DEGRADATION OF METHYL RED – AN AZO DYE BY H_2O_2/UV PROCESS

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TÓM TẮT

TỐC ĐỘ SUY GIẢM METYL ĐỎ - THUỐC NHUỘM AZO BẰNG H_2O_2/UV

Trong bài báo này, sự oxi hóa metyl đỏ (MR) – một chất azo trong thuốc nhuộm bởi UV/H_2O_2 được nghiên cứu. Ảnh hưởng của thể tích dung dịch và nồng độ ban đầu được nghiên cứu. Với điều kiện tối ưu, chiếu tia UV qua đáy của dung dịch chứa MR. Tốc độ thay đổi màu tỉ lệ thuận với sự tăng của nồng độ H_2O_2. Sau 50 phút, hiệu quả khử màu với 16 ppm H_2O_2 là 38%, cao hơn một chút so với hàm lượng 14 ppm H_2O_2. Tuy nhiên, sự mất màu đạt tới 97%, cần 380 phút đối với dung dịch MR với nồng độ 16 ppm của H_2O_2, so với 320 phút khi nghiên cứu ở cùng điều kiện với dung dịch MR với nồng độ 14 ppm của H_2O_2. Sau khi chọn được điều kiện tối ưu 200 mL MR 10^{-4} M và 14 ppm H_2O_2, hiệu quả oxi hóa được so sánh bằng quá trình Fenton và Photo-Fenton. Quá trình Photo-Fenton có hiệu suất cao nhất, đạt 97% sau 70 phút, so với 270 phút và 320 phút đối với quá trình Fenton và oxi hóa bằng H_2O_2/UV. Tuy nhiên, dung dịch sau xử lý bằng H_2O_2/UV mất màu hoàn toàn, trong khi hai dung dịch xử lý bằng hai phương pháp còn lại vẫn có màu vàng do có mặt ion sắt.

***Từ khóa:** metyl đỏ, nước thải dệt nhuộm, azo.*

1. INTRODUCTION

The textile industry has always been an important and indispensable component of the economy of Vietnam. In 2013, the textile industry ranked the second place in the export turnover rate[1]. However, the wastewater of textile industry becomes a serious threat to the environment.

In the article *Treatment of Textile wastewater by AOPs – A review*[2], Al-Kdasi et al mentioned that 47% of 87 dyestuffs are biodegradable, leaving 53% of the dyeing colors are non-biodegradable. Another reason for the low biodegradability of textile wastewater is that they have complex organic structure along with the strong azo bond (-N=N-). When the textile wastewater is released into the environment, they will still have the color residues. The colored waste is dangerous to the aquatic life in rivers, lakes and sea[3]. Colored water also hinders light penetration, and, as a result, will disturb the biological processes in water-bodies. Furthermore, because of the huge numbers of chemical additions, the dyes themselves are toxic to organisms and human if they are in contact with the water.

Researches have shown high interest in the removal of dyes and chemicals in the textile effluent. Many traditional methods, such as filtration, adsorption, or activated carbon, are no longer effective for many wastewater treatment facilities[4,5]. According to the study of Amin et al, one of the most common methods used nowadays is conventional activated sludge, which is effective but rather "not originally used for treatment of industrial wastes, particularly textile wastes containing dyes and surfactants".

Several methods have been applied, but most of them bring unsatisfied results, in terms of cost and outcomes. Advanced Oxidation Processes (AOPs), however, have been reported successfully to degrade organic pollutants into environmental friendly products without the high cost and the advanced operations[6-9]. AOPs are based on the generating of reactive radical species such as hydroxyl radicals, •OH that will oxidize organic pollutants non-selectively and in high speed under certain conditions.

In this project, H_2O_2/UV, one of AOPs processes was chosen to study due to the availability of the reagents and the great promising effects for degradation of Methyl Red (MR). Its presence is important in the biological and chemical assays. It is useful in coloring textiles (cotton, wool, silks, and acrylics), china clay, leather, printing inks producing, and in photography[3].

