

Decolorization of Acid Red 1 by heterogeneous Fenton-like reaction using Fe-ball clay catalyst

H. Hassan

Faculty of Chemical Engineering
Universiti Teknologi Mara (UiTM)
Permatang Pauh, 13500 Pulau Pinang, Malaysia
e-mail: hamizura179@ppinang.uitm.edu.my

B.H. Hameed

School of Chemical Engineering, Engineering Campus
University of Science Malaysia (USM)
14300 Nibong Tebal, Pulau Pinang, Malaysia
e-mail: chbassim@eng.usm.my

Abstract—In this work, the Fenton-like decolorization of an azo dye, Acid Red 1 (AR1) by Fe-ball clay (Fe-BC) catalyst was studied. The effects of different reaction parameters such as initial iron ions loading on ball clay (BC), catalyst dosage and initial concentration of hydrogen peroxide (H_2O_2) and AR1, and solution pH on the decolorization of AR1 were assessed. The results indicated that by using 12 mM of H_2O_2 and 5.0 g L^{-1} of the 1.0 wt.% iron ions on BC at pH 2.5, 99% of decolorization efficiency was achieved within 180 min in a batch process. The results indicated that Fe-BC was a promising catalyst for the heterogeneous Fenton system.

Keywords—Decolorization, Acid Red 1; Fe-ball clay, Fenton-like, Heterogeneous Fenton

I. INTRODUCTION

Azo dyes, characterized by the presence of one or more azo groups (-N=N-) bound to aromatic rings, are the largest and most important class of synthetic organic dyes. It has been estimated that more than 50% of all dyes in common use are azo dyes because of their chemical stability and versatility [1]. About 10-15% of the synthetic textile dyes used are lost in waste streams during manufacturing or processing operations [2]. The effluents are strongly colored which not only created environmental and aesthetic problems, but also posed a great potential toxic threat to ecological and human health as most of these dyes are toxic and carcinogenic [3]. Azo dyes are not biodegradable by aerobic treatment processes [4]. In addition, under anaerobic condition, they are reduced to potentially carcinogenic aromatic amines which cause long term health concerns [5]. The new environment regulations concerning textile products have banned the discharge of colored waste in natural water bodies [6]. Therefore, an effective and economic treatment of effluents containing diversity of textile dyes has become a necessity for clean production technology for textile industries [7].

Fenton technology is widely studied and reported as an interesting alternative for the treatment of industrial wastewater containing non-biodegradable organic pollutants. However, the homogeneous Fenton process has significant disadvantages: (i) iron ions have to be separated from the system at the end of the process by precipitation, which is expensive in labor, reagents and time; (ii) it is limited by a narrow pH range (pH 2–3); and (iii) iron ions may be

deactivated due to complexation with some iron complexing reagents such as phosphate anions and intermediate oxidation products [8]. To overcome the disadvantages of Fenton type processes, heterogeneous Fenton and Fenton like catalyst have recently received much attention. In heterogeneous Fenton process, iron salts, were adsorbed onto the surface of supported catalysts, and in a suitable aqueous medium; the reduction-oxidation reactions between Fe(II)/Fe(III) take place in presence of hydrogen peroxide which promote the formation of reactive components such as ($\cdot OH$) and hydroperoxyl ($\cdot OOH$) radicals [9]. The radicals generated by the decomposition of hydrogen peroxide can oxidize organic compounds adsorbed over the catalyst or degrade soluble organic compounds in the vicinity of active iron ions present at both the catalyst surface and in the bulk liquid phase. Thus, the Fe(III)/Fe(II) complex formed on the surface of support can react with H_2O_2 thus allowing iron ions to participate in the Fenton catalytic cycle [10].

Being inexpensive and widely available, clays represent an attractive substrate for iron immobilization. Clays are natural minerals with hydrous aluminum phyllosilicates and feature a layered structure composed of silicate (Si_2O_5) sheets bonded to aluminum oxide/hydroxide ($Al_2(OH)_4$) sheets (also called gibbsite sheets). The wide usefulness of clay minerals is essentially a result of their high specific surface area, high chemical and mechanical stabilities, and a variety of surface and structural properties [11].

