Decolorization of Acid Red 1 using natural zeolite via heterogeneous fenton-like oxidation

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Abstract. Fenton process can be regarded as powerful and effective method in decolorization and mineralization of dye pollutants. However, this method is restricted with the generation of iron waste sludge which require secondary treatment. This limitation can be overcome by utilizing heterogeneous Fenton process where iron ions are immobilized onto the catalyst support. In the present study, the heterogeneous Fenton-like oxidation using Fe-natural zeolite (Fe-NZ) was investigated in decolorization of azo dye Acid Red 1 (AR1). The effects of iron ions loading, catalyst dose and initial pH on the decolorization of AR1 were evaluated. The maximum decolorization efficiency of 99.60% was achieved at 0.80 wt% of iron ions loading, 5.0 g/L of catalyst dose, and at 2.5 initial pH. The Fe-NZ showed high catalytic performance for decolorization of AR1 and could be regarded as a suitable low-cost catalyst in heterogeneous Fenton-like reaction.

1. Introduction
Textile, dyestuff, plastic, and paper industries consume large volume of water to color their products and consequently generates substantial amount of colored wastewater [1]. Untreated colored effluents from these industries interfere the natural growth activity of aquatic life by hindering sunlight and oxygen transfer into water bodies [2,3]. Azo dyes, which represents more than 50% global dye production are the largest synthetic organic dyes due to their widely used in dyeing industries. Generally, azo dyes which contain nitrogen to nitrogen double bond (-N=N-) are not biodegradable by biological treatment and persistent in water bodies. Numerous treatments have been extensively used to eliminate the effect of azo dyes contamination such as physicochemical treatment (e.g. coagulation, precipitation, and adsorption), bacterial and fungal treatment, synthetic biology and oxidative processes [4,5]. Advanced oxidation processes (AOPs) have transpired as a potential alternative for the elimination of organic pollutants derived from industrial wastewater and are profoundly useful in the case of substances resistant to conventional technologies without producing secondary wastes. AOPs are based on the production of highly reactive hydroxyl radicals (•OH) that possess strong oxidant power (•OH + H+ + e– → H2O; Eo = 2.80 V) and non-selectivity attack that able to decolorize and degrade recalcitrant pollutants in dye wastewater [6].

Fenton process is one type of AOPs that comprise of reaction between iron ions (e.g Fe(II)/Fe(III)) with hydrogen peroxide (H2O2) to form active oxygen species such as (•OH) and hydroperoxyl
(•OOH) radicals that able to oxidize organic or inorganic compounds under mild conditions [5]. The iron ions act as a catalyst to break-down the H₂O₂ molecules to generate the •OH. The production of •OH is generally accelerated by combining UV radiation, O₃, TiO₂, ultrasound, and electron-beam irradiation [7]. However, in the treatment of real dyeing wastewater, the homogeneous Fenton is restricted by the narrow pH range (pH 2-3), difficulties in catalyst recovery and hydrolysis of iron ions that require further treatment after each run [3,8]. To overcome these limitations, the heterogeneous Fenton-like catalyst have gained much attention in recent years [9,10]. In heterogeneous Fenton, the iron species is deposited onto and in the pore/ interlayer space of support. By using this technique, the catalyst can continuously generate •OH from H₂O₂ and iron hydroxide sludge is prohibited [3]. A wide range of solid materials, such as bentonite [11], SBA-15 [8], zeolite [3,12] and MCM-41 [13] have been utilized as support for the oxidative degradation of organic compounds through the Fenton reaction. Among the various support, zeolite is widely applied in Fenton process because of its large surface area, distinct ion-exchange capability, high adsorption capacity, promising thermal stabilities and environmental friendly [14,15].

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 [14]. Arimi [6] investigated the removal of colored recalcitrants in molasses distillery wastewater (MDW) by using sulphuric acid-ferrous modified natural zeolite catalyst. The authors reported that about 90% and 60% of color and total organic carbon (TOC) were removed, respectively. In addition, the maximum removals of color and TOC were achieved at higher pH value (pH = 5) as compared to conventional homogeneous Fenton which operated at narrow pH value (pH 2-3). Herein, the feasibility of value-added iron-modified natural zeolite (Fe-NZ) catalyst was investigated in banishment of AR1 dye by heterogeneous Fenton-like reaction. The effect of iron loading, catalyst dose and initial pH were evaluated to optimize the decolorization of AR1.