2. MATERIAL AND METHODS

Methyl Red (MR) ($C_{15}H_{15}O_2N_3$) – an azo dye is also known as 2-((4-dimethylamino)phenyl) azo)-benzoic acid or hydrochloride. It's absorbed at 515-525 nm wavelength. The system was set up in a safe environment to work with UV. The UV lamp was covered by carton box and black tape, placed horizontally. Under the UV lamp, two stirring machines Stirring Hotplate – IKA RCT were placed, allowing two experiments to be carried out at the same time. The H_2O_2 30% solution was stored in the refrigerator during the project.

At the beginning, MR solution was put in a 500-mL beaker and was placed under the UV light; H_2O_2 was added by using the pipette immediately after. After 3-5 seconds, the first sample of Methyl Red was taken out and measured the absorbance by UV-Vis spectroscopy. The sample was continued to be drew out after a certain amount of time until achieving the desired efficiency. UV Spectrophotometer – Shimadzu 1800 was used to measure the decolorization of MR, the maximum absorbance peak was determined by scanning the dye solution with wavelength range from 350 nm to 700 nm.

3. RESULTS AND DISCUSSION

3.1. Effect of bed volume of Methyl Red solution in H_2O_2/UV method

The height of MR solution was considered to be an element affecting the color removal efficiency. The higher the column was, the harder it was for UV light to get to the whole body of MR solution.

In this experiment, different heights MR solution were applied by changing the volumes of MR solutions (100mL, 200mL, and 300 mL) while other parameters such as concentration of MR (10^{-4} M), concentration of H_2O_2 (6 ppm), power of UV light, and room temperature were fixed. Figure 1 presented the effect of bed volume on the decolorization efficiency of MR using H_2O_2/UV system.

Figure 1 showed a trend that the smaller the volume was, the higher the efficiency of treatment process was. The efficiencies were 94.7%, 68.7%, 55.2%, corresponding to bed volume of 100 mL, 200 mL and 300 mL, respectively.

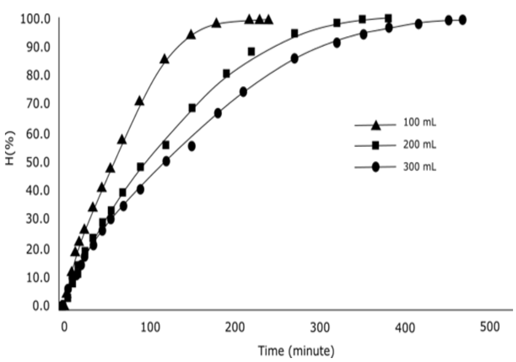


Figure 1: Effect of bed volume on the decolorization efficiency of MR solution using H_2O_2/UV system

As mentioned above, to be able to measure the absorbance by UV-Vis spectroscopy, the sample was taken out of the beaker more than 16 times (3-3.5 mL/time). For reaction set up at volume 100 mL, it would lead to a huge change on the bed volume of solution, affecting severely to the data set. Therefore, all reaction at 200 mL solution was chosen to be the optimum condition for the following experiments.

3.2. Effect of Methyl Red concentration

The effect of Methyl Red concentration on decolourization efficiency was studied. Experiments with different Methyl Red concentrations changing from 10^{-5} M, to 10^{-4} Mwere carried while stabilizing all other conditions of reactions as follow: power of UV light, volume of dye solution (200 mL), H_2O_2 concentration (10 ppm), and room temperature. The results were presented in Figure 2.