In this work, the decolorization of the non-biodegradable azo dye, Acid Red 1 (AR1) by heterogeneous Fenton-like process using Fe-ball clay (Fe-BC) catalyst were determined. The effects of different initial iron ions loading on ball clay (BC), initial concentration of H_2O_2 and AR1, catalyst dosage and initial pH solution on the decolorization efficiency of the process were discussed.

II. EXPERIMENTAL

A. Chemical and reagents

Azo dye, AR1 and hydrogen peroxide (30%, w/w) was purchased from Sigma-Aldrich (M) Sdn Bhd, Malaysia. The ferrous sulfate ($Fe\ SO_4 \cdot 7H_2O$) was obtained from Merck, Germany. The pH of the solution was adjusted by 1.0 M H_2SO_4 or 0.10 M NaOH. All of chemicals used were

analytical grade without any further purification. Distilled water was used throughout the study.

B. Preparation of Fe-ball clay (Fe-BC)

Ball clay was obtained from School of Material Science Universiti Sains Malaysia, Malaysia and was used as received. The Fe-BC was prepared by the impregnation method [12]. In this process, Fe SO₄.7H₂O (Merck) was dissolved in a beaker containing distilled water. Then, ball clay was added to this aqueous solution and was stirred by a glass rod uniformly in the water bath until all water was evaporated. The resulted products were finally dried at 85°C for 12 h and then calcined at 500°C for 4 h in a muffle furnace.

C. Catalytic activity

All experiments were carried out in a 250 mL-stoppered glasses (Erlenmeyer flask) filled with 200 mL diluted solutions (50–100 mg/L). The pH was adjusted to the desired value by using 1.0 M H₂SO₄ or 1.0 M NaOH which was followed by the addition of catalyst. The reactions were initiated by adding predetermined amounts of H₂O₂ solution to the flask. The flasks were then placed in a thermostated water bath shaker and agitation was provided at 130 rpm. The samples were taken out from the flasks periodically by using disposable syringes and were filtered by using BOECO filter (SFCA-membrane, 0.45 μm) for the separation of catalysts from the aqueous solution. The concentrations of dyes were measured using a double beam UV/Vis spectrophotometer (Shimadzu, model UV 1601, Japan) at 532 nm wavelength. At each stage, the samples withdrawn were returned into the conical flask to prevent any loss of contents.

The effect of iron ions loading on BC was studied by varying the iron ions loading range from 0.20 to 1.0 wt. %. Furthermore, the activity of this catalyst to decolorize AR1 was tested by varying other parameters such as pH in the range of 2.0-5.0, initial concentration of H₂O₂ between 4.0-20 mM, initial concentration of AR1 from 25-50 mg L⁻¹. Similarly, the concentration of catalyst dosage in the range of 1.0-5.0 g L⁻¹ was also studied. The solutions were agitated in a thermostated water bath shaker at 130 rpm and samples were withdrawn for analysis at intervals of time. In all the experimental runs, as described above, other parameters were kept constant and samples were being withdrawn at regular intervals of time for the analysis.

The decolorization efficiency of AR1 was defined as follows:

$$\text{Decolorization efficiency (\%)} = \left(\frac{C_o - C_t}{C_o} \right) \times 100 \% \quad (1)$$

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

III. RESULT AND DISCUSSIONS

A. Effect of iron ions loading on BC

The effect of iron ions loading on the BC was investigated by varying the iron ions concentration from 0.20

to 1.0 wt.% and the results was shown in Fig.1. By increasing iron ions loading on the BC, the decolorization rate increasing efficiently and 99% decolorization was achieved for 1.0 wt.% within 120 min. Hence, 1.0 wt.% of iron ions loading was found to be optimum for maximum efficiency. The fact that higher decolorization efficiency achieved at high iron ions concentration was mainly attribute to the higher production of ·OH with the increase of iron ions concentration.

