EXTRACTING IRON FROM RED MUD (TAN RAI, LAM DONG) TO DECOMPOSE METHYLENE BLUE (MB) USING THE MODIFIED FENTON SYSTEM OF FERRIOXALATE/H_2O_2/SUNLIGHT

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Hoàng Thị Thu Thảo, Bùi Xuân Vững
Chemistry Department, Education University, The Danang University

TÓM TẮT

NGHIÊN CỨU CHIẾT SẮT TỪ BÙN ĐỎ ĐỂ PHÂN HỦY METHYLENE XANH BẰNG HỆ FENTON CẢI TIẾN FE(III)-OXALAT/H_2O_2/MẶT TRỜI

Bài báo này trình bày nghiên cứu về việc chiết sắt từ bùn đỏ thải ra từ nhà máy Bauxit Tân Rai, Lâm Đồng bằng axit oxalic 1M dưới dạng phức sắt(III) oxalate. Phức này được sử dụng cho quá trình Fenton cải tiến, hệ phức $Fe(C_2O_4)_3^{3-}$/H_2O_2/ánh sáng mặt trời, để xử lý thuốc nhuộm xanh metylen trong dung dịch nước. Các nghiên cứu được tiến hành ở qui mô phòng thí nghiệm. Kết quả thực nghiệm cho thấy phương pháp đun sau đó ngâm chiết cho hiệu suất tách sắt dưới dạng phức oxalat cao nhất. Hiệu suất sắt chiết đạt 86% khi đun 2.000 g bùn đỏ trong 40mL axit oxalic 1 M trong 2h ở 70^0C, sau đó ngâm trong 20h. Khi xử lý 200 mL xanh metylen 100 ppm với $[Fe(C_2O_4)_3]^{3-}$ = 0,5mM; $[H_2O_2]$ = 20 mM; pH = 4, dung dịch mất màu hoàn toàn sau 25 phút phơi nắng ở thời điểm giữa trưa . Kết quả nghiên cứu cho thấy bùn đỏ và ánh sáng mặt trời có thể được tận dụng để xử lý nước thải dệt nhuộm với giá thành hợp lý.

1. INTRODUCTION

Red mud is a byproduct of the production of alumimum from bauxite ore in the Bayer process [1], patented in 1888 by Karl Joseph Bayer. On average the Bayer process requires 2.65 kg of bauxite ore to produce 1 kg of alumina, while about 1 kg of dry red mud is discharged into the environment, by far its greatest environmental problem [2]. Although red mud is classified by EC as a non hazardous waste [3], its small particle size (dust-like, mean particle size 0.49 μm [4]), high alkalinity and very large amounts makes its disposal a lot of serious problems for the environment such as groundwater pollution, air pollution by dust, substantial land use for disposal, red mud spill… For the purpose of exploiting the increasing red mud source, we investigate to extract iron from red mud by oxalic acid to obtain ferrioxalate complex that was used in the modified Fenton system of $Fe(C_2O_4)_3^{3-}/H_2O_2$/sunlight for decomposing methylene blue (MB), a common dye. Dyes in textile wastewater are toxic and carcinogenic [5]. They have been treated using such methods as absorption, coagulation-floculation, advanced oxidation processes (O_3/H_2O_2, Fenton, UV/H_2O_2, UV/TiO_2…)[6]. This study is performed to aim at finding a novel method based on red mud to treat dye wastewater with both reasonable cost and high efficiency, and contributing to solving the environmental pollution by red mud and textile wastewater.

2. EXPERIMENTAL

2.1. Material and chemicals

Raw red mud was obtained from the alumin Tan Rai factory that is located in Lam Dong province, neutralized to pH 8 by seawater taken from a local sea of Danang city, dried by sunlight, ground and then sieved to < 0.01mm. The content of Fe_2O_3 in the neutralized red mud was 38.19%, derived from the analysis of Danang National Center for Hydro-Meteorological Forecasting using the F-AAS method. Pure analytical grade chemicals of $FeCl_3$, $H_2C_2O_4.2H_2O$, H_2O_2 30%, concentrated H_2SO_4, MB were purchased from China. Prepared H_2O_2 solutions were titrated using the permaganate method.

