

Degradation of Reactive Blue 181 Dye by Heterogeneous Fenton Technique Using Modified Fly Ash

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In this paper, the heterogeneous Fenton technique using modified fly ash used for the degradation of Reactive Blue 181. The catalysts were prepared supporting the metal by the incipient impregnation method using iron(III) nitrate. Several properties of raw and modified fly ashes were characterized by SEM, EDX and XRD techniques. Effects of some key operating parameters such as catalyst dose, pH and the concentration of hydrogen peroxide on the treatment efficiency were studied and discussed. Kinetic rate constants of treatment process were also determined. The experimental results show that the heterogeneous Fenton technique using modified fly ash/H₂O₂ is a suitable method for removing Reactive Blue 181 from aqueous solution. At the optimum conditions include pH 3; catalyst dose of 0.4 g/L, hydrogen peroxide concentration of 3.92 mM, treatment time of 90 min, approximately 90 % of Reactive Blue 181 was removed from aqueous solution. The kinetic data fitted well for pseudo first-order reaction.

Key Words: Heterogeneous Fenton, Fly ash, Modified fly ash, Fly ash/H₂O₂, Kinetic, Reactive Blue 181.

INTRODUCTION

Textile is one of the mainstream industries with important strategic position in the development of the national economy in Vietnam¹. However, due to the specific characteristics of a complex manufacturing industry that utilizes much water, chemicals, materials, *etc.* The risk of environmental pollution caused by the textile industry is inevitable. Wastewater from the textile industry is one of major environmental problems in Vietnam and many other countries¹⁻⁴. The environmental pollution due to the textile industry is multidimensionally causing serious problems not only to the land mass fertility but also to the natural flora, fauna, as well as the aquatic bodies. Consequently, dyes have to be removed from textile wastewater before discharge^{3,4}.

Basically, dyes can be removed from aqueous solution by many different techniques, typically chemical and physical techniques such as flocculation⁵⁻⁸, electric coagulation, adsorption, membrane; anaerobic and aerobic biotechnology^{6,9,3}, chemical techniques such as advanced oxidation processes^{4,7-15}. Among the advanced oxidation processes, Fenton process is known as a powerful tool to solve the pollution problem of organic pigments. This solution is said to have many advantages such as efficient decomposition of pollutants, low cost price; it operates under favourable condition and chemicals used in the treatment process does not affect the environment. However,

this method has its limitations such as it forms a large amount of iron sludge after the treatment process and the cost of disposing iron sludge is usually high: iron ions can be inactivated when they interact or create complex forms with ions such as phosphate or some intermediate oxidation products¹⁶. The heterogeneous Fenton processes with lower cost and friendly with the environment can overcome those disadvantages of the homogeneous Fenton processes. Several Fenton heterogeneous catalysts are synthesized on the basis of minerals or iron-containing solid waste products such as kaolin³, pyrite ash, fly ash^{2,8} and red mud.

Fly ash is an industrial solid waste of burning power plants, produced approximately 300 million tons per year globally. In many places, fly ash is taken directly to the landfills, causing serious environmental pollution¹⁶. Currently, fly ash can be used as additives or construction materials, sorbents or catalysts for the oxidation of H₂S, methane, sodium sulfite. However, few information involving the uses of fly ash as the catalyst for the purpose of decomposing dye in the water are published.

In this article, fly ash was modified and used as a catalyst for heterogeneous Fenton process, which is applied in the degradation of Reactive Blue 181 dye.

EXPERIMENTAL

Reactive Blue 181 dye, was purchased from Shimi Boyakhsaz Co., Iran, which is used in the dyeing procedure of

Mua Dong Textile and Garment Company, Hanoi, Vietnam. Hydrogen peroxide solution (30 %) and other chemicals which are pure analysis. Fly ash taken from Uong Bi Thermal Power Plant in Quang Ninh province, Vietnam.

Catalyst preparation: In this work, catalyst was prepared supporting the metal by the incipient impregnation method as the report of Yolanda Flores *et al.*⁸. Dissolve 6 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 20 mL of distilled water. After that, add 10 g of fly ash to the solution. Stir the mixture on the magnetic stirrer with the speed of 20 rpm and heated at 100 °C until the water completely evaporates. Dry the sample at 100 °C in an oven overnight. The catalyst samples will be obtained after heating at 500 °C for 4 h.