Fig. 1 also showed some sorts of delayed establishment of the heterogeneous Fenton oxidation during the initial reaction time followed by rapid oxidation of AR1. An induction period is defined as a period of time during which no measurable reactions occurs or a time before a reaction suddenly increases in rate [13]. Here the induction period probably has two causes. First, it is thought as activation process of surface iron species, which are thus enabled to form complexes with the reactants (AR1) before the oxidation process can occur. Second, it is attributed to the time needed to dissolve enough iron for homogeneous Fenton reaction to take place. The second cause is less likely because, the concentration of dissolved iron was low (1.234 mg L⁻¹) so that the homogeneous Fenton reaction is negligible [14]. Carriazo et al. [15] suggested that the induction period is related to the adsorption of reactant onto the catalyst surface. In the present study the best iron ions loading for the decolorization of AR1 was experimentally determined to be 1.0 wt.%.

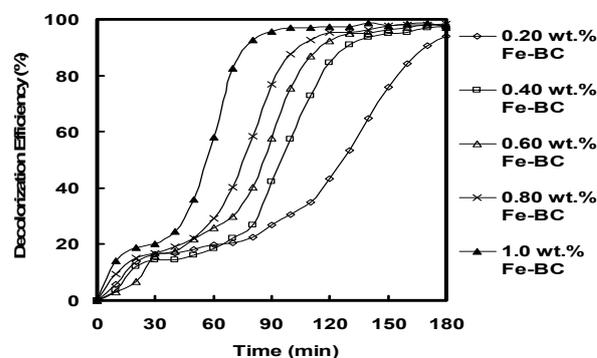


Fig. 1. Effect of iron ions loading on BC on the decolorization of AR1. Reactions conditions: [AR1]_o = 50 mg L⁻¹, [H₂O₂]_o = 4 mM, pH = 2.5, catalyst = 2.0 g L⁻¹, temperature = 30 °C and 130 rpm.

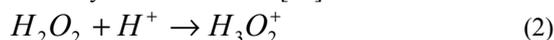
B. Effect of catalyst dosage

The influence of catalyst dosage on AR1 decolorization was studied by varying the catalyst dosage from 1.0 to 5.0 g L⁻¹. The result is presented in Fig. 2. The result indicated that the decolorization of AR1 was significantly influenced by the dosage of catalyst and the optimum dosage was observed at 5.0 g/L of catalyst with 99% decolorization efficiency. An increase in the amount of catalyst dosage will provide more iron sites on the catalyst surface for accelerating the decomposition of H₂O₂ which in turn increase the number of hydroxyl radical significantly. This is in agreement with the

results observed by Zhang et al. [16] when Acid Orange 7 was degraded by ultrasound enhanced Fenton-like process using goethite as catalyst.

C. Effect of pH

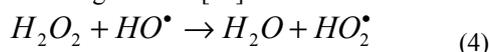
The effect of initial pH solutions on the decolorization of AR1 was studied in the pH range of 2.0-5.0 and the result was shown in Fig. 3. The results indicated that the decolorization of AR1 was significantly influenced by the pH of the solution. The optimum solution pH for decolorization of AR1 was achieved at pH 3 with 99% decolorization efficiency within 180 min reaction time. At low pH (pH < 2.0), the reaction of hydrogen peroxide with Fe²⁺ (ferrous ion) could be slowed down because H₂O₂ can stay stable probably by solvating a proton to form an oxonium ion (e.g., H₃O₂⁺) as presented by Eq. (2). An oxonium ion (H₃O₂⁺) makes H₂O₂ electrophilic which enhance the stability and presumably reduce substantially the reactivity with ferrous ion [17].



At the same time the formed complex species [Fe(H₂O)₆]²⁺ and [Fe(H₂O)₆]³⁺ also react more slowly with H₂O₂. In addition, the scavenging effect of the [•]OH radical by H⁺ is severe Eq. (3) [18]. On the other hand, in case of pH>3.00, the oxidation efficiency decreased rapidly due to the stability of H₂O₂ which starts to rapidly decompose into molecular oxygen without formation of appreciable amounts of hydroxyl radical. It is expected that the formed O₂ is not capable to efficiently oxidize the organics in the mild operating conditions used [19].

