KINETICS OF THE TREATMENT OF ORGANIC DYE BASED ON MODIFIED RED MUD

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SUMMARY
In this paper, red mud denatured by Iron (III) sulfate is used for researching decomposition reaction kinetics of Reactive Yellow 160 (RY 160) dye using Heterogeneous Fenton Technique. Basic characteristics of red mud before and after denaturation are determined through scanning electron micrograph (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). In the appropriate conditions on catalyst content (1.5 g/L), hydrogen peroxide content (2.29 mM), pH = 2, with more than 99.2% of RY 160 dye is eliminated at 30°C with a rate constant of 0.0383 min^{-1} (R^2 = 0.9939); surveying temperature in the range of 30°C - 50°C, the reaction follows first order kinetics with activation energy 31.9 kJ/mol (R^2 = 0.9804); surveying catalyst content, the largest rate constant is k = 0.0381 min^{-1} with catalyst content of 1.5 g/L; surveying hydrogen peroxide content, the largest rate constant is k = 0.0367 min^{-1} with hydrogen peroxide concentration of 2.29 mM; surveying pH, the largest rate constant is k = 0.0391 min^{-1} at pH = 2.
Keywords: Catalyst, Heterogeneous Fenton, Reactive Yellow 160, Red mud.

I. INTRODUCTION

Activities in the textile and dyeing production have currently generated a large amount of wastewater containing persistent organic compounds which seriously affects the scenic, reduces the amount of dissolved oxygen in the water, reduces photosynthesis process, causes serious impact on the environment, ecology and the lives of many aquatic species, animals and human (Đặng Trấn Phòng, 2004; Đặng Trấn Phòng, 2005). More recently, researchers have discovered toxicity and danger of azo compounds for the ecological environment and human, especially this type of dye may cause cancer to product users (Y.M. Slokar and A.M. Le Marechal, 1998). Research on treatment of wastewater containing azo compounds is a very important issue in order to eliminate all these substances before discharging into the environment, protect human and ecological environment.

In such techniques being applied to treat textile and dyeing wastewater as flocculation, adsorption (Yolanda Flores, Roberto Flores, and Alberto Alvarez Gallegos, 2008); anaerobic (Esther Forgac, Tibor Cserhát, and Gyula Oro, 2004), aerobic; biological techniques; advanced ozonation, oxidation, heterogeneous Fenton technique using oxidizing agent ($OH^{\bullet}$) is an appropriate technique to treat structurally reliable, toxic organic dyes with high efficiency without special equipment; especially with certain types of dyes that are non-biodegradable and difficult to eliminate with conventional chemical and physical methods (Behin Jamshid, Farhadian Negin, Ahmadi Mojtaba, and Parvizi Mehdi, 2015; Bento Natálya, Santos Patrícia S., De Souza Talita, Oliveira Luiz C., and Castro Cínthia, 2016; Gulkaya I., Surucu G.A., and Dilek F.B, 2006). However, the high cost of chemicals is considered a basic restriction of oxidation techniques in general and Fenton techniques in particular.

Unique features of the method of Fenton heterogeneous as hydroxyl created with the ability to react fast and selective with most organic compounds (constant reaction rate between 10^7 and 10^{10} $mol^{-1}.l.s^{-1}$) on the surface of the solid phase. Features non-selective oxidation is extremely important, allowing to expand the scope of application of the method with heterogeneous waste water, which contains compounds of different pollutants. The fast activation capability is consistent with the short shelf life and low instantaneous concentration of hydroxyl radicals.

In order to overcome limitations of Fenton technique, scientists have still been focusing on research to find highly active catalyst materials with low cost of preparation and production, applicable on an industrial scale, such as fly ash, red mud, kaolin, pyrite slag (Đào Sỹ Đức, 2012; Đào Sỹ Đức, 2013; Đào Sỹ Đức et al, 2009). Use of solid wastes as catalysts not only reduces treatment cost for Fenton process but also helps solve part of hazardous solid wastes.

