Decomposition of methyl orange by Heterogeneous Electro-Fenton technology using ferrimagnetic oxide on activated carbon support as the catalyst

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ABSTRACT

The treatment of methyl orange in this study was carried out by application of Electro-Fenton process using Fe_3O_4*/AC catalyst and electrode cells in an area of 100* cm^2*. The efficiency of removing methyl orange was 98.86% with optimal conditions including: pH of solution 3.0, potential difference between two electrodes 15 V, initial concentration of methyl orange 20 ppm, catalyst dosage 0.8 g/L. The synthesized material has the ability to be reused, achieving the treatment efficiency of 78.5% after 4 reuses. The experimental results showed the potential of application the heterogeneous Electro-Fenton process for treatment of persistent organic compounds.*

Keywords: Heterogeneous Electro-Fenton; Methyl orange; Magnetic activated carbon.

1. INTRODUCTION

Dye pollutants from dye manufacturing, printing, and textile industries are sources of water pollution [1]. Residual dyes in wastewater discharged into the environment will harm aquatic animals and humans due to toxic, carcinogenic and mutagenic effects. Azo dyes, characterized by the presence of one or more azo groups (-N=N-) linked to aromatic rings, are the largest and most common class of synthetic organic dyes [2]. More than 50% of commonly used dyes are estimated to be azo dyes, valued for their chemical stability and versatility. Currently, wastewater treatment technologies for dyeing wastewater including physical, chemical, and biological [3]. Biological method is a widely used, cost-effective technology, but it has some drawbacks such as it's inability to degrade persistent organic compounds. Physical methods like sedimentation, filtration, adsorption and ion exchange are also ineffective for treatment of persistent pollutants and can produce secondary waste. Advanced oxidation processes are a suitable method for treatment of persistent organic pollutants [4]. Among them, electro-Fenton is one of the technologies that is currently being studied due to its fast reaction rate, low toxicity and environmental friendly. This process is based on the reaction between Fe^{2+} ions and H_2O_2 called the Fenton reaction to generate hydroxyl radicals ($OH^{\bullet}$) to conduct a series of non-selective reactions and is capable of oxidizing all organic molecules until they are completely mineralized into CO_2 and H_2O [5]. Previous studies have shown that some azo dyes can be effectively degraded by the Fenton reaction [6, 7]. The degradation efficiency of dyes mainly depends on their chemical properties and the generation of hydroxyl radicals during the reaction. This study was carried out to investigate the effect of operation parameters on the degradation efficiency of methyl orange dye and the reusability of the catalyst material in the heterogeneous Electro-Fenton process.

2. MATERIALS AND METHODS

2.1. Materials

Chemicals employed in the synthesis of magnetic activated carbon include activated carbon (0.5-1 mm particle size powder – China), ferrous chloride tetrahydrate ($FeCl_2.4H_2O$ 99.5% – China), ferric chloride hexahydrate ($FeCl_3.6H_2O$ 99.7% – China), ammonia solution (NH_3 28-30%

– China), acid hydrochloric (HCl 36.5% – China).

2.2. Synthesis of magnetic activated carbon

The activated carbon was immersed in HCl 1M solution to remove impurities. Next, 10 g of pre-treated activated carbon was added to 150 mL of a $FeCl_3$ and $FeCl_2$ solution (2:1 molar ratio). The mixture was heated and stirred, maintaining a temperature of 70–80 °C in an oxygen-free environment by flowing nitrogen gas. After adding 30 mL of NH_3 30% solution, the mixture was stirred for 30 minutes, then aged at room temperature for 24 hours. The solid was filtered, washed with distilled water until the pH reached the neutral region, dried at 70 °C for 10 hours to obtain the magnetic activated carbon [8].

2.3. Characterization techniques

The morphology of material was obtanined by using scanning electron microscopy SEM (Hitachi S-4800, Japan), Investigate the crystal structure of the material by the X-ray diffraction (XRD) technique (D2 Phaser, Bruker, Germany), The specific surface area was analyzed using the nitrogen adsorption/desorption method at 77.35 ^oK (PMI's BET Sorptometer, India) [8].

2.4. The experimental procedure

The experimental model was setuped including a DC power supply, graphite electrodes (10 × 10 cm) placed at a distance of 4 cm apart, a reaction tank (10 × 10 × 4 cm), and 300 mL of wastewater containing methyl orange as the simulated solution. After the reaction, the catalyst is separated from the solution, and the water is analyzed to determine the concentration of methyl orange using a colorimetric method on a UV-Vis spectrophotometer at a wavelength of $\lambda = 464$ nm [9]. Methyl orange degradation efficiency is determined by using the following expression:

$$H\% = \left(1 - \frac{C_t}{C_0}\right) \times 100\%$$

Where, C_t and C_0 are the concentrations at the sampling time and the initial concentration of methyl orange, respectively.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the magnetic activated carbon

The results of the surface morphology analysis of the magnetic activated carbon and the initial activated carbon are shown in figures 1 and 2.