Characterization of raw fly ash and prepared catalyst:

The morphology was observed with scanning electron microscope (SEM, JSM5410LV JEOL, Japan) at an accelerating voltage of 20 kV. The crystalline form of the catalyst was identified by X-ray diffractometer on a Siemens D5000 (Germany) with CuK_α radiation in the angle range $2\theta = 15\text{--}85^\circ$. EDX analysis was carried out with a JED-2300 JEOL (Japan).

Degradation experiment: Degradation experiments were conducted by adding a specific amount of modified fly ash to the reactor. Continue to add 500 mL of water with Reactive Blue 181 dye (with adjusted pH). The reaction starts when adding hydrogen peroxide.

Analytical procedures: The concentration of Reactive Blue 181 in water is determined by the photometric method at a wavelength of 609.5 nm (characterized wavelength absorption of dye, determined by experiments) using UV-1650 PC UV-visible spectrophotometer (Japan). Colour removal performance is determined by the formula:

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

In which C_0 and C_t are Reactive Blue 181 concentrations in water at the initial time and after t minutes of treatment, respectively.

RESULTS AND DISCUSSION

Physicochemical properties of these raw fly ash and prepared catalyst: In this study, the characteristics of fly ash before and after modification were studied and focused on SEM image analysis (Fig. 1) and EDX spectrum (Fig. 2).

SEM images of raw fly ash samples (Fig. 1a) and prepared catalyst (modified fly ash) (Fig. 1b) shows the prepared catalyst has porous structure with many empty niches, which facilitates favourable for adsorption, catalysis.

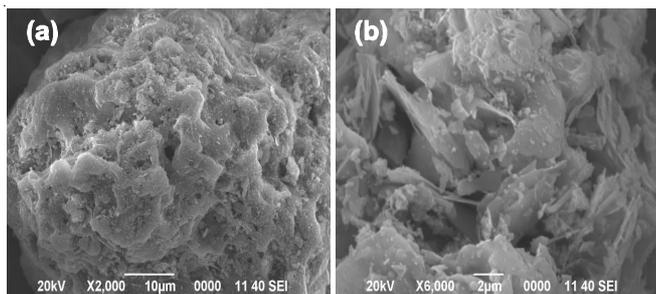


Fig. 1. SEM images of raw fly ash (a) and modified fly ash (b)

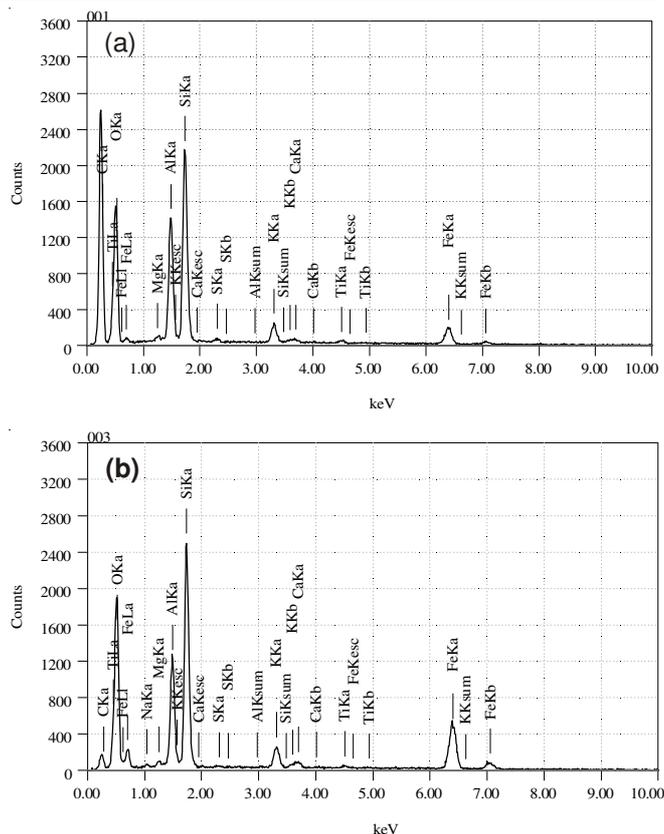


Fig. 2. EDX spectrum of raw fly ash (a) and catalyst (b)

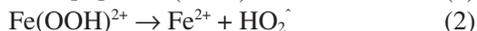
In this study, chemical composition of fly ash samples before and after preparation are determined through EDX spectrum; corresponding results are shown in Fig. 2 a and b.