In-depth research on heterogeneous Fenton reaction kinetics by waste materials is relatively new, providing a source of documents of critical significance in calculation and design of textile and dyeing wastewater treatment system and further research on the mechanism of heterogeneous Fenton technique. In this paper, the focus is placed on the research of kinetics parameters for decomposition of Reactive Yellow 160 (RY 160) by heterogeneous Fenton process with the catalyst as denatured red mud.

II. EXPERIMENT

2.1. Chemicals and experiment

All kinds of chemicals are of pure type and used without further purification. Red mud is taken in the red mud lake of Tan Rai Aluminate Factory, Bao Lam, Lam Dong, Vietnam. Chemical structure and UV-vis spectrum of RY 160 are given in Figure 1.

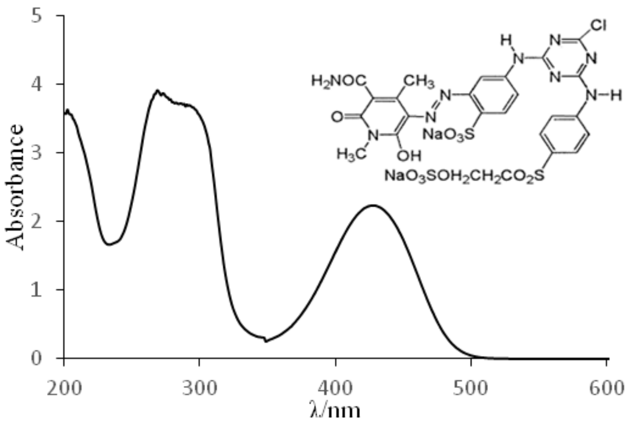

Fig. 1. Chemical structure and UV-vis spectrum of RY 160. [RY 160] = 200 ppm

2.2. Denaturation process of red mud

Finely grind 10 g of red mud and 2.5 g of $Fe_2(SO_4)_3$ dissolve in a glass containing 50 mL of water. This mixture is stirred mechanically 120 rpm for 2 hours at room temperature, and then increase the temperature to 100°C and stir until the water is completely evaporated. The mixture is washed with distilled water twice, dried overnight at room temperature and then grinded and mixed in about 10 mins; baked at 200°C for 2 hours. Leave to cool and we obtain the catalyst.

2.3. Treatment process

Accurately weigh m grams of red mud into a glass containing 50 mL of water, then add 500 mL of water containing pH adjusted 160 RY and evenly stir at a speed of 120 rpm. Start the reaction by adding hydropeoxit 30% (by volume). At the time of need to determine RY 160 concentration in the solution, sample is extracted and determined Optical Absorption combined with the standard curve of RY 160 in Fig. 2. Then, determine RY 160 concentration at time t (C_t).

2.4. Kinematic treatment method

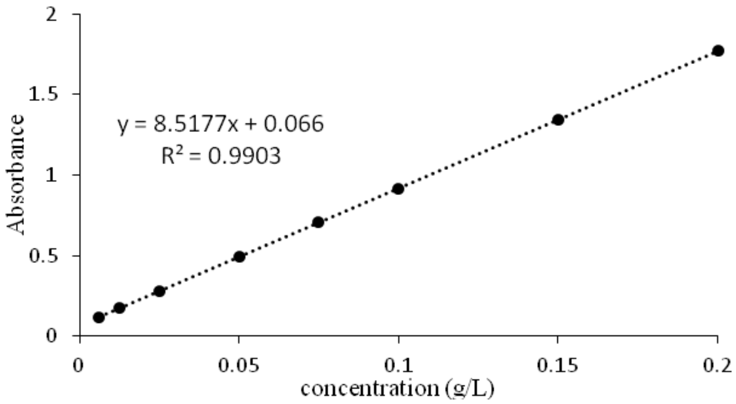

Fig. 2. Standard curve of Optical Absorption of RY 160 at characteristic wavelength λ_{max} = 428 nm