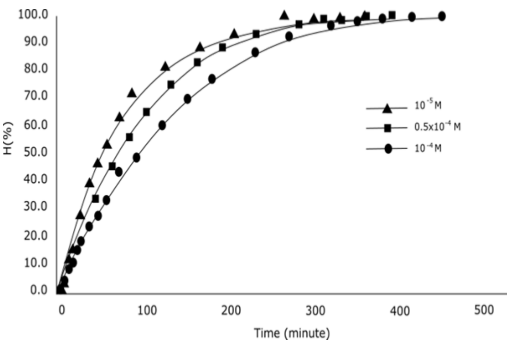


Figure 2: Effect of Methyl Red concentration on the decolorization efficiency

Before the combination of hydrogen peroxide and UV light happened, some researches had been carried with the oxidization of textile wastewater using solely hydrogen peroxide. They all showed an ineffective result for both acid and alkali medium[2]. Yet, under the presence of UV irradiation, hydrogen peroxide is “photolyzed to form two hydroxyl radicals that react with organic contaminants”.

The decolorization efficiency rate increased rapidly in first 100 minutes. The result showed that by increasing the MR concentration from 10^{-5} M to 10^{-4}M, the removal efficiency decreased from 75% to 55%. To reach the stationary state (H = 98%), the experiment at 10^{-5} M of dye needed 250 minutes, 1.32 times and 1.52 faster than its at 0.5×10^{-4} M (330 minutes) and 10^{-4} M (380 minutes), respectively.

Although the experiment with 10^{-5} M of MR showed the higher efficiency comparing to the other two experiments, 10^{-4} M of MR was more related to the wastewater from industry, as effluent from dye industry always had high concentration. For this reason, 10^{-4} M of MR was chosen for the following experiments.

3.3. Effect of H_2O_2 concentration

Effect of different H_2O_2 concentration (ranging from 6 to 14 ppm) was also studied. These conditions were: power of UV light, volume of dye solution (200 mL), MR concentration (10^{-4} M), and room temperature. Figure 3 presented the effect of different H_2O_2 concentration on the decolorization efficiency.

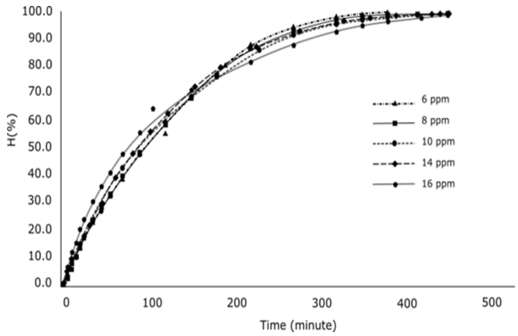


Figure 3: Effect of H_2O_2 concentration on MR solution decolorization efficiency using H_2O_2/UV system

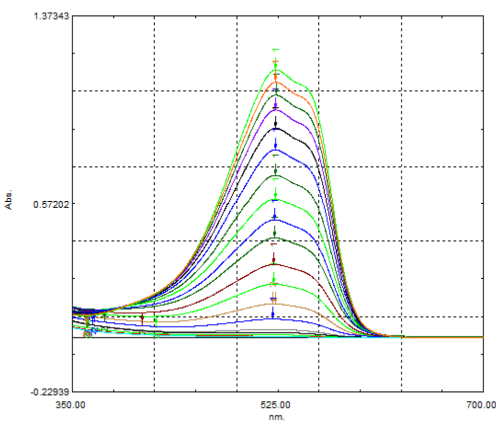
There was an increase in the color removal with the increasing of H_2O_2 concentration[2]. The results showed the efficiency of reaction was 38% with 16 ppm H_2O_2 and 32% with 14 ppm H_2O_2 after 50 minutes. On the contrary, it needed a longer period to attend the stationary state. It took 380 minutes to reach efficiency of 97%, while with 14 ppm H_2O_2, it took only 320 minutes to reach the same efficiency. With lower concentration of H_2O_2, not enough hydroxyl radicals was produced, resulting in a decrease in the removal rate. In contrast, high concentration of hydrogen peroxide produced enough ·OH for the oxidation, leading to an increase in efficiency. H_2O_2 was a “scavenger” for hydroxyl radicals[5].