D. Effect of initial concentration of H₂O₂

H₂O₂ plays the role of an oxidizing agent in this process. The selection of an optimal H₂O₂ concentration for the decolorization of AR1 is important from practical point of view due to the cost of H₂O₂ [20]. The effect of H₂O₂ dosage on the decolorization of AR1 was examined by varying initial concentration of H₂O₂ from 4 to 20 mM and the result was shown in Fig. 4. As it can be seen, the effect of increasing initial concentration from 4 to 12 mM was first positive for the decolorization of AR1. This is due to the oxidation power of Fenton-like process which was improved with increasing [•]OH radical amount obtained from the decomposition of increasing H₂O₂. However, with continuous increasing of H₂O₂ concentration more than 12 mM, the decolorization rate of AR1 was reduced. This may be explained by the fact that the very reactive [•]OH radical could be consumed by H₂O₂ and results in the generation of less reactive [•]OOH radical which can be expressed by the following reaction [21].



Such reaction reduces the probability of attack of organic molecules by hydroxyl radicals, and causes the

decolorization rate to drop. It is important to control the initial concentration of H₂O₂ since the high concentration would be adverse to the decolorization of dye and would increase the cost of the wastewater treatment. Hence, 12 mM appears as an optimal initial concentration of H₂O₂.

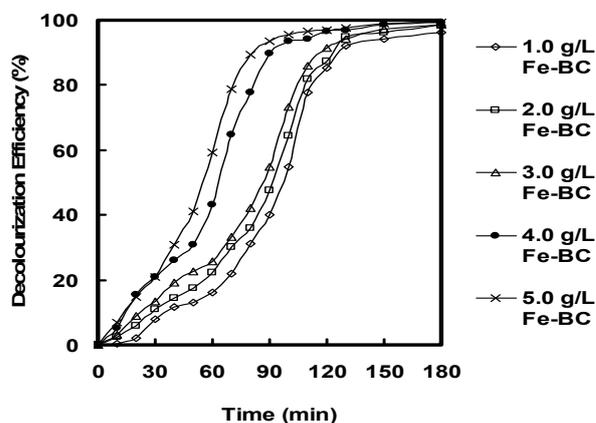


Fig. 2. Effect of catalyst dosage on the decolorization of AR1. Reactions conditions: [AR1]₀ = 50 mg L⁻¹, [H₂O₂]₀ = 4 mM, pH = 2.5, 1.0 wt.% of Fe-BC, temperature = 30 °C and 130 rpm.

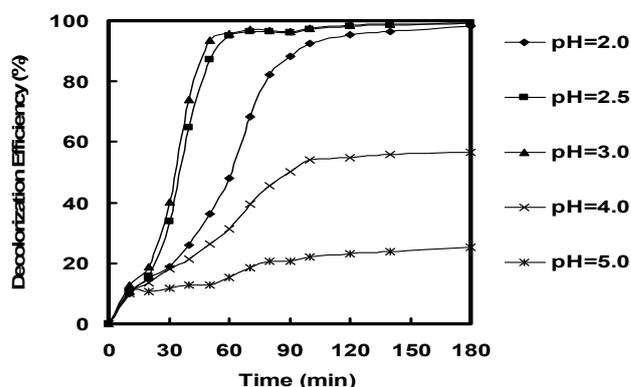


Fig. 3. Effect of pH on the decolorization of AR1. Reactions conditions: [AR1]₀ = 50 mg L⁻¹, [H₂O₂]₀ = 4 mM, 1.0 wt.% of Fe-BC, catalyst = 5.0 g L⁻¹, temperature = 30 °C and 130 rpm.

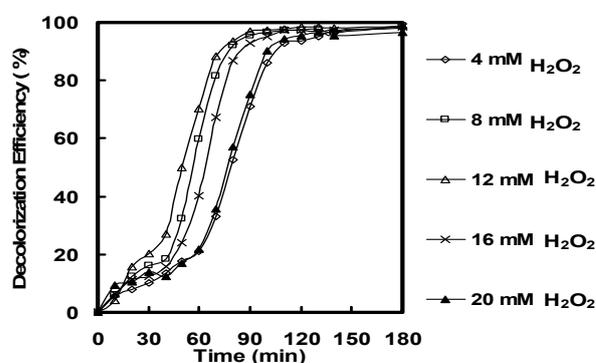


Fig. 4. Effect of initial concentration of H₂O₂ on the decolorization of AR1. Reactions conditions: [AR1]₀ = 50 mg L⁻¹, 1.0 wt.% of Fe-BC, catalyst = 5.0 g L⁻¹, pH = 3.0, temperature = 30 °C and 130 rpm.

