REMOVAL OF METHYLENE BLUE FROM WATER BY ELECTROCOAGULATION

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ABSTRACT
This paper deals with the removal of methylene blue from water by the electrocoagulation process. The parameters such as electrode material, current density, and initial pH affecting the removal process were investigated in detail. The results showed that the Fe(anode)-Al(cathode) pair is the most proper electrode pair for the removal of methylene blue. The current density had a noticeable effect on the removal efficiency and the optimal value for application in practice was 70 A/m^2. The removal efficiency significantly depended on the initial pH of the solution. At pH of 7.0, more than 99% of methylene blue was removed after 40 min. The finding in this study indicates that electrocoagulation is a promising approach that can be applied for the removal of organic dyes from water.
Keywords: *methylene blue; electrocoagulation; removal efficiency; electrode; organic dyes*

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LOẠI BỎ XANH METYLEN TRONG NƯỚC BẰNG KEO TỤ ĐIỆN HÓA

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TÓM TẮT
Bài báo này nghiên cứu quá trình loại bỏ xanh metylen khỏi nước bằng quá trình keo tụ điện hóa. Các thông số như vật liệu điện cực, mật độ dòng điện và pH của dung dịch có ảnh hưởng đến quá trình xử lý được nghiên cứu chi tiết. Kết quả cho thấy cặp điện cực Fe(anôt)-Al(catôt) là cặp điện cực phù hợp nhất cho quá trình xử lý xanh metylen. Mật độ dòng điện có ảnh hưởng đáng kể đến hiệu suất xử lý. Cường độ dòng điện tối ưu cho quá trình ứng dụng trong thực tế để loại bỏ xanh metylen là 70 A/m^2. Hiệu suất xử lý cũng phụ thuộc rõ rệt vào pH ban đầu của dung dịch. Tại pH = 7.0, hơn 99% xanh metylen được loại bỏ sau 40 phút. Các kết quả trong nghiên cứu này cho thấy keo tụ điện hóa là một phương pháp có nhiều tiềm năng để ứng dụng vào việc loại bỏ chất màu hữu cơ trong nước.
Từ khóa: *Xanh metylen; Keo tụ điện hóa; Hiệu suất loại bỏ; Điện cực; Chất màu hữu cơ*

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1. Introduction

Methylene blue (MB) has been widely used in different industries such as paper and plastics, leather, pharmaceuticals, cosmetics, dyestuffs, textiles, etc. to color the products [1], [2]. Consequently, the wastewater of these industries contains a considerable amount of MB. This dye is difficult to degrade because of its complex structure which contains aromatic amines, such as nitro-aromatic and phenolic compounds [3], [4]. The existence of MB in water even with a low concentration is highly visible and undesirable. The degradation by-products of MB have serious effects on the environment because they are toxic aromatic compounds [3]. Therefore, the removal of MB from wastewater before discharged into the environment is essential, otherwise, it will cause many problems with human health and environmental pollution [5].

MB can be removed from water by various methods such as adsorption, coagulation, filtration, ion exchange, oxidation, and biodegradation [6]. However, the drawbacks of the mentioned methods including chemical expense, difficult operation, production of new pollutants, and time consumption limit the application in practice [7]. In recent years, electrocoagulation (EC) has been insensitively and applied for the removal of organic dyes from wastewater [8]. The reported results show that it is a promising approach for the prevention of pollution problems from industrial effluents. In the contribution [9], the authors used EC to remove congo red from wastewater and found that the removal efficiency reached 98% with the energy consumption of 0.46 KWh per 1000 L of congo red solution. In the study [10], EC was used for removal of color from the solution containing dye Basic Yellow 28 and the results showed that the color can be completely removed after about 7 minutes. The main advantage of this technology is its environmental compatibility, high efficiency, and safety because it operates at the ambiance conditions [11].

In the present work, the EC process is studied and utilized to eliminate MB from water. The key factors such as electrode material, current density, and initial pH which govern the removal process are investigated in detail.

