Fe-Natural Zeolite as Highly Active Heterogeneous Catalyst in Decolorization of Reactive Blue 4

H. Hassan and B. H. Hameed

Abstract—Heterogeneous Fenton-like reaction using Fe-natural zeolite (Fe-NZ) was investigated for the decolorization of Reactive Blue 4 (RB4). The effect of iron ions loading, H₂O₂ concentration and initial pH value were investigated. The maximum decolorization efficiency of 98.71% was achieved at 0.60 wt% of iron ions loading, 16 mM H₂O₂ concentration and an initial pH of 2.5. The high performance of Fe-NZ indicates that the heterogeneous Fenton-like could be efficiently employed for the treatment of wastewater containing azo dye.

Index Terms—Natural zeolite, reactive blue 4, heterogeneous fenton, decolorization.

I. INTRODUCTION

Textile industries have become a high priority environmental concern among other industries due to the intense color of the dyes that lead to serious water resource problem including loss of water purity, and obstruct the light penetration which reduce the photosynthetic activity of marine life [1]. Yearly, about 7 × 10⁹ ton of dyes has been produced worldwide and 10-15% of them have reached the water bodies through the industrial pollutants [2]. Azo dyes are one of the important class of commercial organic colorants and create serious problems in textile wastewater due to their versatility, brilliant color shades, low cost and strong bind with dyed materials [3]. Azo dyes are carcinogenic, mutagenic, recalcitrant, non-biodegradable by aerobic treatment and become toxic to human and animals [4].

Advanced oxidation process (AOPs) based on the in-situ generation of strong and non-selective oxidant species including hydroxyl radical (•OH) become potential alternative technologies to degrade and mineralize organic pollutants to carbon dioxide (CO₂) and water (H₂O) at mild pressure and temperature condition [5], [6]. The AOPs can be broadly classified into: Fenton, Photo-Fenton, UV/H₂O₂, ozonation and natural sunlight [1], [7]. Among the AOPs, Fenton is the most effective and promising technique to generate •OH radical due to its simple operation, low energy consumption, and use of environmental-friendly reagents (Fe³⁺ and H₂O₂) [8]. The classical Fenton involves the reaction between Fe²⁺ or Fe³⁺ with the presence of H₂O₂ for the generation of •OH radical that able to degrade various persistent organic pollutants including azo dyes [9]. However, the process has challenge for application in industries due to the formation of stable ferric complexes (Fe-OOH²⁻ Eq. (1)) which impede the catalytic reaction due to their slow decomposition to generate Fe²⁺ (Eq. (2)) [10].

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \leftrightarrow \equiv \text{Fe} – \text{OOH}^{2+} + \text{H}^+ (k = 3.1 \times 10^{-3}) \]  

(1)

\[ \equiv \text{Fe}-\text{OOH}^{2+} \rightarrow \text{OOH} + \equiv \text{Fe}^{2+} (k = 2.7 \times 10^{-3}) \]  

(2)

Moreover, the application of homogeneous Fenton is limited by the requirement of large amount of H₂O₂ as well as low pH condition (3-5). Therefore, secondary treatments are required for catalyst separation and neutralization which resulted in large-amount of iron-containing sludge that are resistant for disposal [8], [11]. These weaknesses can be overcome by heterogeneous Fenton process where the active phase species such as iron were immobilized onto the catalyst support. By using this technique, the iron leaching could be reduced and the formation of iron hydroxide sludge is prohibited and the spent catalyst can be recovered from the effluent [12]. Different materials such as clay [13], activated carbon [14], synthetic zeolite [15] polymer [16], and mesoporous silica [17] has been applied as catalyst support in heterogeneous Fenton oxidation. Synthetic zeolite is widely used as supported material in heterogeneous Fenton process due to its distinct ion-exchange capability, large surface area, high adsorption capacity, and promising thermal stabilities [15], [18]. Aleksić et al., [15] reported that more than 80% of TOC removal and 100% color removal were achieved when synthetic zeolite was utilized as heterogeneous Fenton catalyst. However, the high cost of synthetic zeolite limits its application especially in developing countries.