However, the final solution of 16 ppm had many bubbles proving that it contained exceeded H_2O_2. Al-Kdasi[2] discussed a "critical value" where the upward trend of decolorization efficiency stopped. At this certain point, the efficiency reached its maximum, and then started to go down. Because HO_2• was less reactive than •OH radical, the exceeded H_2O_2 would start to compete with the dye for reaction with •OH radicals, causing the reaction rate to decrease. Furthermore, the •OH radicals generated at a high local concentration would combine to create H_2O_2[5]. Economically, H_2O_2 concentration 14 ppm was chosen to be a optimal condition for the following experiments.

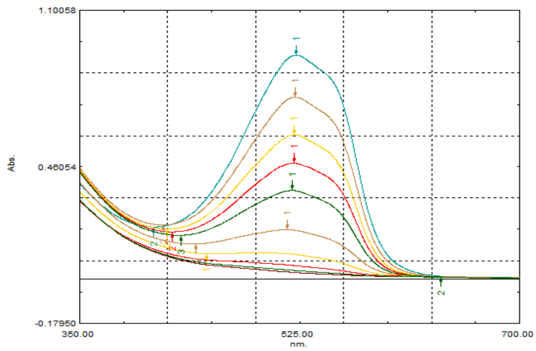
3.4. Comparative study of H_2O_2/UV, Fenton, Photo-Fenton process for degradation of MR

Effect of different processes on MR degradation was carried out. These experiments were carried after determining the optimum concentration of H_2O_2 (14 ppm). Besides, the Fenton's reagent (H_2O_2 and Fe^{2+}) dose initial and $[H_2O_2]/[Fe^{2+}]$ ratio is an important factor to decolorization, the molar ratio 1:1 of $H_2O_2/FeSO_4.7H_2O$ was chosen. The results were presented in Figure 4. The concentration of MR at different reaction time was monitored by the UV-Vis spectrum. Figure 5 showed the UV-Vis spectrum of MR in term of time in Fenton, Photo-Fenton, and H_2O_2/UV processes.

According to the Figure 4, Photo-Fenton process showed the higher efficiency in Methyl Red degradation than Fenton and H_2O_2/UV process.. The efficiency of Photo-Fenton was 96% after 70 minutes of reaction, while that of H_2O_2/UV was the lowest (H = 96%; 320 minutes). The rate of MR degradation by Photo-Fenton was 3.4 times faster than Fenton system (H = 96%; 240 minutes), and 4.2 times faster than H_2O_2/UV.



(a)



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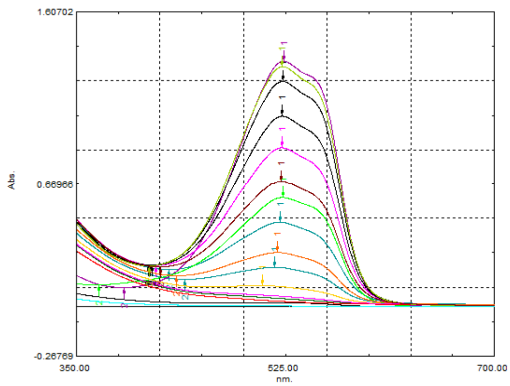

(c)

Figure 5: UV-Vis spectrum of MR in terms of time in a) Photo-Fenton process, b) Fenton and c) H_2O_2/UV process

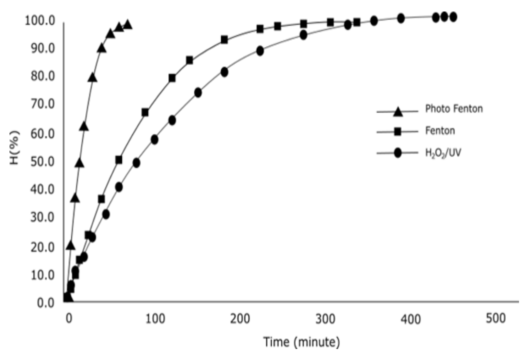

Figure 4: Effect of different processes on Methyl Red degradation

However, the resulting solution obtained from Photo-Fenton and Fenton was yellowish due to the presence of Fe^{2+}, while the same solution of H_2O_2/UV was colorless.