UV-Vis spectrum in Fig. 1 shows that RY 160's characteristic absorption is at wavelength 428 mm. This wavelength is used to construct standard curve indicating the relationship between optical absorption and dye concentration. Experimental result in Fig. 2 shows that concentration of RY 160 concentration can be determined when knowing optical absorption value (Abs) by the following formula:

$$C = \frac{\text{Abs-0.066}}{8.5177} \text{ (g/L)}$$

Reaction kinetics is handled according to first order kinetics with RY 160 concentration and first order kinetics with H_2O_2 concentration which is shown in Fig. 5 and Fig. 6. Rate constant of the reaction is determined by the slope of dependence curve ln (Co/Ct) over time:

$$\ln (C_o/C_t) = k.t$$

in which C_o, C_t: RY 160 concentration at initial time and time (mol/L); k: rate constant (min^{-1}), t: time (min)

Activation energy of the reaction is determined by the Arrhenius equation of the influence of temperature to the reaction rate constant:

$$\ln (k_T) = -E_a/(R.T)$$

In which E_a: activation energy of the reaction (J), R = 8.314 $J.mol^{-1}.K^{-1}$, T: reaction temperature (K)

III. RESULTS AND DISCUSSION

3.1. Characteristics of materials

In this research, basic characteristics of red mud before and after denaturation are analyzed through scanning electron micrograph (SEM) (Fig. 3) and Energy Dispersive X-Ray Spectroscopy (EDX) (Fig. 4).

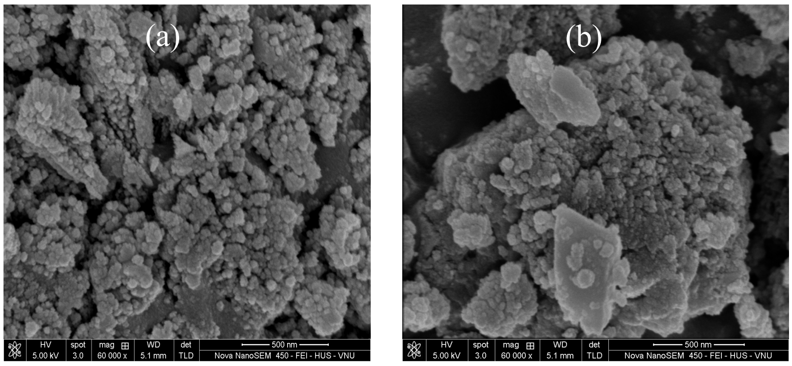

Fig. 3. Scanning electron micrograph of red mud sample before (a) and after (b) denaturation

SEM image of the red mud sample before denaturation (Fig. 3a) and after denaturation (Fig. 3b) shows that red mud surface after denaturation is more structurally tight, small pieces bind to materials due to iron oxides going into holes, filling surface of red mud and some particles sticking outside red mud; there are also large gaps on structural surface of red mud due to the dissolution of alkali and earth metal hydroxides in the composition of the red mud. This is also confirmed by EDX spectrum of red mud sample when Fe content increases from 38.83% to 42.26%.

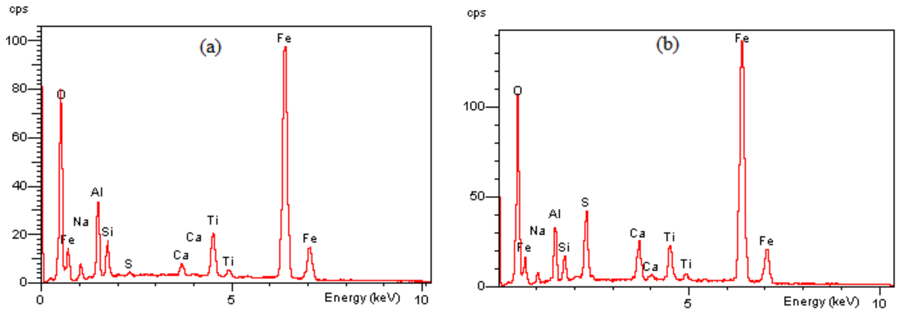

Fig. 4. Energy Dispersive X-Ray Spectroscopy of red mud sample before (a) and after (b) denaturation