2.2. Instruments

UV-VIS LAMBDA25 (USA), Branson pH meter (England), Precisa-XR125SM analytical balance (German) with the precision of ± 0.1 mg. 3. RESULTS AND DICUSSION

3.1. Setting up calibration curve for ferrioxalate complex concentration

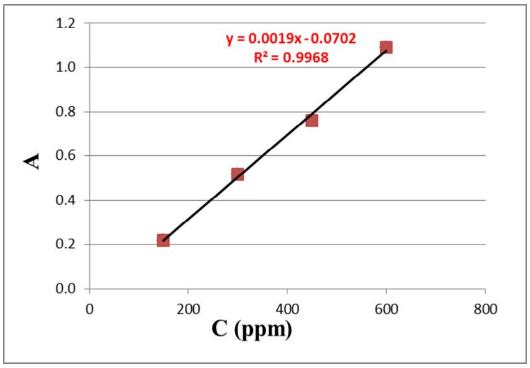

Figure 3.1: The calibration curve for ferri oxalate complex concentration

Standard ferrioxalate complex solutions were prepared from 1000 ppm $FeCl_3$ and 1 M $H_2C_2O_4$ and then measured spectrometrically using UV-VIS LAMBDA25 spectrometer at the maximum wavelength λ_{max} of 403 nm. The calibration curve is y = 0.0019x – 0.0702 with the regression coefficient of 0.9968. Here y is absorbance, and x is concentration of ferrioxalate complex. This equation was used to determine quantities of ferrioxalate complex that was extracted from the red mud, and then to calculate extraction efficiency based on the initial and extracted amounts of iron.

3.2. Effect of the sequence of ways of extracting iron on the extraction efficiency

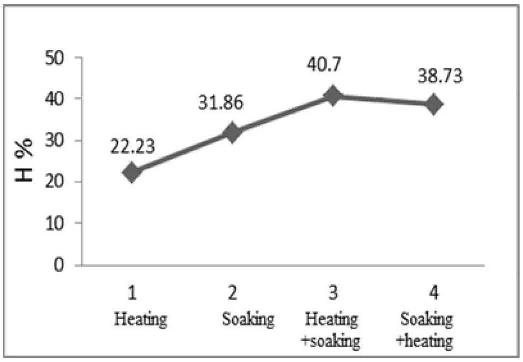

Figure 3.2: Effect of the ways of extracting iron on the extraction efficiency H%

2.000g of the neutralized red mud was added to 50mL of 1M $H_2C_2O_4$ and carried on respectively by one of the following ways of extraction: 1 h heating; 20h soaking; 1h heating and then 20h soaking; 20h soaking and then 1h heating. Here heating temperature was 60^{o}C. As can be seen from Figure 3.2, the iron extraction efficiency gets the maximum at 40.7% when extracting iron from the neutralized red mud using the way of 1h heating at 60^{o}C and then 20h soaking, which was chosen to investigate for the next factors.

3.3. Effect of heating time on the extraction efficiency

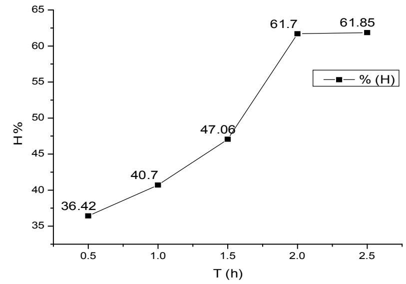

Figure 3.3: Effect of heating time on the extraction efficiency H%

Mixtures of 2.000g of the neutralized red mud with 50mL of 1 M $H_2C_2O_4$ were respectively heated at 60^{o}C in the following time intervals: 0.5h, 1h, 1.5h, 2h, 2.5h, and then each mixture was soaked in 20h. Figure 3.3 shows that the extraction efficiency increases gradually when increasing the heating time, and after 2h heating the extraction efficiency is nearly the same as that after 2.5h heating. Because the difference on the extraction efficiency between these two cases is insignificant, the way of 2h heating and then 20 h soaking was chosen to investigate for the next factor.