E. Effect of initial concentration of AR1

Fig. 5 shows the changes of AR1 concentration with the reaction time. The efficiency of the Fenton-like process as a function initial concentration of dye was evaluated. The results indicated that decolorization efficiency increased when the initial dye concentration increased.

Concentration plays a very important role in reactions according to the collision theory of chemical reactions. The collisions theory state that for a chemical reaction to occur, the reacting particles must collide in correct orientation with each other so that the breaking and formation of chemical bonds can occur and they also should possess energy that is equal to or more than the minimum energy called activation energy. It was two reactants being in a closed container. All the molecules contained within are colliding constantly. By increasing the concentration of one or more reactants, the frequency of collisions between reactants molecules is increased and the frequency of effective collisions that causes a reaction to occur will also be high. The lifetime of hydroxyl radicals is very shorts (only a few nanoseconds) and they can only react where they are formed. Therefore, as increasing the quantity of dyes molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the decolorization efficiency [22]. Similar result was also reported by Kasiri et al. [23] in their study of degradation of Acid Blue 74 by using Fe-ZSM5 zeolite as heterogeneous photo-Fenton catalyst.

IV. CONCLUSIONS

Fe-ball clay has been proved to be an effective heterogeneous catalyst for decolorization of azo dye, (AR1), in an aqueous solution. The optimal operation parameters for the Fenton-like oxidation of AR1 were 0.80 wt. % of iron ions loading on BC, 5.0 g/L of catalyst dosage, and 12 mM of H₂O₂ for 50 mg/L initial dye concentration at an initial pH of 3.0 with 30°C temperature. Under these conditions, 99%

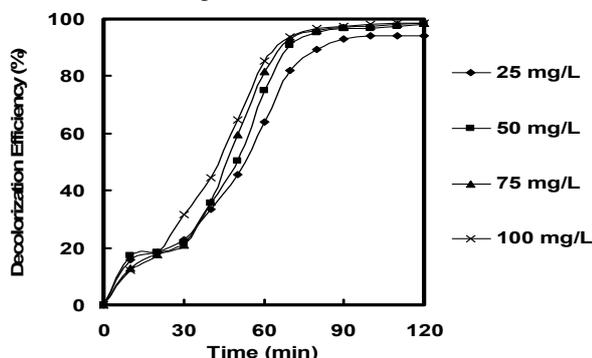


Fig. 5. Effect of initial concentration of AR1 on the decolorization of AR1. Reactions conditions: [H₂O₂]₀ = 4 mM, 1.0 wt.% of Fe-BC, catalyst = 5.0 g L⁻¹, pH = 3.0, temperature = 30 °C and 130 rpm

decolorization efficiency of AR1 in aqueous solution was achieved within 180 min.