3.2. Reaction kinetics

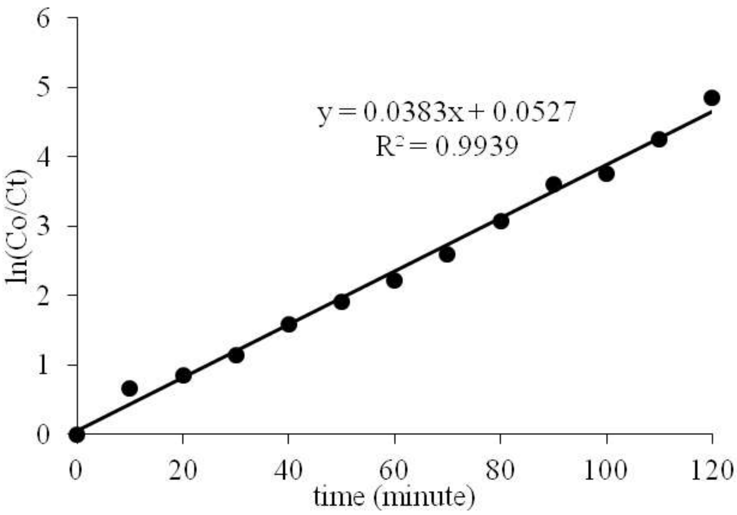

Fig. 5. Results determined constant decomposition rate by first order of RY 160

([RM] = 1,5 g/L; [H_2O_2] = 2,29 mM, pH = 2, t° = 30°C, stirring rate of 120 rpm)

The heterogeneous Fenton process is based on the general reaction as follows:

$$RY160 + H_2O_2 \xrightarrow{RM\text{-}Fe(III)} Product \quad (1)$$

Main goal of this paper is to present kinetic parameters of heterogeneous Fenton reaction using denatured red mud catalyst including: reaction order of RY 160, reaction order of H_2O_2, effects of temperature, RY 160 concentration, catalyst concentration, H_2O_2 concentration to rate constant of heterogeneous Fenton reaction and activation energy of the reaction.

Kinetic parameters are examined assuming first order according to RY 160 concentration: Log base e graph of initial RY 160 concentration ratio (Co) and at time t (Ct) versus time shown in Fig. 5 is linear with a slope of 0.0383 (R^2 = 0.9939), which suggests that the reaction is first order kinetics for RY 160 concentration with rate constant of k = 0.0383 min^{-1}.

3.3. Effect of denatured red mud concentration

In heterogeneous Fenton reaction, the reaction rate is influenced powerfully by catalyst content. In this research, catalyst content was surveyed in values of 0.5 g/L; 1.0 g/L; 1,5 g/L; 2.0 g/L; 2.5 g/L, other factors were fixed such as pH = 2, H_2O_2 concentration of 2.29 mM and RY 160 concentration of 200 ppm.

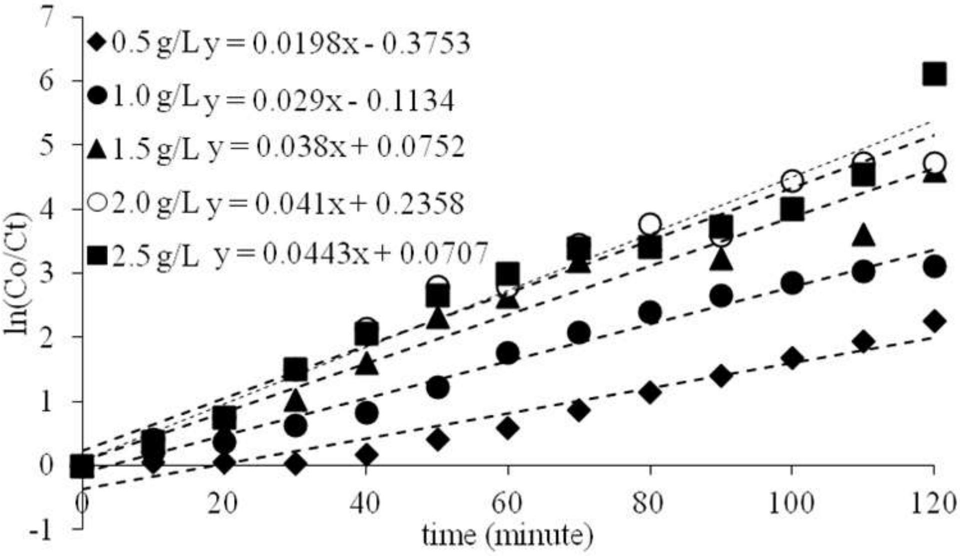

Fig. 6. Effect of catalyst content

($[H_2O_2]$= 2.29 mM; pH = 2; $t^o = 30^oC$; stirring rate of 120 rpm)