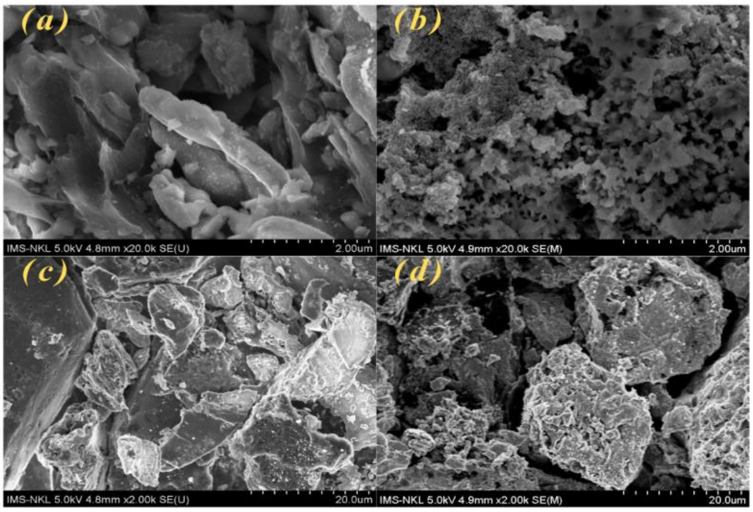
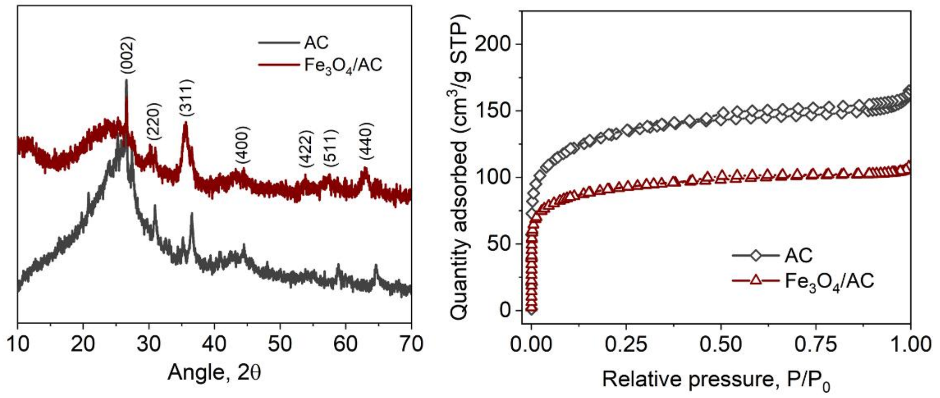


Figure 1. *SEM image of activated carbon (a, c) and magnetic activated carbon (b, d).*

The SEM images of the material samples clearly reveal differences in their surface structures. Activated carbon has a surface morphology with large, nonhomogeneous pores. Meanwhile, Fe_3O_4/AC material has more pores and tends to be uniform with smaller pore sizes than activated carbon. This can be attributed to the incorporation of Fe_3O_4 into the activated carbon, which causes the iron oxide to penetrate the pores and disperse randomly across the surface. The Fe_3O_4/AC material has a darker, rougher surface due to the larger molecular weight of Fe_3O_4 molecules adhering to the activated carbon [10]. This suggests that the iron oxide molecules are strongly attached and uniformly distributed on the activated carbon surface.

The X-ray diffraction (XRD) results have shown that the initial activated carbon contain graphene phases, with the characteristic miller plane (002) predominantly present, along with amorphous components lacking a crystalline structure. The Fe_3O_4/AC contain graphene phases with the characteristic miller plane (002) and crystalline phases of Fe_3O_4 in cubic form, with miller planes (220), (311), (400), (422), (511), and (440) [11]. This demonstrated the successful attachment of Fe_3O_4 crystalline components to the surface of the activated carbon.



(a) (b)

Figure 2. *(a) XRD spectrum and (b) N_2 adsorption – desorption isotherm.*

The results of nitrogen adsorption-desorption analysis of the initial activated carbon and the magnetic material follow the Langmuir Type II isotherm [12]. This indicates that the pores of the material are stable and primarily consist of micropores and mesopores. The similarity between the isotherms also suggests that the Fe_3O_4 crystalline phases are evenly coated on the surface of the activated carbon support.