2. Materials and Methods

The chemicals including MB, NaCl, NaOH, and HCl were analytical grade and used directly without any further purification. The electrode materials used in this study were Fe (99%) and Al (99.5%). All solutions were prepared with double-distilled water (DDW). A 1000 mg/L solution of MB was prepared by dissolving 1 g of methylene blue in 1 L of DDW and the obtained solution was used to prepare working solutions by diluting with DDW. The electrocoagulation system used in this study is presented in Figure 1.

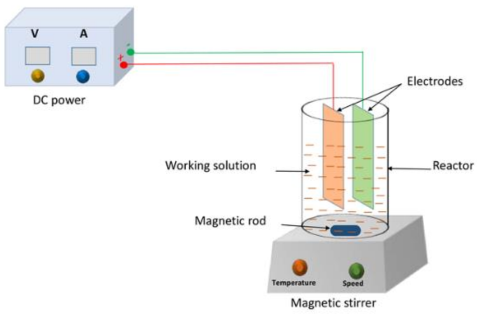

Figure 1. *Electrocoagulation system*

In this system, two electrodes with 2cm in width and 5 cm in length were placed in a 250 ml reactor containing 200 mL of the working solution. The distance between two electrodes was 15 mm and the electrodes were connected to a DC power by electric wires. A magnetic stirrer was used to homogenize the reaction system. To study the effect of the electrode and, the experiments were carried out at pH = 7, with current density (J) of 50 A/m^2, MB initial concentration (C_o) of 30 mg/L, and electrolyte (NaCl) concentration of 1%. The materials used for electrodes were steel (Fe) and aluminum (Al). Four pairs of electrodes including Fe-Fe, Al-Al, Al (anode) –Fe (cathode), and Fe(anode)-Al(cathode) were used to find the optimum electrode pair and the reaction time were changed from 5 to 90 minutes. In the study of the effect of current density, the experiments were carried with electrodes pair Fe(anode)-Al(cathode) and the current density was varied from 50 to 100 A/m^2. Reaction time was changed from 5 to 60 minutes. To study the effect of pH on MB removal performance, the experiments were performed the under the following conditions: MB initial concentration of 30 mg/l, the current density of 70 A/m^2), electrolytes (NaCl) of 1%, electrode pair of Fe(anode)-Al(cathode) and the initial pH of the solution was adjusted from 3.0 to 11.0. The samples after treatment were centrifuged at 4000 rpm. The concentration of MB in the remained in the solutions was determined by photo spectroscopy method. The analyses were performed on a V-770 photo spectrometer. The standard line was built in the concentration range of 0-10 ppm with a radiation wavelength of 664 nm. The obtained solutions were diluted (if it is necessary) to lie in the standard range and measured at 664 nm. Each sample was analyzed three times and the reported results were average values. The dye removal efficiency was calculated by the following equation:

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} 100, \quad (1)$$

where C_o is the MB initial concentration (mg/L) and C_t (mg/L) is the MB concentration after treated in *t* minutes.

3. Results and Discussion

3.1. Effect of electrode materials

The electrode material is one of the key factors that affect electrocoagulation because the electrochemical reaction significantly depends on the nature of the electrodes used in a system [12]. In this study, four pairs of electrodes were tested. From the results, we found that the MB removal efficiency is remarkably low, below 10% after treated in 90 minutes when the electrodes pairs Al-Al and Al(anode)-Fe(cathode) were used, indicating that these pairs are not suitable for removing MB from the solution. The low efficiency in these cases can be explained by the passivation of the aluminium electrode in the electrolysis process, resulting in a small amount of flocs formed.

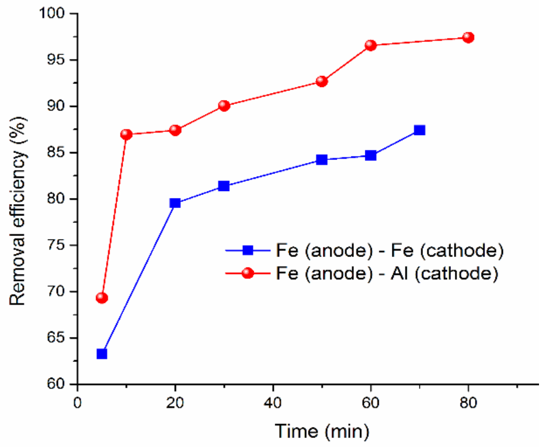

Figure 2. *Effect of electrode on MB removal efficiency: pH=7, C_o=30 mg/L, 1% of NaCl, J=50 A/m^2*