Experimental result in Fig. 6 shows that when denatured red mud content increases from 0.5g/L to 2.5g/L, RY 160 treatment rate tends to increase, k increases from 0.0198 min^{-1} to 0.0443 min^{-1}. This can be explained by basic reactions during heterogeneous Fenton process:

$RM\text{-}FeOOH + 3H^+ \rightarrow X\text{-}Fe^{3+} + 2H_2O$ (2)

$RM\text{-}Fe^{3+} + H_2O_2 \rightarrow X\text{-}Fe(OOH)^{2+} + H^+$ (3)

$RM\text{-}Fe(OOH)^{2+} \rightarrow X\text{-}Fe^{2+} + HO_2^{\bullet}$ (4)

$RM\text{-}Fe^{2+} + H_2O_2 \rightarrow X\text{-}Fe^{3+} + HO^- + HO^{\bullet}$ (5)

$RM\text{-}Fe^{3+} + HO_2^{\bullet} \rightarrow X\text{-}Fe^{2+} + H^+ + O_2$ (6)

$RM\text{-}Fe^{2+} + HO^{\bullet} \rightarrow X\text{-}Fe^{3+} + HO^-$ (7)

Sharp increase of catalyst rate from 0.5 g/L to 1.5 g/L is explained by the reason that in the range of this catalyst concentration, catalyst content increases with increased free radical OH • formed. Meanwhile, difference between rate constant of 2 concentrations as 1.5 g/L (k = 0.0381 min^{-1}) and 2 g/L (k = 0.0443 min^{-1}) is not large after treatment time of 120 mins. These results indicate that suitable catalyst content is 1.5 g/L.

3.4. Effect of H_2O_2 concentration

In Fenton reaction system, heterogeneous or homogeneous, H_2O_2 concentration is one of the factors that significantly influence on the formation and consumption of hydroxyl groups, so it also determines the treatment rate. Effect of H_2O_2 concentration to reaction rate constant was surveyed at concentrations 2.29 mM; 3.55 mM; 4.75 mM; 7.11 mM and 9.40 mM, while other conditions were fixed such as pH = 2, temperature of 30 oC, red mud content of 1.5 g/L and RY 160 concentration of 200 ppm.

Results determining the effect of H_2O_2 concentration to RY 160 decomposition rate are shown in Fig. 7. At research conditions at pH = 2, catalyst content of 1.5 g/L, rate constant reaches the maximum value (k = 0.0367 min^{-1}) when H_2O_2 concentration is 2.29 mM, this can be explained by hydroxyl radical partially consumed by the equation (8):

$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O$ (8)

Appropriate hydrogen peroxide content is 2.29 mM.

