

# Fenton-like oxidation of reactive black 5 solution using Fe-rice husk ash catalyst

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**Abstract-** In this work, the decolorization of the azo dye Reactive Black 5 (RB5) was studied, making use of a Fenton-like oxidation process. For that, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) activation was achieved by means of one supported material-based catalysts, which have been immobilized with 0.070 wt. % of Fe (III) oxide on rice husk ash (Fe-RHA). The effects of different parameters such as iron loading (Fe<sup>3+</sup>) on rice husk ash (RHA), catalyst dosage, solution pH, initial concentration of H<sub>2</sub>O<sub>2</sub> on the decolorization efficiency of the process were studied. The results indicated that by using prepared catalyst with optimum condition (3.5 g L<sup>-1</sup> catalyst dosage of 0.070 wt.% Fe-RHA at pH 2.5 and 20 mM of H<sub>2</sub>O<sub>2</sub>), 99 % of the 50 mg L<sup>-1</sup> of RB5 was decolorized within 150 min. Leaching test indicated that the leached iron from the catalyst was less than 5 mg L<sup>-1</sup> which is within the Malaysia regulation of Environmental quality Act 1974.

**Keywords:** Decolorization; Reactive Black 5; Fenton-like process; Fe-rice husk ash; Hydrogen Peroxide Activation.

## I. INTRODUCTION

Colored dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile industry [1]. Dyes are chemicals which on binding with a material will give color to the material. Over 7 x 10<sup>5</sup> tons and approximately 10,000 different types of dyes and pigments are produced world wide annually and it is estimated that 10-15 % of the dyes are lost in the effluent during the dyeing process [2].

Reactive Black 5 (RB5) is the types of azo reactive dye which are the dominant type of the dyes are widely used in the textile industries. These are designed to produce long lasting color and have very simple dyeing procedure. Colored effluents can cause problems in several ways; dyes can have acute and/or chronic effects on exposed organisms in many rivers and waterways [3]. This kind of effluent is also resistant to biological treatment. Therefore, removal of such colored agents from aqueous effluents is a significant environmental issue. There is currently wide range of treatment technologies for these types of wastewaters. Precipitation, ion exchange, solvent extraction, filtration and electrochemical treatment are the conventional methods for the removal of dyes from aqueous solutions [4-7]. All these methods have significant disadvantages such as incomplete ion removal, high-energy requirements and production of toxic sludge or other waste products that require further disposal.

The efficiency and simplicity of advanced oxidation processes make them a suitable choice for the removal of toxic chemicals from wastewaters in the recent years [8-11]. The use of H<sub>2</sub>O<sub>2</sub> and Fenton reagents has been

extensively reported [12-13]. Fenton's reagent (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) has been one of the most common homogeneous systems proposed for the treatment of textile wastewaters. However homogenous Fenton systems have some well-known drawbacks, e.g. a limited pH range, the production iron-contained sludge to dispose and the catalyst deactivation by iron complexing agents [14]. The use of heterogeneous solid Fenton catalysts such as iron oxide-contained rice husk ash (RHA) can be an alternative. The abundance of agricultural by-products in most continents of the world and also its low cost make it a strong candidate as supported catalysts for the removal of many pollutants from wastewaters. The Fenton-like processes have been used as a powerful source of hydroxyl radicals with H<sub>2</sub>O<sub>2</sub> in the presence of metal cations, in very effective reaction conditions [15-16]. Iron salts, were adsorbed onto the surface of RHA, the reduction-oxidation reactions between Fe(III)/Fe(II) take place in presence of hydrogen peroxide which promote the formation of reactive components such as the hydroxyl (·OH) and the hydroperoxyl (·OOH) radicals. 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 iron active ions present at both the catalyst surface and in the bulk liquid phase. Thus, the formed Fe<sup>2+</sup>/Fe<sup>3+</sup> complexes on the surface of RHA can react with H<sub>2</sub>O<sub>2</sub> thus allowing iron ions to participate in the Fenton catalytic cycle [17].