The more detailed analysis shows that the iron content increased significantly after the preparation process, from 3.35 % to 17.97 %. Iron exists in the structure of the product as completely denatured form of Fe_2O_3 . This was confirmed through X-ray diffraction diagram of the modified fly ash samples. The XRD of raw fly ash also appeared to reflect specific lines of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and particles of quartz (SiO_2); while only records the presence of mineral mullite reflections ($\text{Al}_6\text{Si}_2\text{O}_{13}$); it has background noise and do not record the present of iron in the structure. The XRD results confirm that fly ash has been successfully modified.

Effect of the content fly ash: In heterogeneous Fenton process, catalyst concentration is a factor that significantly influenced the treatment performance. Effect of fly ash were surveyed in the values 0.2, 0.3, 0.4, 0.5 and 0.6 g/L, in about 150 min and the concentration of H_2O_2 (3.92 mM), pH 3.

From the experimental result (Fig. 3), it can be seen that when the catalyst concentration increases, the decomposition performance of Reactive Blue 181 dye tend to increase. However, this is only true when the catalyst concentration and treatment time do not exceed 0.4 g/L and 90 minutes. If continue to increase the amount of catalyst on 0.4 g/L, not only did the processor performance not increase significantly but it even tended to decrease (0.5 g/L). The effectiveness of the treatment almost remained unchanged after 90 min of treatment at all levels of catalyst.

Effect of fly ash can be explained by the correlation between the speeds of the following reactions¹⁷⁻¹⁹:



When fly ash content is greater than 0.4 g/L, the consumption of a hydroxyl radical (according to reaction (5)) is the direct cause leading to reduced performance.

Effect of pH: pH is one of the strongest factors influencing the performance of the decomposition of organic matter of advanced oxidation techniques. Typically, in the Fenton process homogeneous, heterogeneous took place favourably in an acidic environment. Study of the effect of pH was conducted at the values 2, 3, 4 and 5; at the content values of H_2O_2 (3.92 mM) and fly ash (0.4 g/L). Experimental results in 150 min are shown in Fig. 4.