REFERENCES

- [1] M. Neamtu, I. Siminiceanu, A. Yediler, A. Kettrup, Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H₂O₂ oxidation, *Dyes and Pigments* 53 (2002) 93–99.
- [2] L. Gomathi Devi, S. Girish Kumar, K. Mohan, Reddy, C. Munikrishnappa, Photo degradation of Methyl Orange an azo dye by Advanced Fenton Process using zero valent metallic iron: Influence of various reaction parameters and its degradation mechanism, *J. Hazard. Mater.* 164 (2009) 459–467.
- [3] S.-P. Sun, C.-J. Li, J.-H. Sun, S.-H. Shi, M.-H. Fan, Q. Zhou, Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: Effect of system parameters and kinetic study, *J. Hazard. Mater.* 161 (2009) 1052–1057.
- [4] U. Pagga, D. Drown, The degradation of dye-stuffs. Part II. Behaviour of dyestuffs in aerobic biodegradation test, *Chemosphere* 15 (1986) 479–491.
- [5] D. Brown, B. Hamberger, Degradation of dye stuffs. Part III. Investigation of their ultimate degradability, *Chemosphere* 16 (1987) 1539–1553.
- [6] C. Maximo, M.T.P. Amorim, M. Costa-Ferreira, Biotransformation of industrial reactive azo dyes by *Geotricum* sp. CCMI 1019, *Enzyme Microb Technol.* 32 (2003) 145–151.
- [7] M.S. Khehra, H. S. Saini, D.K. Sharma, B. S. Chadha, S.S. Chimni, Biodegradation of azo dye C.I. Acid Red 88 by an anoxic-aerobic sequential bioreactor, *Dyes and Pigments* 70 (2006) 1–7.
- [8] J. Deng, J. Jiang, Y. Zhang, X. Lin, C. Du, Y. Xiong, FeVO₄ as a highly active heterogeneous Fenton-like catalyst towards the degradation of Orange II, *Appl. Catal. B: Environ.* 84 (2008) 468–473.
- [9] N.K. Daud, B.H. Hameed, Decolorization of acid red 1 by Fenton-like process using rice husk ash based catalyst, *J. Hazard. Mater.* 176 (2009) 938–944.
- [10] O.S.N. Sum, J. Feng, X. Hu, P.L. Yue, Novel bimetallic catalyst for the photoassisted degradation of Acid Black 1 over a broad range of pH, *Chem. Eng. Sci.* 59 (2004) 5269–5276.
- [11] S.H. Lin, R.S. Juang, Y.H. Wang, Adsorption of acid dye from water onto pristine and acid-activated clays in fixed beds, *J. Hazard. Mater. B* 113(2004) 197–202.
- [12] Y. Flores, R. Flores, A.A. Gallegos, Heterogeneous catalysis in the Fenton-type system reactive black 5/H₂O₂, *J. Mol. Catal. A: Chem.* 281 (2008) 184–191.
- [13] M. Lou, D. Bowden, P. Brimblecombe, Catalytic property of Fe-Al pillared clay for Fenton oxidation of phenol by H₂O₂, *Appl. Catal. B* 85 (2009) 201–206.
- [14] J. Carriazo, E. Guelou, J. Barrault, J.M. Tatibouet, R. Moilina, S. Moreno, Catalytic wet peroxide oxidation of phenol by pillared clays containing Al–Ce–Fe, *Water Res.* 34 (2000) 327–333.
- [15] J. Carriazo, E. Guelou, J. Barrault, J.M. Tatibouët, S. Moreno, Catalytic wet peroxide oxidation of phenol over Al–Cu or Al–Fe modified clays, *Appl. Clay Sci.* 22 (2003) 303–308.
- [16] H. Zhang, H. Fu, D. Zhang, Degradation of C.I. Acid Orange 7 by ultrasound enhanced heterogeneous Fenton-like process, *J. Hazard. Mater.* 172 (2009) 654–660.
- [17] B.G. Kwon, D.S. Lee, N. Kang, J. Yoon, Characteristics of *p*-chlorophenol oxidation by Fenton's reagent, *Water. Res.* 33 (1999) 2110–2118.
- [18] M. Muruganandham, M. Swaminathan, Decolorisation of reactive Orange 4 by Fenton and photo-Fenton oxidation technology, *Dyes Pigments* 63 (2004) 315–321.

- [19] J. Gou, M. Al-Dahhan, Catalytic wet oxidation of phenol by hydrogen peroxide over pillared clay catalyst, *Ind. Eng. Chem. Res.* 42 (2003) 2450–2460.
- [20] J. H. Sun, S.P. Sun, G. L. Wang, L.P. Qiao, Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process, *Dyes Pigment* 74 (2008) 647–652.
- [21] N. Kang, D.S. Lee, J. Yoon, Kinetic modeling of Fenton oxidation of phenol and monochlorophenol, *Chemosphere* 47 (2002) 915–924.
- [22] M. Kitis, S.S. Kaplan, Adsorption of natural organic matter from waters by iron coated pumice, *Chemosphere* 66 (2007) 1846–1853.
- [23] M.B. Kasiri, H. Aleboyah, A. Aleboyah, Degradation of Acid Blue 74 using Fe-ZSM5 zeolite as a heterogeneous photo-Fenton catalyst, *Appl. Catal. B* 84 (2008) 9–15.