The aim of this study is to investigate applicability of iron oxide-rice husk ash catalyst for decolorization of reactive dye solution by Fenton-like process. The efficiency of the oxidation process was evaluated by examining temperature, pH, H<sub>2</sub>O<sub>2</sub> dosage, iron ions loading on the supported catalyst, catalyst dosage and initial concentration of dye.

## II. EXPERIMENTAL PROCEDURES

**Materials-** The reactive dye, Reactive Black 5 (Fig. 1) (CAS number = [17095-24-8](#), Synonyms = Remazol Black B, empirical formula = C<sub>26</sub>H<sub>21</sub>N<sub>5</sub>Na<sub>4</sub>O<sub>19</sub>S<sub>6</sub>, molecular weight = 991.82, and λ<sub>max</sub> = 597 nm), was provided by Sigma-Aldrich, Malaysia and used without purification. H<sub>2</sub>O<sub>2</sub> solution (30 %) was of analytical grade and purchased from Merck Chemicals, Malaysia. Distilled water was used throughout the experiments. The initial pH of the solution was adjusted using 1.0 M NaOH or 1.0 M H<sub>2</sub>SO<sub>4</sub> to explore the effect of the pH.

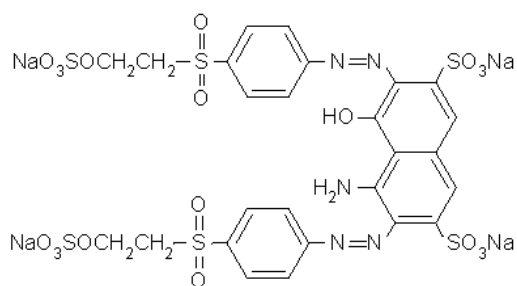


Fig. 1: Chemical structure of RB5

Rice husk used in this study was obtained from BERNAS Company Malaysia Bhd. The rice husk was then washed with distilled water for several times to remove all the dirt and dried in a hot air oven at 60 °C for 12 h and then burned in the Carbolite Furnace at 500 °C at a heating rate 10 °C min<sup>-1</sup> under air atmosphere. The burning process was maintained at this temperature for 3 h. The ash obtained was grinded and finally sieved through sieve no. (125 μm) using a sieve shaker (Analysensieb, RETSCH, D-42759 HAAN/Germany). The Fe-RHA catalyst was prepared by the incipient impregnation method [18], in which distilled water is used to solubilize the Fe (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck). Then, RHA was added to this aqueous solution and was stirred constantly in the water bath until all water was evaporated. After impregnation, the sample was dried at 105 °C for 12 h, followed by calcination at 500 °C for 4 h in a muffle furnace.

**Catalyst characterization-** Specific Brunauer Emmett-Teller (BET) surface area and pore size distribution for Fe-RHA was determined with a Micromeritics ASAP 2020, surface area and porosity analyzer by nitrogen adsorption at 77 K.

The x-ray diffraction (XRD) patterns of the catalysts (before and after impregnated) were measured with SIEMENS XRD D5000 equipped with Cu K $\alpha$  radiation.

**Catalytic activity of prepared catalysts-** All experiments were carried out in 250 mL-stoppered glasses (Erlenmeyer flask) placed in a thermostated water-bath with an agitation of 130 rpm for 150 min. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by dilution with distilled water to 200 mL. Predetermined amounts of impregnated catalyst were then added to the flask. Also, initial solution pH values were adjusted to the desired values by using prepared 1.0 M H<sub>2</sub>SO<sub>4</sub> or 1.0 M NaOH solution. The reactions commenced when predetermined amounts of H<sub>2</sub>O<sub>2</sub> solution were added to the flask. Thereafter, 3 mL volume of samples were withdrawn periodically and analyzed using a UV-vis spectrophotometer (Shimadzu, model UV 1601, Japan) with the maximum absorbance wavelength for RB5 at 597 nm. At each stage, the samples withdrawn were returned into the conical flask to prevent any loss of contents. Thus, the concentration of dye in the reaction mixture at different reaction times were determined by measuring the absorption intensity at  $\lambda_{\text{max}} = 597$  nm and with a calibration curve. Prior to the measurement, a calibration curve was obtained by using the standard RB5 solution with known concentration. The decolorization efficiency of RB5 is defined as follows:

$$\text{Decolorization efficiency (\%)} = [1 - (C_t/C_o)] \times 100 \quad (1)$$

where C<sub>o</sub> (mg L<sup>-1</sup>) is the initial concentration of RB5 and C<sub>t</sub> (mg L<sup>-1</sup>) is the concentration of RB5 at reaction time, t (min).

The total iron concentration in the solution was determined using Atomic Absorption Spectrophotometer (AAS) model Shimadzu AA 6650 with the maximum absorbance wavelength ( $\lambda_{\text{max}}$ ) of iron ion obtained at 248.35 nm. Similarly, prior to the measurement of the iron concentration, a calibration curve was obtained by using the standard iron ion solution in 0.10 M HNO<sub>3</sub> solution with known concentration. Finally, when the decolorization of RB5 was completed, the samples were analyzed to determine the total iron ion leached from the catalyst.

### III. RESULTS AND DISCUSSION

#### Catalysts characterization

The BET surface area, pore size and pore volume for Fe-RHA are 61.33 m<sup>2</sup> g<sup>-1</sup>, 135.52 Å, 0.21 cm<sup>3</sup> g<sup>-1</sup>, respectively. Despite the relatively low BET surface area, the sample is within the range of mesopores system that is appropriately good for removal organic pollutants from wastewater.

Fig. 2 shows the XRD spectra for RHA and impregnated RHA. The spectra show two broad bands located at around  $2\theta = 8.5^\circ$  and  $22^\circ$ , respectively. The XRD spectra recorded on the sample obtained at 500 °C revealed that the amorphous and porous structure of RHA was retained after the incorporation of Fe ion [19]. Additionally, compared to the RHA, the peak of the Fe-RHA is less prominent, which indicates the ordered layered structure of Fe-RHA was subjected to some disruption. However, no peak for Fe ion was detected by XRD spectra. Our results of the deposited iron are in a good agreement with the literature as no indicative peaks relating to the crystalline of metal/metal oxide are found [20]. This is due to the good dispersion of iron on the supported catalysts.

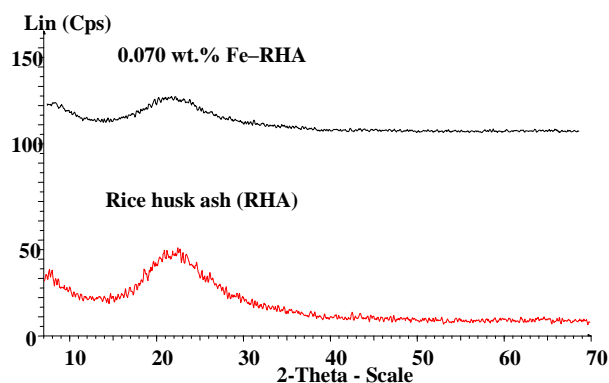


Fig. 2: XRD diffractogram of RHA and Fe-RHA.

## Catalytic activity

### A. Effect of Fe (III) oxide loading on RHA

The effect of iron oxide loading on RHA was investigated by varying the  $\text{Fe}^{3+}$  concentration from 0.010 to 0.070 wt.% for RHA and the result was shown in Fig. 3. The decolorization efficiency increases with increase in  $\text{Fe}^{3+}$  loading and 99 % decolorization of RB5 was observed for 0.070 wt.% Fe-RHA within 150 min reaction to complete. Hence, 0.070 wt.% of  $\text{Fe}^{3+}$  loading on RHA was founded to be optimum for decolorization of RB5. Although original supported catalyst comes with small amount of iron, no decolorization of the RB5 was noticed when using it as a catalyst under the typical condition adopted in this work, which may be related to the inaccessibility of such iron, located in the octahedral positions of the serrated structure for the RHA [21].