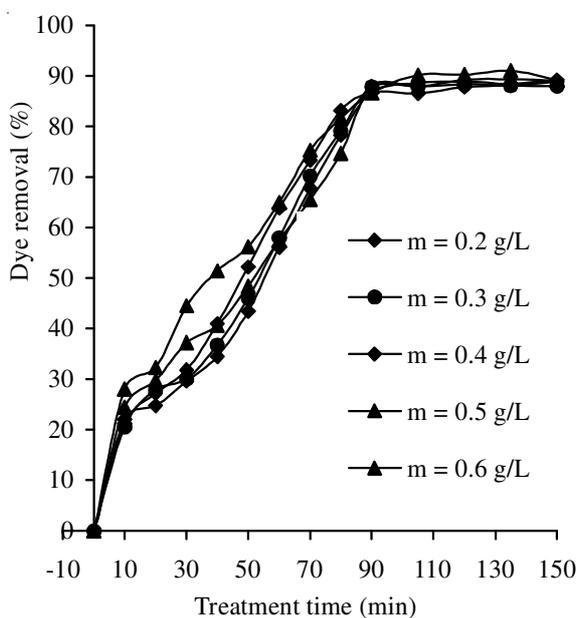


Fig. 3. Effect of catalyst dose on treatment efficiency

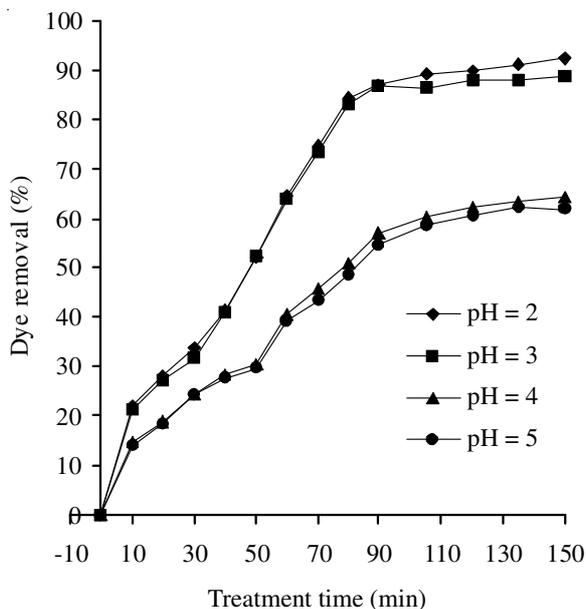
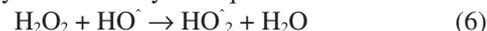


Fig. 4. Effect of pH on treatment efficiency

The experimental results in Fig. 4 show that acidic environment is conducive to the formation of hydroxyl radicals, proven when the effect of the treatment tends to decrease while increasing pH. Here note the different takes on the decomposition efficiency of Reactive Blue 181 dye at pairs of pH 2, pH 3; pH 4, pH 5, but the difference in maximum efficiency is quite high (over 90 % and approximately 60 %). Suitable pH value is defined as 3; appropriate time is 90 min; meanwhile the dye removal efficiency reached 86.67 %.

Effect of hydrogen peroxide concentration: Fig. 5 shows the effect of hydrogen peroxide concentration to the decomposition performance of Reactive Blue 181 dye. It can be seen in the study conditions (pH 3, catalyst dose 0.4 g/L): while increasing the hydrogen peroxide concentration from 1.96 mM to 3.92 mM, performance tends to increase rapidly and strongly increase in about 90 min and then increased slowly, not significantly. However, when increasing concentrations of hydrogen peroxide are greater than 3.92 mM, the effectiveness of the treatment not only continues but also tends to decrease. The decrease in performance of a large concentration of hydrogen peroxide can be explained by hydroxyl radicals partially consumed by the equation^{13,18,20}:



Hydrogen peroxide concentration of 3.92 mM is appropriate.

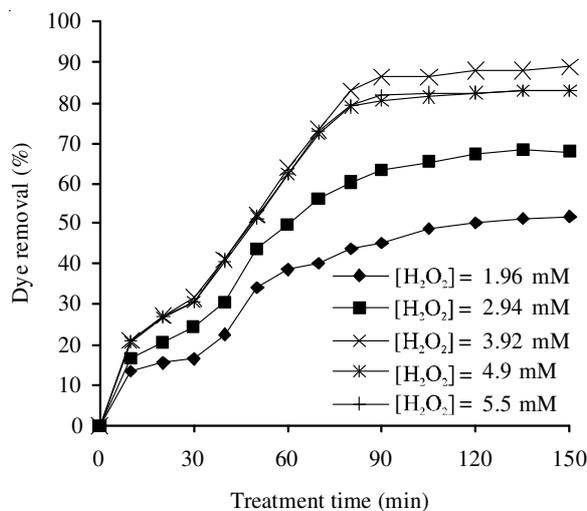


Fig. 5. Effect of catalyst dose on treatment efficiency

Kinetics: Many studies show that the homogeneous and heterogeneous Fenton processes usually follow the pseudo first-order kinetics. However, studies of Karthikeyan *et al.*¹⁹ showed that the heterogeneous Fenton process follows the pseudo second order kinetic¹⁹. In this article, the kinetics of the process are checked with both kinetic models, first-order and second-order kinetics. If the process follows the pseudo first-order and pseudo second-order kinetics, kinetics of the processes are represented respectively by the expressions:

$$\ln C_t = \ln C_0 - kt \quad (\text{pseudo first-order kinetic})$$

$$\frac{1}{C_t} = \frac{1}{C_0} + kt \quad (\text{second-order kinetic})$$

In which C_0 and C_t is the concentration corresponding dye at the time of treatment and after treatment t minutes; k are the reaction rate constants.