3.4. Effect of heating temperature on the extraction efficiency

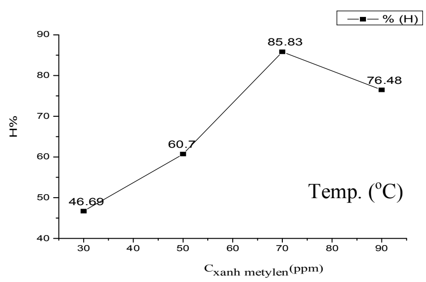

Figure 3.4: Effect heating temperature on the iron extraction efficiency H%

Heat for 2h respectively a mixture of 2.000g of the neutralized red mud with 50mL of 1M $H_2C_2O_4$ at 30^0C; 50^0C; 70^0C; 90^0C, and then soak the suspension for 20h. As can be seen from Figure 3.4, the iron extraction efficiency increases slowly when increasing heating temperature, and it gets the maximum of 85.83% at 70^oC. The decrease in the iron extraction efficiency at temperature higher than 70^oC could be due to the evaporation of water leading to the crystallization of oxalic acid. Thus, heating at 70^oC was chosen for the next investigation.

3.5. Effect of soaking time on the iron extraction efficiency

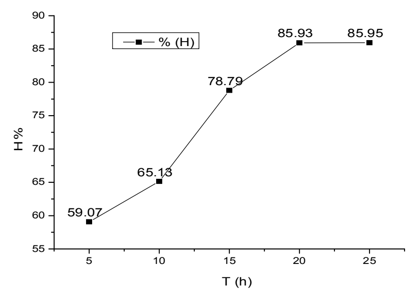

Figure 3.5: Effect of soaking time on the iron extraction efficiency H%

Heat respectively mixtures of 2.000g of the neutralized red mud and 40 mL of 1 M $H_2C_2O_4$ at 70^0C in 2h, and then soak the suspension in the time intervals of 5h, 10h, 15h, 20h, and 25h. Figure 3.5 shows that when soaking time increases from 5 h to 20 h, the iron extraction efficiency gradually increases from 59.07% to 85.93%, respectively. After that the efficiency is almost unchanged. As a consequence, the soaking time of 20h was chosen as the best parameter.

3.6. Effect of oxalic acid volume on the extraction efficiency

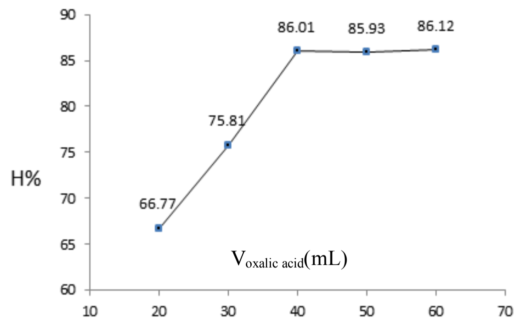

Figure 3.6: Effect of oxalic acid volume on the extraction efficiency H%

Add 2.000g the neutralized red mud to a volume of 1M $H_2C_2O_4$ respectively as follows: 20mL; 30mL; 40mL; 50mL; 60mL. The mixture was heated at 70^0C, and then soaked in 20h. As can be seen from Figure 3.6, the increase in the volume of 1M oxalic acid from 20 mL to 40 mL leads to the iron extraction efficiency going up from 66.77% to 86.0%, and then the efficiency was almost unchanged if the volume of oxalic acid was higher than 40 mL. Thus, the optimal volume of 1M oxalic acid for the extraction of iron from 2.000g of the neutralized red mud under conditions mentioned above was 40mL, and the efficiency was about 86%.