2. Method
2.1 Materials and chemicals
Natural zeolite was attained from the School of Civil Engineering, Universiti Sains Malaysia. The material was shaped in a granular form and was crushed using mortar before being sieved through sieve no. (125 μm). Sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂) (30%, w/w), and ferrous sulfate (FeSO₄·7H₂O) were obtained from Merck, Germany. The commercial Acid Red 1 (AR1) was bought from Sigma-Aldrich (M) Sdn Bhd, Malaysia. All chemicals were used as received without further purification.

2.2 Catalyst preparation and characterization
The Fe-NZ was synthesized using impregnation method [1]. A predetermined quantity of FeSO₄·7H₂O was dissolved in distilled water to make an aqueous solution. Immediately afterwards, the natural zeolite was added into the solution. The mixture was stirred uniformly in the water bath until all water was evaporated. The resulting sample was dried at 100 °C for 12 h and calcined at 500 °C for 4 h. Then the sample was crushed by mortar and stored in a desiccator prior to use. The textural properties (pore size and pore volume) of the catalyst were analysed using nitrogen adsorption–desorption method. The characterization was carried out by using a surface area analyzer Autosorb 1 (Quantachrome Corporation, USA). The pore volume and surface area of the prepared catalyst were calculated based on Brunauer-Emmett-Teller (BET) theory while the average pore width and pore size distribution were characterized by the Barret–Joyner–Halenda (BJH) method. The crystal phase and structure of the natural zeolite and Fe–NZ were examined using X-ray diffraction with Siemens d-5000 diffractometer and a graphite secondary beam monochromator operated at 30 mA and 40 kV with filtered CuKα radiation (λ=1.5418 Å). The diffraction angle of the samples was observed in the 2θ scan range of 10° to 90°.
2.3 Catalytic activity
The catalytic activity was performed in a 250 mL-stoppered glasses (Erlenmeyer flask) filled with 200 mL diluted solutions (25–100 mg/L). The pH was modified using 1.0 M H₂SO₄ and 1.0 M NaOH before the introduction of catalyst. The reactions were started once calculated volume of H₂O₂ solution was added to the flask. Then, the flask was transferred to water bath shaker where the solutions were stirred at 130 rpm. After certain time interval, the solutions were withdrawn and the concentration of AR1 were measured using a double beam UV/Vis spectrophotometer (Shimadzu, model UV 1601, Japan) at 532 nm wavelength. The effect of iron loading on supported catalyst in the decolorization of AR1 was evaluated over the iron loading varied from 0.20 to 1.0 wt. %. The H₂O₂ concentration and solution pH were fix at 4 mM and 2.8, respectively. On the other hand, the effect of catalyst dose was studied by varying the amount of dosage used (0.50, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 g/L), while pH, agitation speed, initial dye concentration and temperature were set at 2.8, 130 rpm, 50 mg L⁻¹ and 30 °C, respectively. In addition, the activity of Fe-NZ in decolorization of AR1 was further tested by varying the pH of the solution in the range of 2.0-5.0. The decolorization degree of AR1 can be calculated based on Equation (1):

\[
\text{Decoloration degree (\%)} = \left( \frac{C_o - C_t}{C_o} \right) \times 100\%
\]  

(1)

where \( C_o \) (mg/L) is the initial concentration of AR1 and \( C_t \) (mg/L) is the final concentration of AR1 at treatment time, \( t \) (min).

3. Results and discussion
3.1 Characterization of catalyst
Figure 1 shows the nitrogen adsorption isotherm for 0.60 wt.% Fe-NZ and BJH pore distribution of Fe-NZ catalyst. According to IUPAC classification, Fe-NZ displayed type IV isotherm which suggested a mesoporous nature. The hysteresis loops of FE-NZ resembled H4 type which can be related to porous material in the form of narrow slit-like pores [2]. The BET surface area, pore volume and average pore size of Fe–NZ are 31.9 m² g⁻¹, 0.068 cm³ g⁻¹ and 85.08 Å, respectively.

![Figure 1. Nitrogen adsorption desorption isotherms of Fe-NZ.](image)
X-ray diffraction measurement was utilized to examine the iron chemical state and the dispersity of Fe ion in catalysts. Figure 2 shows the XRD pattern for natural zeolite (NZ) and impregnated natural zeolite (Fe-NZ). The result shows that impregnation with iron ions does not lead to significant structural changes. The diffraction diagram shows that both samples in crystalline phase. The comparative analysis of both NZ and Fe-NZ shows that decrease in intensity at 2θ = 22.69°, 27.14°, 28.33° and 30.22° in the NZ spectrum. No new peaks are appearing and three sharp peaks due to iron phases are observed in the diffractograms at 2θ = 28.33°, 30.22° and 32.30° after calcinations of the impregnated catalyst. It can be deduced that impregnated catalyst (Fe-NZ) mainly consists of Fe₂O₃.