Fig. 6 shows that the change of $\ln C_t$ as a function of treatment time; while $1/C_t$ varied as a function of time was presented in Fig. 7. As can be seen from Figs. 6 and 7, the reaction kinetics fitted well for pseudo first-order reaction with regression coefficient approximately 0.95 (due to the correlation coefficient R^2 is larger than second order). In the first 90 minutes of treatment, the reaction rate constants are greater than ($k_1 = 0.0219 \text{ min}^{-1}$; $R_2 = 0.9414$) that at 60 min later ($k_2 = 0.004 \text{ min}^{-1}$; $R_2 = 0.957$).

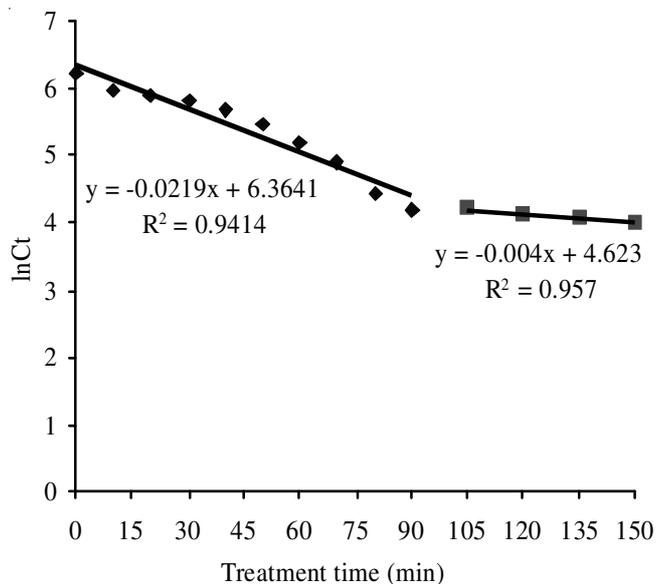


Fig. 6. Determination of reaction rate constant for heterogeneous Fenton oxidation of wastewater (pseudo first-order reaction)

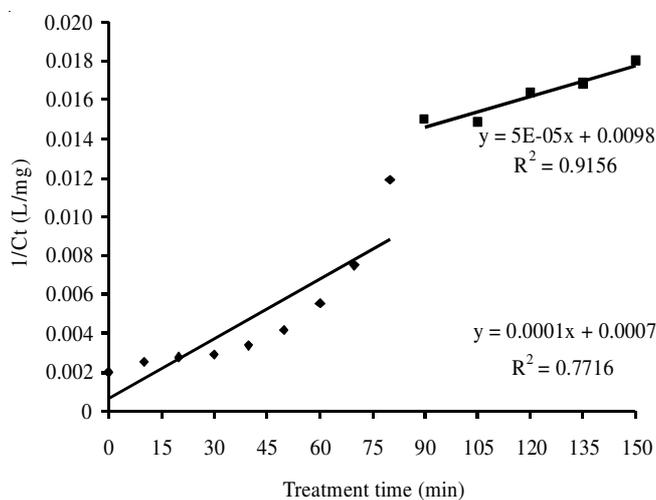


Fig. 7. Determination of reaction rate constant for heterogeneous Fenton oxidation of wastewater (pseudo second-order reaction)

Conclusion

The heterogeneous Fenton technique using modified fly ash/ H_2O_2 is a suitable method for removing Reactive Blue 181 from aqueous solution. Experimental results show that under suitable conditions, specifically the catalyst dose of 0.4 g/L ; $\text{pH } 3$; hydrogen peroxide concentration of 3.92 mM , treatment time of 90 min , the degradation performance of Reactive Blue 181 reach 86.67% ; the reaction kinetics fitted well for pseudo first-order reaction with regression coefficient approximately 0.95. In the first 90 min . of treatment, the reaction rate constants are greater than ($k_1 = 0.0219 \text{ min}^{-1}$; $R^2 = 0.9414$) that at 60 min later ($k_2 = 0.004 \text{ min}^{-1}$; $R^2 = 0.957$).

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