For the Fe-Fe electrode system (Figure 2), the removal efficiency increases rapidly at the beginning of the electrolysis process. Nearly 80% of MB was removed in 20 minutes, after that the process was slowed down with the removal efficiency after 70 minutes. The mechanism for removing MB in this electrode system is indicated by the reactions that occur on the electrode surface as the following:

Anodes: $Fe - 2e \rightarrow Fe^{2+}$ (2)

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ (3)

$2Fe(OH)_2 + H_2O + O_2 \rightarrow 2Fe(OH)_3$ (4)

Cathodes:

$2H_2O + 2e \rightarrow 2OH^- + H_2$ (5)

The overall reaction during electrolysis is as follows:

$4Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3$ (6)

Newly formed Fe(OH)3 flocs have large surface areas, which are favored for the effective adsorption of dissolved organic compounds and capturing of suspended particles [13].

For the Fe(anode) - Al(cathode) electrode system, the MB removal rate is much faster in comparison to the Fe-Fe system. More than 85% of MB was removed in only 10 min, after that, the rate is slower and finally reaches 97.34 % after 90 min.

Anodes:

Anodes: $Fe - 2e \rightarrow Fe^{2+}$ (7)

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ (8)

$2Fe(OH)_2 + H_2O + O_2 \rightarrow 2Fe(OH)_3$ (9)

Cathodes:

$2H_2O + 2e \rightarrow 2OH^- + H_2$ (10)

$Al + OH^- + H_2O \rightarrow [Al(OH)_4]^- + H_2$ (11)

$[Al(OH)_4] \leftrightarrow Al(OH)_3 + OH^-$ (12)

The overall reaction during electrolysis is as follows:

$Fe + Al + O_2 + 4H_2O \rightarrow Fe(OH)_3 + Al(OH)_3 + H_2$ (13)

Like the above electrode system, $Fe(OH)_3$ are generated adsorbs dissolved organic compounds in the solution and captures suspended particles, reducing the concentration of MB. However, one difference in this electrode system is that it produces not only $Fe(OH)_3$ but also $Al(OH)_3$. $Al(OH)_3$ also works as $Fe(OH)_3$, reducing the concentration of MB. Therefore, MB removal efficiency in the Fe-Al electrode system is higher than that of the Fe-Fe electrode system. From the results, it can be also seen that the MB removal efficiency significantly depends on the electrolysis time. This dependence is reasonable because the amount of flocs formed relates to the amount of metal ion released during electrolysis which is proportional to the electrolysis time (Faraday's law). When compared two equations (6) and (13), it can be found that in the Fe-Al system, besides the $Fe(OH)_3$ flocs, there are additional $Al(OH)_3$ flocs, although two systems consume the same amount of charge. Therefore, concerning the electric efficiency in the production of flocs, the Fe-Al system more efficient that the Fe-Fe system. Thus, the Fe-Al system was selected for the next experiments.

3.2. Effect of current density

Current density (J) is an important parameter in the EC process because it affects the cost of the system operation [14]. J (A/m^2) is calculated as the following equation:

$$J = \frac{I}{S} \quad (14),$$

where I (A) is the current intensity and S (m^2) is the surface area of the electrode. In this work, to find the optimal condition, J was varied in the range of 50-100 A/m^2, respectively. The dependence of the MB removal efficiency on J is shown in Figure 3.