4. CONCLUSION

The study described the degradation of Methyl Red using three treatment methods: H_2O_2/UV, Fenton and Photo-Fenton. These approaches were found to degrade Methyl Red effectively with the decolorization efficiency of nearly 100%.

Among of them, Photo-Fenton process had the highest yield. To h]ve the decolorization efficiency of 97%, Photo-Fenton took 70 minutes, comparing to 270 minutes and 320 minutes of that for Fenton and H_2O_2/UV systems respectively. However, Photo-Fenton required UV light, which consumed a large amount of energy. Despite wasting time, final solution obtained from H_2O_2/UV was colorless, while the two other methods needed another method to be colorless. It can be concluded that each treatment has its own pros and cons, yet they still gave better results than other methods.

The work also investigated the importance of some parameters in the degradation efficiency. Favorable operating conditions were estimated by H_2O_2/UV process. The height and the concentration of Methyl Red solution were modified to allow the UV light go through. The higher concentration of H_2O_2 was used, the faster the reaction occurred. However, the amount of H_2O_2 excess was not environmentally-friendly and economically. As a result, for different cases and circumstances, it is important for the experimenters to find the relevant amount of H_2O_2 concentration. Industrial factories that use these processes must take into consideration the parameters to ensure they are at the optimum conditions. For that, the effective and economic aspects of the project are guaranteed.

In the future, many ideas can be considered to improve three methods. For example, sunlight can be an option to replace UV light. More investigation can be proceeded to examine the other standards to transform textile wastewater to drinking water.

REFERENCES

1. Nguyễn, N., (2014), 'Textile Dye Treatment Technology – Experiences from the Reality', *Vietnam Environment Administration Magazine*, vol. 10.

2. Al-Kdasi, A., Idris, A., Saed, K., Guan, C., (2004), 'Treatment of Textile Waste Water by Advanced Oxidation Processes – A review', *Global Nest: the International Journal*, vol. 6, no.3, pp 222-230.

3. Ali, A., Dakhil, I., (2012), 'Photocatalytic Decolorization of Methyl Red dye under solar light', *Journal of Kerbala University*, vol. 10, no. 3, pp 88-95.

4. Sundararaman, T., Ramamurthi, V., Partha, N., (2009), 'Decolorization and COD Removal of Reactive Yellow 16 by Fenton Oxidation and Comparison of Dye Removal with Photo Fenton and Sono Fenton Process', *Modern Applied Science*, vol. 3, no. 8, pp 15-22.

5. Amin, H., Amer, A., Feckly, A., Ibrahim, I., (2008), 'Treatment of Textile Waste Water using H_2O_2/UV system', pp 17-28.

6. Deng, Y., Zhao, R., (2015), 'Advanced Oxidation Processes (AOPs) in Wastewater Treatment', *Current Pollution Reports*, vol. 1, no. 3, pp 167-176.

7. Fadzil, N., Zainal, Z., Abdullah, A., (2012), 'Ozone-assisted Decolorization of Methyl Orange via Homogeneous and Heterogeneous Photocatalysis', *International Journal of Electrochemical Science*, vol. 7, pp 11993 – 12003.

8. Kumar, M., Sharma, P., Sharma, K., (2012), 'Photochemical Treatment of Methyl Red WasteWater by Photo-Fenton Reagent', *International Journal of Research in Chemistry and Environment*, vol. 2, no. 4, pp 87-92.

9. Mahmoud M., Poncherib A., Abd M., Waheda E., (2009), *South Africa Journal of Science*, 'Photocatalytic degradation of methyl red dye', vol. 105, pp 299-303.