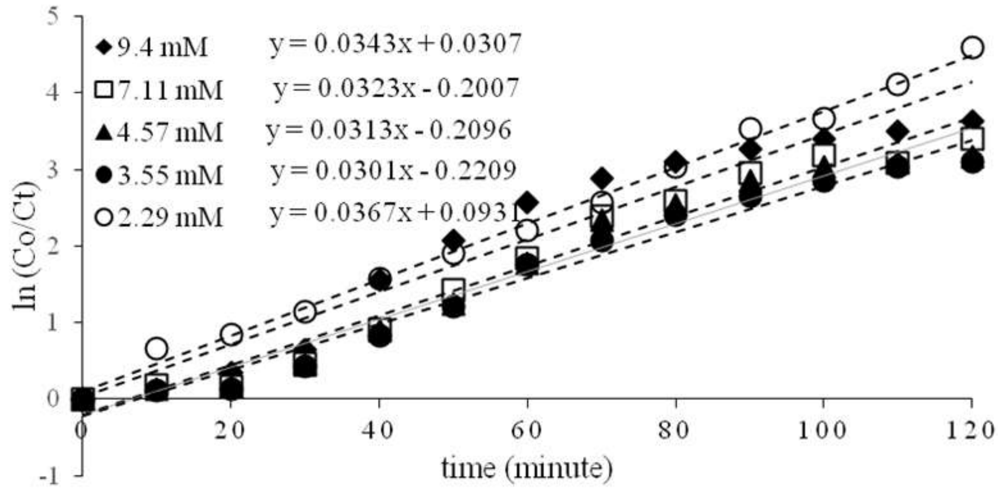

Fig. 7. Effect of H_2O_2 concentration

([RM] = 1.5 g/L; pH = 2, $t^o = 30^oC$, stirring rate of 120 rpm)

3.5. Effect of pH

pH is one of the factors most strongly affecting organic decomposition efficiency of Fenton technique. Typically, Fenton processes take place smoothly in an acid environment. Research on the effect of pH was carried out at values 1; 2; 3; 4 and 5 and appropriate conditions about dye concentration, catalyst content and H_2O_2 concentration as examined above.

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \quad (9)$$

$$OH^{\bullet} + H^+ + e^- \rightarrow H_2O \quad (10)$$

Experimental result in Fig. 8 shows that pH has a strong influence on treatment process, at pH 1 and pH 4, low treatment rate and small reaction constant (k = 0.0168 min^{-1} and 0.0164 min^{-1}, respectively), smallest at pH 5 (k = 0.0043 min^{-1}) and largest at pH = 2 (k = 0.0391 min^{-1}). At pH < 2, treatment rate is reduced by the occurrence of reactions (9) in which Hydrogen peroxide can be stabilized because it exists as solvation ($H_3O_2^+$), oxonium ions when formed will reduce the ability to react with iron ions. In addition, when conducted at a pH below 2, hydroxyl radicals can be consumed by ion H^+ (10) and in contrast, precipitation of iron hydroxide (II, III) will appear when conducted in high pH. Thus, appropriate value is pH = 2.

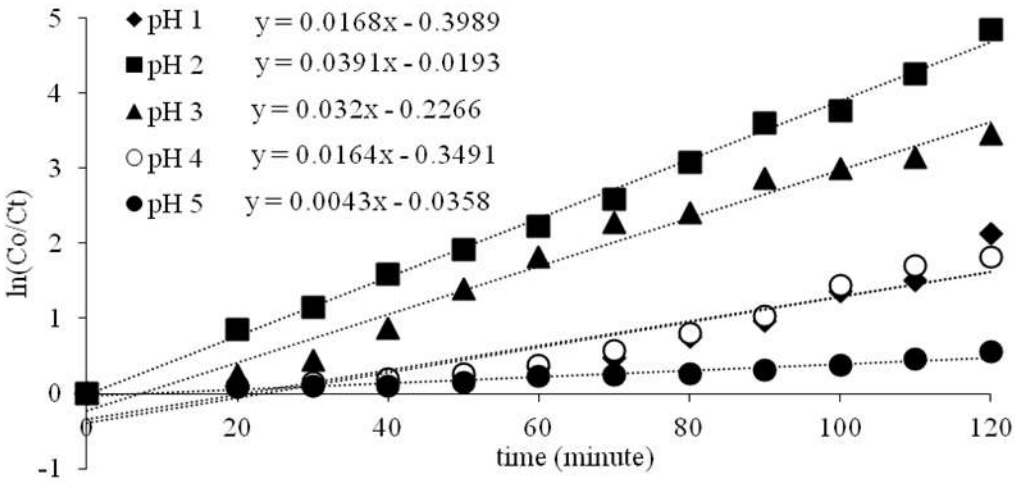

Fig. 8. Effect of pH

([RM] = 1,5 g/L; $[H_2O_2]$ = 2,29 mM; $t^o = 30^oC$; stirring rate of 120 rpm)