3.7. Effect of pH on the decomposition of MB by Fe(III)-oxalate/H_2O_2/sunlight

The Fe(III) oxalate complex extracted from the neutralized red mud mentioned above was used for the modified Fenton system of Fe(III)-oxalate/H_2O_2/sunlight to decompose MB dye. Prepare 6 beakers in which each beaker contains 200 mL of 200 ppm MB, 0.3 mM $Fe^{III}(C_2O_4)_3^{3-}$, and 25 mM H_2O_2. The pH of each beaker was adjusted to 2, 3, 4, 5, 6, and 7, respectively by 0.1M H_2SO_4. These solutions were stirred magnetically and illuminated by sunlight within 25 minutes at noontime at Danang Education University. The MB solutions before and after the illumination were measured spectrometrically at the wavelength of 628 nm to calculate the MB decomposition efficiency H%. The solutions before measuring spectrometrically were added izopropylic alcohol to prevent the further decomposition of MB due to the attack of OH radicals.

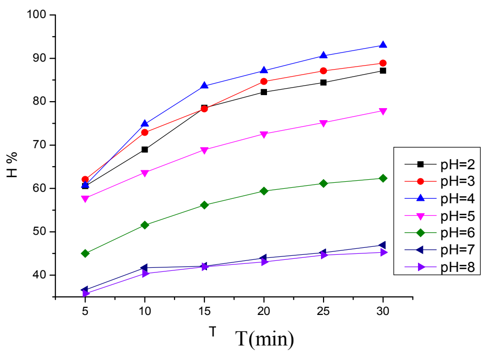

Figure 3.7: Effect of pH on the MB treatment efficiency H%

Figure 3.7 shows that after 30 min illumination of sunlight the decomposition of MB increases when the pH of solutions increases from 2 to 4, and then decreases rapidly when the pH increases from 4 to 8, respectively. Thus, the decomposition efficiency of MB gets the maximum of about 93% at pH 4. At the low pH (pH 2) $HO^{\bullet}$ radical will be reduced by the following reaction: $HO^{\bullet} + H^+ + e^- \rightarrow H_2O$ leading to the decrease in the decomposition rate of MB. Furthermore, at the low pH the ferrioxalate complex exists mainly the form of $Fe^{III}(C_2O_4)^+$ that has low quantum efficiency leading to low decomposition efficiency. Otherwise, At pH 4 the ferrioxalate complex exists mainly the forms of $Fe^{III}(C_2O_4)_2^-$ and $Fe^{III}(C_2O_4)_3^{3-}$ having high quantum efficiency, meaning that $HO^{\bullet}$ radicals were more generated resulting in the highest decomposition efficiency of MB [7]:

$$Fe^{III}(C_2O_4)_2^- + h\nu \longrightarrow Fe^{2+} + C_2O_4^{2-} + C_2O_4^{\bullet -}$$
$$Fe^{III}(C_2O_4)_3^{3-} + h\nu \longrightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{\bullet -}$$
$$Fe^{2+} + H_2O_2 + 3C_2O_4^{2-} \longrightarrow Fe^{III}(C_2O_4)_3^{3-} + OH^- + OH^{\bullet}$$

At pH > 5 the decomposition rate was decreased rapidly because of the formation of hydroxides of iron leading to the decrease in the formation of OH radicals. Thus, the modified Fenton system of Ferrioxalate/H_2O_2/sunlight has the optimal pH of 4 compared to pH 2 of the normal Fenton reagent meaning that the modified Fenton system spends less chemical to adjust pH of treatment solution than the common Fenton reagent.

3.8. Effect of the concentration of iron(III) oxalate complex on MB decomposition efficiency

Each of 6 beakes contains 200 mL of 200 ppm MB, 25 mM H_2O_2, pH 4, and its $Fe(C_2O_4)_3^{3-}$ concentration changes from 0.1mM to 0.9mM, respectively.