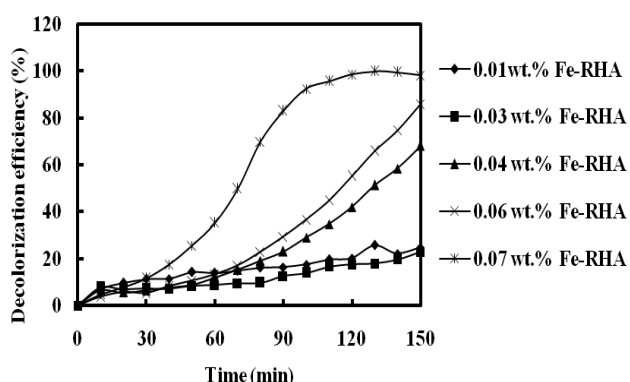


Fig. 3: Effect of iron loading on RHA on the decolorization of RB5. Reaction conditions: initial concentration of RB5,  $[\text{RB5}]_0 = 50 \text{ mg L}^{-1}$ , initial concentration of hydrogen peroxide,  $[\text{H}_2\text{O}_2]_0 = 4 \text{ mM}$ ,  $\text{pH} = 2.5$ , dosage of catalyst =  $2.0 \text{ g L}^{-1}$ , temperature =  $30 \text{ }^\circ\text{C}$  and agitation speed =  $130 \text{ rpm}$ .

### B. Effect of catalyst dosage

Dosage of catalyst is also one of main parameters to influence in the Fenton-like process. The influence of the catalyst dosage on decolorization efficiency against time is presented in Fig. 4. From the result shown, the optimum dosage for decolorization of RB5 using 0.070 wt.% Fe-RHA was  $3.5 \text{ g L}^{-1}$ . All the reaction completed in time-span of 150 min with the decolorization efficiency of 99 %. An increase of the dosage of catalyst will increase the amount of Fe ions involved in the process, which in turn increase the number of  $\cdot\text{OH}$  significantly. When the amount of catalyst employed increases, RB5 elimination rates also increase, due to the increasing amount of active sites for  $\text{H}_2\text{O}_2$  decomposition and less important but also concern, for organic compounds adsorption [22].

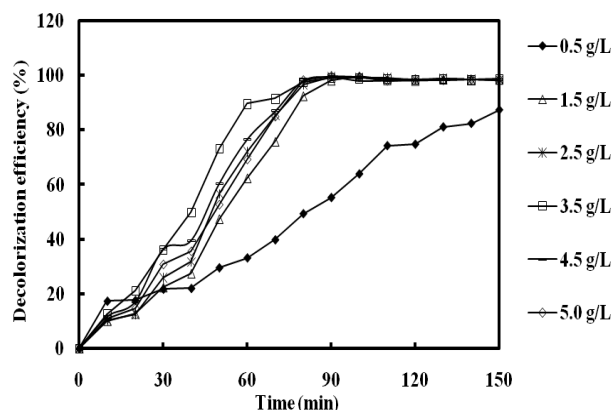


Fig. 4: Effect of dosage of 0.070 wt.% Fe-RHA catalyst on the decolorization of RB5. Reaction condition: initial concentration of RB5,  $[\text{RB5}]_0 = 50 \text{ mg L}^{-1}$ , initial concentration of hydrogen peroxide,  $[\text{H}_2\text{O}_2]_0 = 4 \text{ mM}$ ,  $\text{pH} = 2.5$ , temperature =  $30 \text{ }^\circ\text{C}$  and agitation speed =  $130 \text{ rpm}$ .