Natural zeolite is a hydrated aluminosilicate minerals with some good physicochemical features such as molecular sieving, cation exchange, catalysis and sorption. Because of its valuable properties, they are commercially used as adsorbents to eliminate dyes [19] and heavy metals [20]. These studies concluded that natural zeolite has a great potential as an adsorbent in removing the organic pollutant. The use of natural zeolite as support for Fenton-like process appears more beneficial than synthetic zeolite due to their low cost, abundance and reduced chemical pollution during production [21]. This study aims to investigate the decolorization of Reactive Blue 4 (RB 4) by Fe-natural zeolite via heterogeneous Fenton-like reaction. The effect of major operating conditions such as iron ions loading, catalyst dosage, initial pH solution and H₂O₂ concentration were studied for optimization of decolorization of RB 4 via heterogeneous Fenton-like reaction.
II. EXPERIMENTAL

A. Materials

Natural zeolite (NZ) was obtained from the School of Civil Engineering, Universiti Sains Malaysia. The material was formed in the granular form and was crushed using mortar and sieved to produce particles sizes of 125 µm in diameter. RB 4 was obtained from Sigma-Aldrich Malaysia. Ferrous sulfate supplied by Sigma-Aldrich was used as iron source of the catalyst. Other chemical used were sulfuric acid (98% purity), 30 wt% hydrogen peroxide and sodium hydroxide (99% purity). All chemicals were used without further purification.

B. Preparation of Fe-Natural Zeolite

Impregnation method was used to immobilize the iron onto the NZ. In this process, required amount of ferrous sulfate salt was dissolved in distilled water to make an aqueous solution followed by the addition of NZ. The resultant suspension was continuously stirred at 70 °C in water bath until all water was evaporated. The sample was further dried overnight at 105 °C and subsequently calcined at 500 °C in a muffle furnace for 4 hr. Finally, the catalyst was stored in a desiccator to prevent moisture absorption.

C. Characterization of Fe-Natural Zeolite

The porosity, shape, and roughness of the NZ and Fe-NZ were characterized by scanning electron microscopy (SEM). The analysis was carried out using a scanning electron microscope (Model Leo Supra 50VP Field Emission, UK). The elemental composition present in the catalyst was determined using Energy Dispersive X-ray (EDX) microanalysis system (Oxford INCA 400, Germany) connected to the SEM.

D. Catalytic Activity Test

Experiments were conducted in a 250 mL-stoppered glasses (Erlenmeyer flask). The volume of reaction solution was 200 mL. The RB4 solution was freshly prepared at room temperature by dissolving suitable amount of powder in distilled water. In a typical experiment, 200 mL of 50 mg/L of reaction solution was fixed. The initial pH of the solution was adjusted by an addition of 1.0 M sulfuric acid or 1.0 M sodium hydroxide. Then, the catalyst was added into the solution and this solution was withdrawn by a syringe and the catalyst was filtered through 0.45 µm membrane for analysis.

The concentration of RB4 was measured using using a double beam UV/Vis spectrophotometer (Shimadzu, model UV 1601, Japan) at 595 nm wavelength. To prevent any loss of content, the samples withdrawn at each time interval were returned into the conical flask. The effect of iron ions loading (0.20 – 1.0 wt%), catalyst dosage (1.0 – 5.0 g / L)-1, initial pH value (2.0–5.0), initial H2O2 concentration (4–20 mM) on the decolorization of RB4 were evaluated. The decolorization efficiency of RB4 was calculated according to Eq. (3):

\[
\text{Decolorization efficiency (\%) = } \frac{C_0 - C_t}{C_0} \times 100 \%
\]

where \(C_0\) is the concentration of RB4 before the heterogeneous Fenton reaction and \(C_t\) is the concentration of RB4 at the time of withdraw.