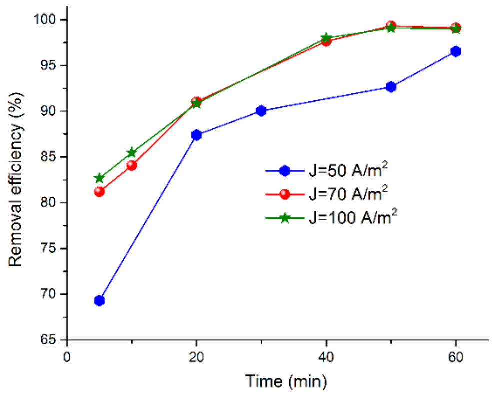

Figure 3. *Effect of current density on the MB removal efficiency*

It can be seen that when J increases from 50 to 70 A/m^2, the removal efficiency increases remarkably, more than 12% after 5 min. When the time increases, the difference reduces with 97.41 % for J of 50 A/m^2 and 99.10% for J of 70 A/m^2 after 70 min of the treatment. This trend can be explained from the fact that the amount of flocs depends on the amount of metal ions formed at the electrodes which are directly related to the current passing through the electrodes according to Faraday's law.

Inversely, when J increases from 70 to 100 A/m^2, the removal efficiency of both cases is similar, indicating that J of 70 A/m^2 is sufficient to produce the flocs which are enough for the removal of MB. Concerning energy efficiency, J of 70 A/m^2 is the most proper value for this process because of the high rate of the process and the saving of energy [15]. Therefore, this value will be used in the next experiments. According to the experimental data, with J of 70 A/m^2, the time required for the removal of more than 99% of MB is 50 minutes.

3.3. Effect of initial pH

In the EC process, the rate of the formation of flocs noticeably depends on the pH of the reaction system because the precipitation of metal ion relies on the concentration of the hydroxyl ion [7]. To study the effect of the initial pH value of the dye solution, the experiments were carried out in three mediums with five values of pH including 3.0 and 5.0 (acidic), 7.0 (neutral), and 9.0 and11.0 (basic). The effect of the initial pH is presented in Figure 4.

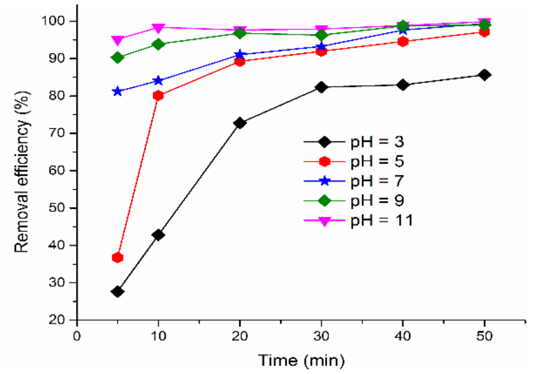

Figure 4. *Effect of pH on the MB removal efficiency*

It can be seen that at the beginning of the process, the removal efficiency is significantly affected by pH value of the solution. Namely, at pH of 3.0, only 27.64 % of MB was removed, while this value for pH of 7.0 and 11.0 is 81.2 and 90.3%, respectively. The effect of pH can be explained that in the acidic solution, ion OH- formed at the cathode will react with ion H+, hence the precipitation of the metal ions is prevented. On other hand, in the basic solution, with an excess of OH^- in the solution at the beginning not only the precipitation of $Fe(OH)_3$ is formed but also aluminum is dissolved to give $Al(OH)_3$, which will accelerate the removal process. When the electrolysis increased, ion OH^- in the acidic and neutral solution increases, resulting in an increase in the removal efficiency. There is no difference between the cases of pH = 7 and pH = 11 after 40 min, indicating that the removal process can be performed well without using the chemical to adjust the pH of the solution.

4. Conclusion

The removal of MB by using the electrocoagulation method has been studied in detail. The removal process is significantly dependent on the material used for electrodes, current density, and initial pH of the solution.

Four electrode pairs including Fe-Fe, Al-Al, Al(anode)-Fe(cathode), Fe(anode)-Al(cathode) pair have been tested for the ability in removing MB in which the Fe(anode)-Al(cathode) pair is the most effective. The effect of current density on the removal efficiency has been evaluated and J of 70 A/m^2 shows the most proper value for practical. The higher pH is the shorter time is required for the removal of MB. According to the obtained data in this study, it can be concluded that the electrocoagulation process with the Fe-Al electrode pair is an effective means to remove cationic dyes as MB from water and is a promising approach that can be applied for the removal of organic dyes from water.

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