### C. Effect of pH

Fig. 5 shows a comparative performance of impregnated catalyst at different pH values. The influence of initial pH of the dye solution on the Fe-RHA/ $\text{H}_2\text{O}_2$  process efficiency was studied with initial pH values of 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 5.0 and without any modifications or control of pH during the process. The results indicated that the decolorization of RB5 was significantly influenced by the solution pH and the optimal solution pH values were achieved at 2.5. With catalyst used, the higher the pH ( $\text{pH} > 3$ ) or the lower the pH ( $\text{pH} < 2$ ), the slower is the reaction rate. The worst performance of both samples at high pH values can be ascribed to the stability of  $\text{H}_2\text{O}_2$ , which starts to rapidly decompose into molecular oxygen without formation of appreciable amounts of hydroxyl radicals [23].

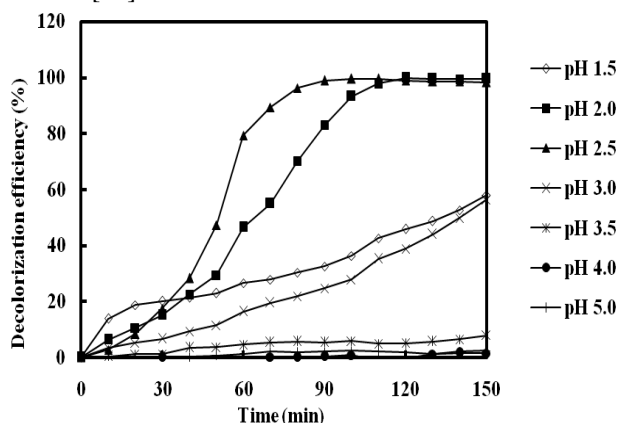
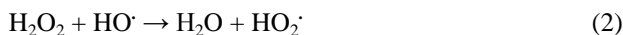


Fig. 5: Effect of pH on the decolorization of RB5 using Fe-RHA as a catalyst. Reaction conditions: initial concentration of RB5,  $[\text{RB5}]_0 = 50 \text{ mg L}^{-1}$ , initial concentration of hydrogen peroxide,  $[\text{H}_2\text{O}_2]_0 = 4 \text{ mM}$ , temperature =  $30 \text{ }^\circ\text{C}$  and agitation speed =  $130 \text{ rpm}$ .

#### D. Effect of initial concentration of H<sub>2</sub>O<sub>2</sub>

H<sub>2</sub>O<sub>2</sub> plays the role of an oxidizing agent in Fenton-like process. The selection of an optimal H<sub>2</sub>O<sub>2</sub> concentration for the decolorization of RB5 by Fenton-like process is important from practical point of view due to the cost of H<sub>2</sub>O<sub>2</sub>. Fig. 6 shows the effect of initial H<sub>2</sub>O<sub>2</sub> concentration on the decolorization of RB5 during the treatment. From the results, the optimum H<sub>2</sub>O<sub>2</sub> concentration for decolorization of RB5 using 0.070 wt.% Fe-RHA was 20 mM. The experiment was conducted in 150 min to achieve the complete reaction. As can be seen, the effect of increasing H<sub>2</sub>O<sub>2</sub> concentration from 4 mM to 20 mM was first positive for the decolorization of RB5. This is due to the oxidation power of Fenton-like process which was improved with increasing ·OH radical amount in solution obtained from the decomposition of increasing H<sub>2</sub>O<sub>2</sub>. However, with continuous increasing of the initial concentration of H<sub>2</sub>O<sub>2</sub> from 24 mM to 32 mM, the decolorization rate of RB5 reduced. This may be explained by the fact that the very reactive ·OH radical could be consumed by H<sub>2</sub>O<sub>2</sub> and the results in the generation of less reactive ·OOH radical (Eq. (2)) [24-26].



Thus, in the condition of excess H<sub>2</sub>O<sub>2</sub>, this would become a scavenger of ·OH radical, and lead the decolorization efficiency of RB5 to decrease.