![XRD diffractograms of the NZ and Fe-NZ catalysts.](image)

**Figure 2.** XRD diffractograms of the NZ and Fe-NZ catalysts.

### 3.2 Effect of iron ions loading on natural zeolite

In heterogeneous Fenton like process, the iron ions (Fe²⁺) activated the decomposition of H₂O₂ on the surface of the support resulting in the generation of hydroxyl radicals (HO•) where the symbol ≡ signifies the iron species that dispersed on the catalyst surface as shown in Equation 2 and 3. These hydroxyl radicals able to degrade the organic pollutants through redox reaction, dehydrogenation and electrophilic addition reactions [3].

\[ \equiv \text{Fe}^{3+} + H_2O_2 \rightarrow \equiv \text{Fe}^{2+} + HOO^- + H^+ \]  \hspace{1cm} (2)

\[ \equiv \text{Fe}^{2+} + H_2O_2 \rightarrow \equiv \text{Fe}^{3+} + HO^- + OH^- \]  \hspace{1cm} (3)

The influence of iron ions loading on natural zeolite in decolorization of AR1 was investigated by varying the iron ions loading between 0.20 wt% and 1.0 wt% and the result was presented in Figure 3. As can be seen in Figure 3, the decolorization of AR1 was increased up to 0.60 wt% of iron ions loading with the maximum decolorization of 95.26% within 150 min reaction time. This behavior can be attributed to the enhancement of 'OH radical production as the iron ions concentration increased [4]. However, the decolorization efficiency of AR1 is declined with further increased in iron ions loading due to scavenging effect of OH radicals by iron ions as shown in Equation 4 [5].

\[ \text{Fe}^{2+} + \cdot OH \rightarrow \text{Fe}^{3+} + OH^- \]  \hspace{1cm} (4)

In heterogeneous catalyst, the iron ions are embedded on the support, which makes the process
more flexible in terms of controlling high sludge formation resulted from coagulation or iron oxyhydroxides deposition. However, this process could have slower kinetic compared to homogeneous Fenton reaction due to less contact area between oxidants and catalyst as the iron ions are embedded onto the support and not freely available in the solution [6].

Figure 3. Effect of iron ions loading on natural zeolite on decolorization of AR1. Reaction conditions: [AR1]₀ = 50 mg L⁻¹, pH = 2.5, [H₂O₂] = 4.0 mM, catalyst dosage = 2.0 g L⁻¹, temperature = 30 °C and agitation speed = 130 rpm.

The decolorization of AR1 by Fe-NZ achieved maximum 99% decolorization with maximum iron ions concentration of 0.60 wt.%. From Figure 3, it is noticeable that there was a kind of delayed formation of the heterogeneous Fenton oxidation mechanism for Fe-NZ catalyst. The Fenton reaction observed here shows an induction period followed by high oxidation of AR1. Induction period occur typically in several aqueous Fenton reactions catalyzed by pillaring clays [7]. An induction period can be outlined as a period of time needed for surface activation of iron species which are then capable of forming complexes with the reactants prior to the initiation of oxidation process. Other possible reason for the existence of an induction period can be associated with the time required to dissolve adequate amount of iron species for homogeneous Fenton reaction to occur [8]. Some researchers relate the induction period with the adsorption process of reactant onto the surface of catalyst [7,9]. Normally, an induction period occur followed by an abrupt surge in the rate of reaction [9]. The observed induction period in the present stipulates the presence of an initial sluggish transfer of iron ions from the BC and NZ surface into the solution. Once it is produced, in presence of H₂O₂, the reaction rate is remarkably increased. Based on the result above, 0.60 wt% Fe-NZ was selected as the optimum iron ions loading for the decolorization of AR1.

3.3 Effect of catalyst dose
The effect of catalyst dose (0.50 to 5.0 g L⁻¹) on decolorization of AR1 was shown in Figure 4. In heterogeneous Fenton type processes, the reaction between ferrous ion or ferric ion with hydrogen peroxide occurs at the solid surface of catalysts which hinges on the specific area of the catalyst. Based on Figure 4, the decolorization efficiency of AR1 increased from 74.57% to 99.60% when the catalyst dose increased from 1.0 to 5.0 g/L within 210 min of reaction time. The plausible reason for such trends is the increasing availability of active sites and total area of Fe(II)/Fe(III) (Equation (5) and (6)) for organic compound adsorption and hydrogen peroxide decomposition as the catalyst dose increased. This would result in the quicker decomposition of H₂O₂ to produce hydroxyl radical (OH⁻) [10].