3.6. Effect of temperature

Conduct experiment survey at optimal conditions about the amount of denatured red mud, H_2O_2 concentration, pH above examined at different survey solution temperatures ranging from 30°C - 50°C. Experimental result shown in Fig. 9 shows that RY 160 treatment rate sharply increases as the temperature increases. Especially when temperature increases to 40°C, rate constant increases to 0.052 min^{-1} and temperature increases to 50°C, rate constant increases to 0.0841 min^{-1}. This can be explained by the reason that when the temperature increases, H_2O_2 decomposes with faster rate, iron ions at high temperatures become more flexible, this combination increases the likelihood of forming $OH^{\bullet}$ hydroxyl radical.

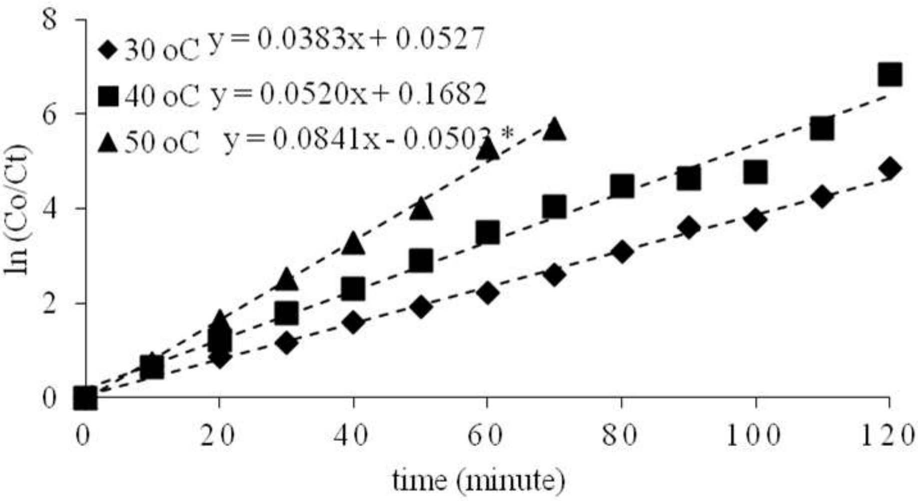

Fig. 9. Effect of temperature

([RM] = 1.5 g/L; $[H_2O_2]$ = 2.29 mM; pH = 2; stirring rate of 120 rpm)

*At 50°C, after 70 min excluding ln (Co/Ct) because this time actual performance achieved 99.67%, remaining amount of RY 160 in the solution is too small.

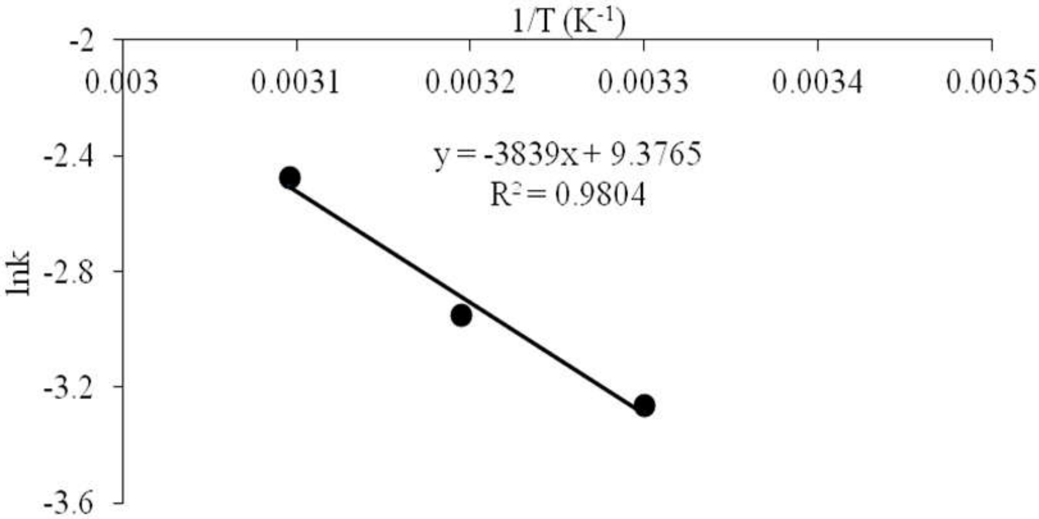

Fig. 10. Linear relationship between lnk and 1/T

([RM]= 1.5 g/L; $[H_2O_2]$ = 2.29 mM; pH = 2; stirring rate of 120 rpm)