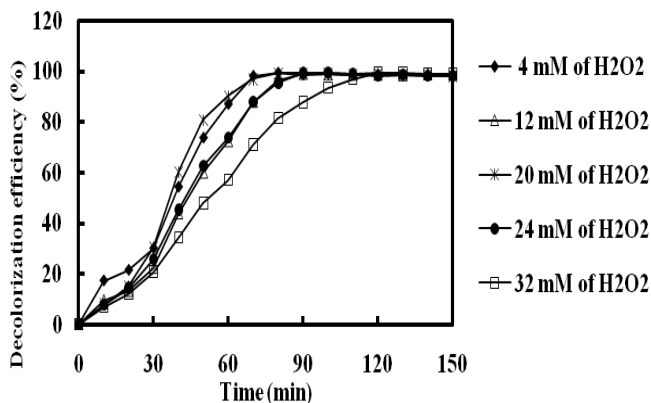


Fig. 6: Effect of initial concentration of H<sub>2</sub>O<sub>2</sub> on the decolorization of RB5 using Fe-RHA. Reaction conditions: initial concentration of RB5, [RB5]<sub>0</sub> = 50 mg L<sup>-1</sup>, temperature = 30 °C, agitation speed = 130 rpm and pH = 2.5.

#### Catalyst stability test

For a practical implementation of a heterogeneous catalytic system, it is crucial to evaluate the stability of the catalysts [27]. For that purpose, a sample that shows a low iron leaching, but presenting simultaneously good catalytic performance, should be selected. The RHA catalyst sample which meets all these criteria was selected. Table 1 shows the concentrations of the leached iron ions in the treated wastewater. It is seen that the highest leached iron concentrations are around 2.85 mg L<sup>-1</sup>. It is observed that the iron leaching concentrations become smaller as the catalyst is repeatedly used. In all of the experiments, concentration of the Fe ion was below 5 mg L<sup>-1</sup> and this

conforms to the standard of Environmental Quality Act 1974. This act relating to the prevention, abatement, control of pollution and enhancement of the environment, and for purposes connected therewith and shall apply to the whole of Malaysia. Therefore, it is feasible and economical to apply the developed catalyst for a long time operation which is environmentally benign to the existing wastewater treatment. Even though slight activity decay was observed, this might be due to the iron loss. Other authors reported similar results, but they attributed the loss of activity to poisoning of the active catalytic sites due to adsorbed organic species [29].

Table 1: Leaching concentrations of Fe-RHA catalysts for the repeated cycles.

Cycle	Concentration of iron, mg L <sup>-1</sup>
	0.070 wt.% Fe-RHA
1	2.85
2	1.49
3	0.20
4	0.02

The Fe (III) impregnated on granite has been tested and used as catalyst in decolorization of AR1 in Fenton-like process. The study showed that the heterogeneous Fenton-like process of Fe/granite can decolorize AR1 effectively. The optimal operational parameters obtained for this study were found to be 0.070 % by weight of Fe (III) oxide loading on granite, 5.0 g L<sup>-1</sup> of 0.070 wt.% Fe/granite, solution pH 3.0, 20 mM H<sub>2</sub>O<sub>2</sub> dosage at 30 °C. Decolorization processes led to 95 % decolorization of AR1 within 100 min. Above all, the process is economical because of the availability of the raw materials (granite) employed.

#### IV CONCLUSION

#### 3. Conclusion

In this work, it was demonstrated that the Fe-RHA obtained through impregnation method serve as a very active heterogeneous catalyst for the decolorization of RB5. The maximum process conditions of 0.070 wt.% Fe-RHA, 3.5 g L<sup>-1</sup> dosage of catalyst, pH 2.5, 20 mM of H<sub>2</sub>O<sub>2</sub>, gave 99 % decolorization of solution containing 50 mg L<sup>-1</sup> RB5 in just 150 min in a batch process. Leaching tests indicated that the activity of the catalyst is not due to the leached iron ions, although an amount of more 2.0 mg L<sup>-1</sup> of Fe ions was found in aqueous solution. Significantly lower concentration of Fe ions in the solution after the treatment could give this system, Fe-RHA/H<sub>2</sub>O<sub>2</sub> a great advantage over the homogeneous Fenton-type system

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