\[
H_2O_2 + Fe(II) \rightarrow OH^- + Fe(III)
\]  
(5)
Similar trend was observed by Adityosulindro et al. [11] on the removal of ibuprofen (IBP) by heterogeneous Fenton reaction using Fe-ZSM-5 catalyst. The authors reported that the increased in catalyst loading from 1 to 4.8 g/L brought a positive impact to IBP and TOC removal due to higher amount of active sites available for \( \text{H}_2\text{O}_2 \) decomposition. This inference was confirmed by the increased in oxidant utilization of 26%, 65% and 79% which correspond to 1 g/L, 3 g/L and 4.8 g/L of catalyst concentration, respectively.

\[
\text{OH}^* + \text{dye} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Mineralization products}
\]  

**Figure 4.** Effect of catalyst dose on the decolorization of AR1. Reaction conditions: \([\text{AR1}]_o = 50 \text{mg/L}, [\text{H}_2\text{O}_2]_o = 4 \text{mM}, \text{pH} = 2.5, \text{catalyst loading} = 0.60 \text{wt.\% of Fe–NZ}, \text{temperature} = 30 \degree\text{C and agitation speed} = 130 \text{rpm}.

3.4 Effect of pH

The influence of the initial solution pH (2.0 –5.0) on the decolorization of AR1 via heterogeneous Fenton like system is depicted in Figure 5. The optimal pH value was obtained at pH 2.5 with 98.36% decolorization efficiency within 180 min reaction. Generally, the optimal pH value for the Fenton and Fenton-like process is obtained at pH value range from 2.5–3.0 [12]. It should be noted that at low pH (pH ≤ 2) value, the H\(_2\)O\(_2\) species might be solvated by the excess of proton (H\(^+\)) to form an oxonium ions (H\(_3\)O\(_2^+\)) as shown in Equation 7 [13] which reduce the reactivity between H\(_2\)O\(_2\) and Fe\(^{2+}/\)Fe\(^{3+}\).
Figure 5: Effect of pH on the decolorization of AR1. Reaction conditions: temperature = 30 ºC, [H$_2$O$_2$]$_0$ = 4.0 mM, [AR1]$_0$ = 50 mg L$^{-1}$, catalyst loading = 0.60 wt. % of Fe–NZ, catalyst dose = 5.0 g/L, and agitation speed = 130 rpm.

The low decolorization efficiency at pH 4 and 5 could be attributed to the formation of iron hydroxide (Fe(OH)$_2$ or Fe(OH)$_3$) which detrimental to the production of $^\cdot$OH due to small amount of Fe$^{2+}$/Fe$^{3+}$ ions to react with H$_2$O$_2$ [13,14].

In addition, the lower decolorization efficiency at pH > 3 could be associated to the scavenging effect of OH$^-$ by H$^+$ (Equation 7), the lower oxidation capacity of OH$^-$ in higher pH solution and unstable condition of H$_2$O$_2$ that decomposed into oxygen (O$_2$) and water (H$_2$O) [5] which incapable to oxidize the organic efficiently [1].

\[
OH^+ + H^+ + e^- \rightarrow H_2O
\]  

(7)

Aleksić et al. [15] reported that more than 90% of decolorization of Reactive Blue 137 (RB 137) was achieved at all tested pH (3-8) except pH 2 while the highest mineralization of RB 137 (57% and 58%) was obtained at pH 4 and 5 under catalysis of Fe-exchanged ZSM-5 zeolite (Fe-ZSM-5). However, as the pH of the solution increased to 6 and 7, the mineralization decreased to 37% due to the formation of stable ferric hydro-complexes that hinders Fenton reaction process. The authors also emphasized that the heterogeneous Fenton reaction using Fe-ZSM-5 could be operated at milder pH value due to the structure of ZSM-5 zeolite that possessed strong electrostatic field of zeolite framework. As pH approaches neutral value, the interaction between negatively charged zeolite with positively charged iron ions could delay the formation of stable hydro-complexes with iron ions.

4. Conclusion
In this study, the feasibility of Fe-NZ as heterogeneous catalyst was investigated in the decolorization of AR1. The results showed that the iron ions loading, catalyst dose and initial pH solution strongly affect the overall decolorization efficiency. The Fe-NZ showed promising catalytic activity with maximum decolorization efficiency of 99.60% was achieved at 0.80 wt% of iron ions loading, 5.0 g/L of catalyst dose, and at 2.5 initial pH. This study showed that the heterogeneous Fenton-like reaction could be considered as promising technique for banishment of dye pollutant and Fe-NZ has proven to be excellent heterogeneous catalyst in decolorization of AR1.
Acknowledgments
The authors would like to thank Universiti Teknologi MARA Cawangan Pulau Pinang for the financial support in publishing this paper.

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