Survey result in Fig. 10 shows a linear relationship between lnk and 1/T with a slope of –Ea/R = -3839 (R^2 = 0.9804), then we calculate Ea = 31.9 kJ/mol. Compared to some other heterogeneous catalyst systems such as CuFeZSM-5 zeolite 24.83 kJ/mol, activation energy of denatured red mud is larger but when compared with nano-iron pipes (35.9 kJ/mol), activation energy of the red mud is lower, reflecting higher catalytic activity. On the other hand, the value of activation energy of thermal reactions generally ranges from 60 to 250 kJ/mol. Research result shows that RY 160 elimination process by heterogeneous Fenton technique needs relatively low activation energy, the process essentially takes place smoothly in terms of chemical kinetics.

IV. CONCLUSIONS

Red mud can be easily denatured by a simple impregnation process. Product after denaturation can be used effectively for destruction and decomposition, eliminating RY 160 dye by heterogeneous Fenton technique. Research result indicates that during elimination of RY 160 dye by heterogeneous Fenton technique, in the appropriate conditions on catalyst content (1.5 g/L), hydrogen peroxide content (2.29 mM), pH = 2, with more than 99.2 % of RY 160 dye is eliminated at 30^oC with a rate constant of 0.0383 min^{-1} (R^2 = 0.9939); surveying temperature in the range of 30^oC – 50^oC, the reaction follows first order kinetics with activation energy 31.9 kJ/mol (R^2 = 0.9804); surveying catalyst content, the largest rate constant is k = 0.0381 min^{-1} with catalyst content of 1.5 g/L; surveying hydrogen peroxide content, the largest rate constant is k = 0.0367 min^{-1} with hydrogen peroxide concentration of 2.29 mM; surveying pH, the largest rate constant is k = 0.0391 min^{-1} at pH = 2.

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ĐỘNG HỌC QUÁ TRÌNH XỬ LÝ PHẨM NHUỘM HỮU CƠ BẰNG BÙN ĐỎ BIẾN TÍNH

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TÓM TẮT

Trong bài báo này, bùn đỏ biến tính bằng muối sắt (III) sunfat được sử dụng cho mục tiêu nghiên cứu động học phản ứng phân hủy phẩm màu Reactive Yellow 160 (RY 160) bằng kỹ thuật Fenton dị thể. Các đặc tính cơ bản của bùn đỏ trước và sau biến tính được xác định thông qua ảnh hiển vi điện tử quét (SEM), phổ tán xạ năng lượng tia X (EDX). Ở những điều kiện phù hợp về hàm lượng xúc tác (1,5 g/L), hàm lượng hydro peoxit (2,29 mM), pH (2), trên 99,2% phẩm màu RY 160 được loại bỏ ở nhiệt độ 30^oC với hằng số tốc độ 0,0383 phút^{-1} (R^2 = 0,9939); khảo sát nhiệt độ trong khoảng 30^oC - 50^oC, phản ứng tuân theo động học bậc một với năng lượng hoạt hóa 31,9 kJ/mol (R^2 = 0,9804); khảo sát hàm lượng xúc tác, hằng số tốc độ lớn nhất k = 0,0381 phút^{-1} với hàm lượng xúc tác 1,5 g/L; khảo sát hàm lượng hydro peoxit, hằng số tốc độ lớn nhất k = 0,0367 phút^{-1} với nồng độ hydro peoxit là 2,29 mM; khảo sát pH, hằng số tốc độ lớn nhất k = 0,0391 phút^{-1} tại pH = 2.

Từ khóa: Bùn đỏ, Fenton dị thể, Reactive Yellow 160, xúc tác.

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