III. RESULTS AND DISCUSSION

A. Catalyst Characterization

The surface of the NZ and 0.60 wt.% Fe-NZ particles were shown in Fig. 1(a)-(b). The image of NZ shows the heterogeneity of the particle size. Most of the particles had a rough surface except a few, which showed a smooth surface. In addition, the natural zeolite has well shaped needles, which represents a well crystallized mordenite. However, after impregnation process, the modified NZ exhibited poorly shaped needles and the surfaces become more porous.

The chemical composition of pristine NZ and 0.60 wt% of Fe-NZ are shown in Table 1. The EDX analysis showed that the oxide and iron content in Fe-NZ were increased by 0.7 % after impregnation process due to transformation of iron containing complexes to iron oxide or hydroxide particles after calcinations. Slight variations between the determined and calculated iron content of the Fe-NZ due to the high hydration degree of solid at the initial stages of the catalyst preparation [22].

B. Role of Different Mechanisms

In order to elucidate the influence of different mechanism
Catalytic activity was studied by varying the iron ions loading from 0.20 to 1.0 wt% and the result was shown in Fig. 3. Based on the result, the decolorization efficiency increased efficiently up to 0.60 wt% iron ions with the maximum decolorization of 93.84% in 120 min. The maximum decolorization at 0.60 wt% could be due to increase of catalytic active site available for the decomposition of H2O2 into •OH [22]. Interestingly, no induction periods are observed and high initial decolorization rate were observed, suggesting Fe-NZ has enough quantity of active sites (Fe2+) for faster production of highly reactive •OH and heterogeneous Fenton reaction react as a main contributor in catalytic activity [24]. Induction period can be defined as a period of time needed for surface activation of metal species (decrease to lower oxidation state) or dissolve of adequate metal for initiation of homogeneous solution [3]. However, the decolorization decreased with further increased in iron ions loading, suggesting the inhibition effect induce by excess of iron ions loading on the •OH as shown in Eq. (4).

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^-$$ (4)

In addition, when the iron ions loading is in excess compared to H2O2, the superoxide radical anion (O_2^−) could be produced in the presence of O2 as in Eq. (5). This radical could be further react with iron ions species as shown in Eq. (6).

$$\text{Fe}^{2+} + \text{O}_2 \rightarrow \text{Fe}^{3+} + \text{O}_2^-$$ (5)

$$\text{Fe}^{2+} + \text{O}_2^- + 2\text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2$$ (6)

All these reaction mechanisms could deaccelerate decolorization of dye [25].
radical able to degrade and oxidize many organic pollutants (Eq. 10). The influence of \( \text{H}_2\text{O}_2 \) (4 – 24 mM) is presented in Fig. 4.

\[
\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (7)
\]

\[
\text{HO}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (9)
\]

E. Effect of Initial pH Value

It can be seen that the decolorization efficiency was increased from 90.53 % to 97.80 % as the \( \text{H}_2\text{O}_2 \) increased from 4 mM to 16 mM due to enhanced generation of reactive \( \cdot\text{OH} \). However, the decolorization efficiency decreased with further increased in \( \text{H}_2\text{O}_2 \) dosage due to scavenging of \( \cdot\text{OH} \) with itself or by the superfluous of \( \text{H}_2\text{O}_2 \) (Eq. (7) and (8)). The superfluous amount of \( \text{H}_2\text{O}_2 \) would react with \( \cdot\text{OH} \) to produce hydroperoxyl radical (\( \text{HO}_2^- \)) which is less reactive (Eq. (7)) [26]. The hydroperoxyl radical is less reactive and did not contribute to the degradation of RB4 which lead to decrease in decolorization efficiency (Eq. (9)).

\[
\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (7)
\]

\[
\text{OH}^- + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad (8)
\]

\[
\text{HO}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (9)
\]

