.5% due to introducing 5% iron into the catalyst. Loss of 0.45% iron may come from preparation and vaporization during calcination.

**Evaluation on performance of heterogeneous Fenton process**

The results in Figure 3 were attributed to two characteristics including clay adsorption of PAPB and oxidation of H$_2$O$_2$, as well as hydroxyl radical (•OH). Decolorization efficiencies of H$_2$O$_2$ oxidation and PAPB adsorption were 6.04±0.78% and 18.12±1.49% at 120 min, respectively. Synergetic effect of PAPB and H$_2$O$_2$ yielded 40.36±3.27% of MO conversion. Decolorization efficiency of MO was increased from 40.36±3.27% to 71.50±5.69% when the iron catalyst was added into PAPB. This was explained by increasing iron content in the catalyst (~4.55%) and by H$_2$O$_2$ which releases •OH in the system; these steps may occur in Equation (1) and (2).

1. FeOOH$_{(s)}$ + 2H$^+$ + $\frac{1}{2}$H$_2$O$_2$ $\rightarrow$ Fe$^{2+}$ + $\frac{1}{2}$O$_2$ + 2H$_2$O (1)
2. Fe$_2$O$_3$$_{(s)}$ + 6H$^+$ $\rightarrow$ 2Fe$^{2+}$ + 3H$_2$O (1-1)
3. Fe$_3$O$_4$_{(s)} + 8H$^+$ $\rightarrow$ 3/2Fe$^{3+}$ + 3/2Fe$^{2+}$ + 4H$_2$O. (1-2)
4. Fe$^{2+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{3+}$ + OH$^-$ + •OH (2)
5. Fe$^{2+}$ + •OH $\rightarrow$ Fe$^{3+}$ + H$_2$O (3)
6. Fe$^{2+}$ + HO$_2^*$ $\rightarrow$ Fe$^{3+}$ + O$_2$ + H$^+$ (4)
7. Fe$^{3+}$ + HO$_2^*$ $\rightarrow$ Fe$^{2+}$ + O$_2$ + H$^+$ (5)
8. C$_{14}$H$_{13}$N$_3$NaO$_3$SH + •OH $\rightarrow$ R + products (8)

However, a small change of MO decolorization efficiencies (80.20±5.69% & 82.10±7.02%) at 15% and 20% of impregnated irons was possibly due to the scavenging effect of HO$_2$ (Equation 5 and 6). In addition, dissolved irons of 2.01±0.48 ppm were observed at 15% of impregnated irons. The amount of impregnated irons in the catalyst should be below 10% to avoid iron leaching and to achieve the national standard limit (2 mg/L). However, change of iron contents in the catalysts need to be further investigated with XRD spectra to confirm reactivity of iron active phases during the heterogeneous Fenton processes.

**Effect of pH on decolorization efficiency**

The active phases of iron oxide, such as goethite ($\alpha$-FeOOH), hematite ($\alpha$-Fe$_2$O$_3$) and maghemite ($\gamma$-Fe$_3$O$_4$) of the PFeAPB, tend to be dissolved in acidic condition to become ferrous and ferric ions, according to Equations 1, 9 and 10. These ferrous and ferric ions promoted •OH radicals to discolor MO. Acidic conditions are known to affect iron phases' reactivity and stability, thus affecting the effectiveness of the Fenton process. It is important to note that these conditions can vary depending on the specific application and the desired outcome.
pH values also shift the equilibrium of Equation 2 to the right which promotes OH radical formation; the high decolorization efficiencies of MO were achieved at pH=2 (80.32 ± 5.26%) and pH=3 (69.10 ± 4.26%). However, if the soluble constant of Fe(OH)$_3$ is theoretically 2.79*10$^{-39}$, precipitation of Fe(OH)$_3$ starts to occur at approximate pH=4.0, thus resulting in decreasing decolorization efficiency (52.05±5.96%) as expected, thus preventing the Fenton process (Equations 1&2). When hydrogen ions in the system are too high (pH=1), these ions may become scavengers of •OH radicals (Equation 11), inducing MO decolorization capability (50.10±5.23%). These results are relatively comparable to other studies$^{1,2,9}$ and indicate a wider range of pH in the heterogeneous Fenton system. A pH=2 was chosen to achieve the highest efficiency for further investigation in this study.

FeOOH$^{(s)}$ + 2H$^+$ + H$_2$O$_2$ → Fe$^{2+}$ + 1/2 O$_2$ + 2H$_2$O (1)

Fe$_3$O$_4$($s$) + 6H$^+$ → 2Fe$^{3+}$ + 3H$_2$O (9)

Fe$_3$O$_4$($s$) + 8H$^+$ → 3/2Fe$^{3+}$ + 3/2Fe$^{2+}$ + 4H$_2$O (10)

H$^+$ + •OH + e$^-$ → H$_2$O (11)
Effect of H$_2$O$_2$ concentration

Effect of H$_2$O$_2$ concentration on MO decolorization efficiencies are contributed by highly oxidation capability of H$_2$O$_2$ species as well as the release of *OH and HO$_2^-$ radicals during reactions between ferrous and ferric ions and H$_2$O$_2$ (Equations 2 & 4). However, when the H$_2$O$_2$ amount is increased over 12.7 mmol/L, the decolorization efficiencies were dropped by 20% due to the scavenging of *OH by H$_2$O$_2$, as shown in Equations 12 &13.