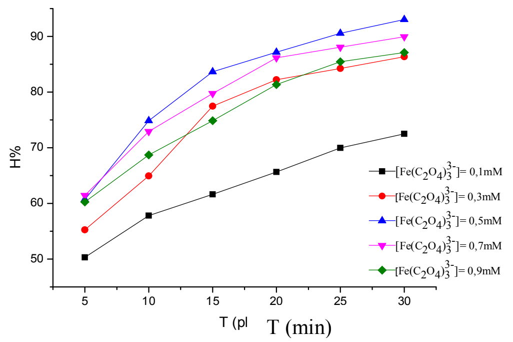

Figure 3.8: Effect of concentrations of the iron (III) oxalate complex

Results from Figure 3.8 show that the MB decomposition efficiency tends to increase when increasing the concentration of $Fe(C_2O_4)_3^{3-}$ complex, but the efficiency tends to decrease when the concentration is larger than 0.5 mM. That is due to the increase in the concentration of $Fe(C_2O_4)_3^{3-}$ leads to a larger amount of $HO^{\bullet}$ radicals generated, yet $HO^{\bullet}$ radicals also react with Fe^{2+} according to the following reaction [8]: $HO^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + HO^{-}$ ($k = 3.0 \times 10^{8}$ L mol^{-1} s^{-1})

3.9. Effect of the concentration of H_2O_2 on MB decomposition efficiency

The H_2O_2 concentration of each of 6 beakers containing 200 mL of 200 ppm MB, 0.5 mM $Fe^{III}(C_2O_4)_3^{3-}$ and pH 4 was respectively changed as follows: 5 mM, 10 mM, 15 mM, 20 mM, 25 mM.

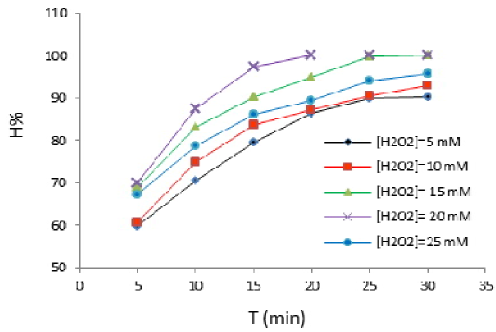

Figure 3.9: Effect of the concentration of H_2O_2

As can be seen from Figure 3.9, the MB decomposition efficiency increases when increasing the concentration of H_2O_2 from 5 mM to 20 mM. However, if the H_2O_2 concentration is higher than 20 mM the efficiency will go down. Thus, the optimal H_2O_2 concentration is 20 mM, and the efficiency for this case is complete after 20 min illumination. The reason why the efficiency increases when the increase in H_2O_2 concentration is up to 20 mM is due to the higher generation of $HO^{\bullet}$ radicals according to the following reaction [7]:

$$Fe^{2+} + H_2O_2 + 3C_2O_4^{2-} \rightarrow Fe^{III}(C_2O_4)_3^{3-} + OH^{-} + OH^{\bullet}$$

However, when H_2O_2 is in much excess, the rate of the reaction between H_2O_2

and $HO^{\bullet}$ will increase according to the following reactions:

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

$HO^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2$

Furthermore, noting that much excess of H_2O_2 not only raises the cost, but also affect the living media of microorganism if using this method before microbiology method for treatment. Thus the optimal concentration of H_2O_2 is 2.0M.

4. CONCLUSION

This study was exploited red mud, a harmfull waste of the Bayer process, to extract iron by 1M $H_2C_2O_4$. The extraction efficiency of ferrioxalate complex was 86% when heating 2.000 g of the neutralized red mud in 1M $H_2C_2O_4$ at 70°C in 2h, and then soaking in 20h. The extracted ferrioxalate complex was used in the modified Fenton system of ferrioxalate/H_2O_2/sunlight to treat 200 mL of MB with the optimal conditions of pH 4, the H_2O_2 concentration of 20 mM, the $Fe(C_2O_4)_3^{3-}$ complex concentration of 0.5 mM, and the MB decomposition efficiency was 100% after 25 min illumination by sunlight at noontime. This is a promising method that uses red mud, inexpensive chemicals, and sunlight to treat MB, a common dye chosen to investigate ability of this method in treating textile wastewater.

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