IV. Conclusion

Fe-natural zeolite showed promising catalytic activity for effective decolorization of Reactive Blue 4 in heterogeneous Fenton-like reaction. Heterogeneous Fenton reaction play a prominent role in decolorization of RB4 where the iron species available on the surface of the catalyst or in the interlayer of catalyst could react with \( \text{H}_2\text{O}_2 \) to generate the highly reactive \( \cdot\text{OH} \) for decolorization of RB4 dye. The maximum decolorization of 98.71 % was achieved in 120 min under the following condition: 0.60 wt % of iron ions loading on natural zeolite, \( \text{H}_2\text{O}_2 \) concentration of 16 mM and initial pH of 2.5. The use of natural zeolite as support for Fenton-like process could be a practical and economical substitute for synthetic zeolite as it is abundant, low-cost and exhibited higher decolorization efficiency.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Hamizura Hassan was involved in experimental works and analysis, compilation results and drafting the manuscript whereas Bassim H. Hameed supervised the project, verifying the result for its intellectual content as well as provided critical feedback. All authors had approved the final version.

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REFERENCES

[1] H. T. Van, L. H. Nguyen, T. K. Hoang, T. P. Tran, A. T. Vo, T. T. Pham, and X. C. Nguyen, “Using FeO-constituted iron slag wastes as heterogeneous catalysts for Fenton and ozonation processes to degrade Reactive Red 24 from aqueous solution,” Separation Purification Technology, vol. 224, pp. 431–432, October 2019.

[2] Z. Oruç, M. Ergüt, D. Uzuno, and A. Özer, “Green synthesis of biomass-derived activated carbon / Fe-Zn bimetallic nanoparticles from lemon (Citrus limon (L.) Burm.f.) wastes for heterogeneous Fenton-like decolorization of Reactive Red 2,” Journal of Environmental Chemical Engineering, vol. 7, pp. 103231, August 2019.

[3] L. Singh, P. Rekha, and S. Chand, “Cu-impregnated zeolite Y as highly active and stable heterogeneous Fenton-like catalyst for degradation of Congo red dye,” Separation Purification Technology, vol. 170, pp. 321–336, June 2016.

[4] E. Guivarch, S. Trevin, and C. Lahitte, “Degradation of azo dyes in water by Electro-Fenton process,” Environmental Chemistry Letters, vol. 1, pp. 38–44, March 2003.

[5] Y. Ahmed, Z. Yaakob, and P. Akhtar, “Degradation and mineralization of methylene blue using a heterogeneous photo-Fenton catalyst under visible and solar light irradiation,” Catalysis Science and Technology, vol. 6, pp. 1222–1232, November 2015.

[6] H. Hassan and B. H. Hameed, “Oxidative decolorization of Acid Red 1 solutions by Fe-zeolite Y type catalyst,” Desalination, vol. 276, pp. 45–52, August 2012.

[7] A. Garcia, “Study of kinetic parameters related to the decolorization and mineralization of reactive dyes from textile dyeing using Fenton and photo-Fenton processes,” Dye Pigment, vol. 75, pp. 647–652, 2007.

[8] S. Adityosulindro C. Julcour, and L. Barthe, “Heterogeneous Fenton processes,” Gharibian, “High efficient Fenton and electro-Fenton reaction,” Applied Catalysis B: Environmental, vol. 4, pp. 2469–2476, April, 2016.

[9] H. S. El-desoky, M. M. Ghoneim, R. El-sheikh, and N. M. Zidan, “Oxidation of Levafix CR aqueous solutions by the photo-Fenton and Fenton-like processes,” Journal of Photochemistry and Photobiology A: Chemistry, vol. 161, pp. 87–93, May 2003.

[10] K. M. Valkaj et al., “Phenol oxidation with hydrogen peroxide using Cu/ZSM5 and CuY catalysts,” Polish Journal of Chemical Technology, vol. 13, pp. 28–36, 2011.

[11] J. Shen, Y. Li, Y. Zhu, Y. Hu, and C. Li, “Aerosol synthesis of Graphene-Fe3O4 hollow hybrid microspheres for heterogeneous Fenton and electro-Fenton reaction,” Journal of Environmental Chemical Engineering, vol. 4, pp. 2469–2476, April, 2016.

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