\begin{align*}
\text{OH} + O_2 &\rightarrow HO_2^- + H_2O \quad (12) \\
HO_2^- + \bullet\text{OH} &\rightarrow H_2O + O_2 \quad (13)
\end{align*}

UV-VIS spectroscopy of MO before and after heterogeneous Fenton reaction under different H$_2$O$_2$ concentrations are shown in Figure 6b. The strongest absorbance of MO molecules was at 464 nm. After 120 min of heterogeneous Fenton reaction, this peak disappeared totally when H$_2$O$_2$ concentration was 12.7 mmol/L. A new peak appeared from 232 to 239 nm, possibly because of \(\pi\rightarrow\pi^*\) transition in aromatic compounds. The results indicate that decolorization of MO molecules may occur at azo site (-N=N-) and that the peaks at 232 – 239 nm are possibly benzylamine compounds such as sulfanilic acid. This result is comparable to standard spectroscopy of pure sulfanilic acid$^{15,18}$. The final products of the heterogeneous Fenton processes need to be further analyzed by GC-MS.

Effect of reaction time

The relatively low decolorization efficiency (60.45 ± 3.26%) and COD removal (30.32 ± 3.69%) of MO at the beginning of the heterogeneous Fenton processes (15 min) were possible due to MO molecule diffusion and adsorption on the surface of the catalysts. Once MO molecules were adsorbed on the active sites of irons, heterogeneous Fenton process occurred in the presence of H$_2$O$_2$, thus increasing MO decolorization with time. However, this process was slowed after 120 min because the low catalytic activity, possibly relating to the formation of intermediate oxidation products which inhibited *OH released at iron active sites$^{19}$. Efficient differences between MO decolorization and COD removal efficiencies were from 30 to 40%. The maximum COD removal efficiency was 50.27±6.05% at 150 min while the decolorization efficiency was 88.68±5.69% (Figure 7). These results indicate that heterogeneous Fenton processes using the PFeAPB catalysts may oxidize MO molecules into smaller organic molecules and partly mineralize into CO$_2$ and H$_2$O. Mineralization of azo dyes occurred slowly compared to the decolorization processes. The COD of the MO solution cannot be removed completely, only 50.27±6.05% in 150 min, possibly due to formation of some persistent by-products and short lifetime of radicals. Dissolved irons were increased with reaction time; however, the concentration (max. 1.13±0.068 ppm) was still below the national standard limit in water (2 ppm). Resistance to iron leaching into solution is possibly due to metal complexes between acid organic compounds, such as 2-carboxyphenylacetic acid, phthalic acid, and oxalic acid, which are released as by-products and iron sites on the PFeAPB surface$^{15}$. In addition, iron ions were properly immobilized within the interlayer space and associated with alumina pillars, thus becoming highly resistant to iron leaching$^{20,21}$.

Catalyst reusability and stability

The pillared process between intercalation of aluminum and iron greatly increases accessibility of reactants and reduces their intermolecular collision
and competition at the catalyst sites. Thus, the PFeAPB could be reused two times and yielded 5.22% repeatability (Figure 8). The PFeAPB catalyst activity decreased after 2 runs of reusage (16.39% and 39.08%)- at the 3rd and 4th runs- which may be attributed to iron leaching and intermediate products adsorbed on the active sites.

CONCLUSIONS

This study primarily developed a pellet type of Iron dispersed on Alumina Pillared Bentonite and investigated its capability of MO treatment from water. XRD results showed that there were α-FeOOH, α-Fe₂O₃ and γ-Fe₃O₄ which were supposedly catalyst phases of the heterogeneous Fenton reaction. Because of successful intercalation of Alumina into Bentonite layers, the specific surface area was increased from 57.79 m²/g to 111.22 m²/g, according to the BET results. The PFeAPB catalysts achieved 88.68 ± 5.69% of MO decolorization and 50.27 ± 6.05% of COD removal when experimental conditions of pH, H₂O₂ concentration, catalyst loading, reaction time and initial MO concentration were 2.0 ± 0.1, 12.7 mmol/L, 20 g/L, 150 min and 100 ppm, respectively. The PFeAPB catalyst can be resistant to iron leaching with 11.5% of iron content in the catalyst and can be reused 2 times with 5.22% of repeatability, compared to the new catalyst. The study results indicate that PFeAPB can be a potential catalyst for the heterogeneous Fenton process and applied in textile wastewater with low loss of iron leaching into water. This catalyst should be further investigated in a continuous system.
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LIST OF ABBREVIATIONS

COD: Chemical Oxidation Demand
BET: Nitrogen adsorption/desorption isotherm
MO: Methyl Orange
XRD: X-ray diffractometer
XRF: X-ray fluorescence
PFeAPB: Pellet of iron alumina pillared bentonite
UV-VIS: Ultraviolet visible

AUTHORS’ CONTRIBUTIONS

The author Ngo Thi Thuan discussed the results and wrote the manuscript. The author Tran Tien Khoi edited and revised the final manuscript. The author Nguyen Thi My Chi did the experiment. The author Nguyen Ngoc Vinh trained the instrument operations in laboratory. All authors approved the final manuscript.

COMPETING INTERESTS

The authors declare that they have no competing interests.

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