3.2. The effect of the material on the methyl orange degradation efficiency

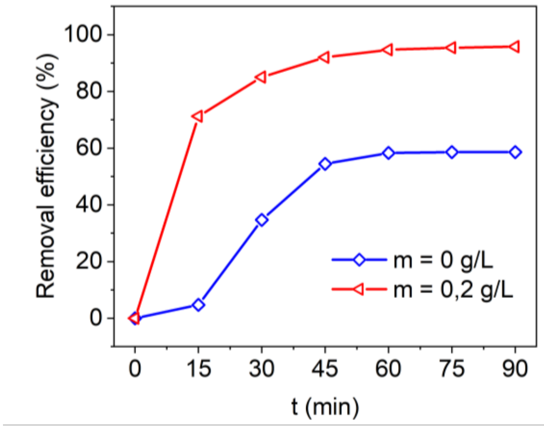


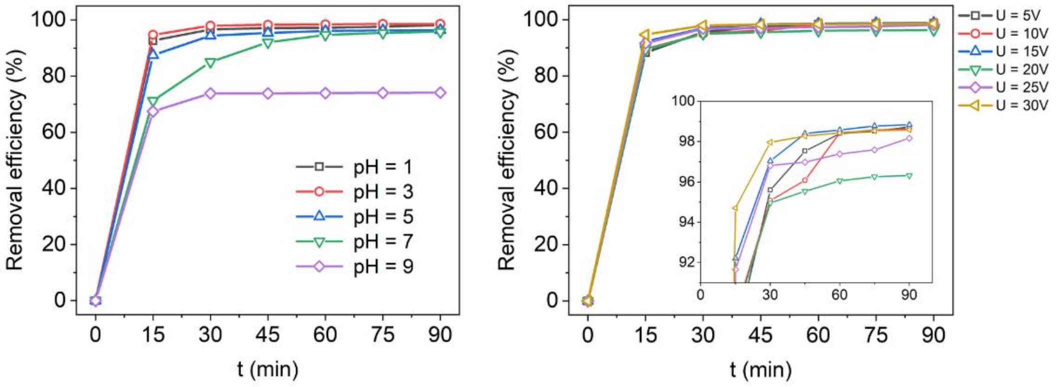
Figure 3. *The effect of magnetic catalytic material on methyl orange degradation.*

The experimental results showed the degradation efficiency of methyl orange occurred rapidly after 15 minutes of reaction (88.65%) by using 0.2 g/L Fe_3O_4/AC material, compared to experiment without material (4.71%). After 90 minutes of reaction, methyl orange was almost completely decomposed, whereas without the magnetic material, the degradation efficiency reached only 58.58%. Magnetic material promotes the generation of hydroxyl radicals through the reaction between Fe^{II} and H_2O_2 formed during the electrochemical process [13]. Consequently, next studies will be cary out with the catalyst material concentration of 0.2 g/L.

3.3. The effect of pH and voltage on the degradation of methyl orange

The experiment was carried out with pH from 1 to 9. The results showed that the degradation of methyl orange occurred quickly under acidic pH conditions. Maximum efficiency was observed at pH 3 (98.59%), whereas at pH 9, the efficiency was limited to 74.12%. Lower pH levels correspond to a higher concentration of H^+ ions, promoting iron dissolution and increasing the generation rate of hydroxyl radicals. Additionally, the neutralization of OH^- ions shifts the equilibrium forward, further facilitating the progression of reaction (1) [14].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{1}$$



(a) (b)

Figure 4. *Effect of (a) pH of the solution and (b) voltage.*

The effect of voltage was examined using values ranging from 5 to 30 V, with the solution pH maintained at 3. Rapid methyl orange degradation was observed within the first 15 minutes, achieving a maximum efficiency of 98.84% at a voltage of 15 V. As the voltage increases, the methyl orange decomposition efficiency tends to decrease, likely due to the dominance of H_2O electrolysis, which produces OH^- ions as outlined in reaction (2).

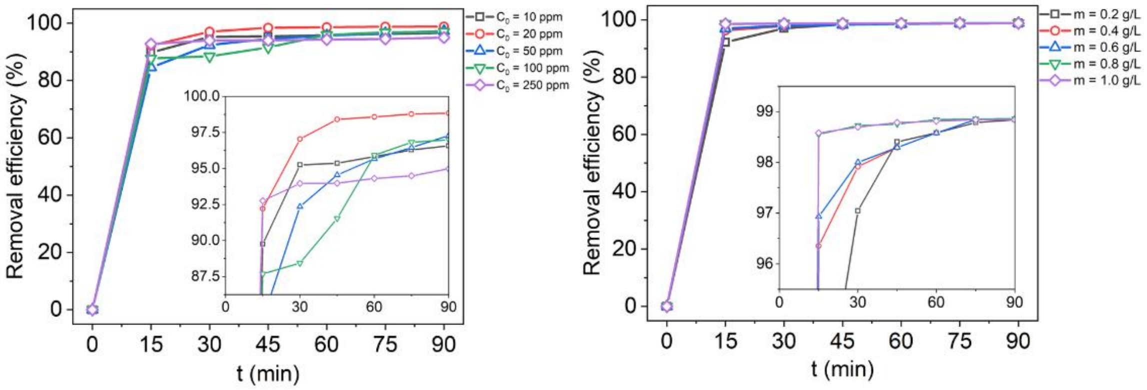
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{3}$$

The higher reaction rate of reaction (2), compared to reaction (3), leads to an increase in the concentration of OH^- ions, which shifts the equilibrium of reaction (1) and reduces the concentration of hydroxyl radicals. This decrease in hydroxyl radicals results in a lower methyl orange degradation efficiency. On the other hand, At lower voltages, fewer electrons are provided for the redox reactions at the electrodes, leading to a reduced production of H_2O_2 which further decreases the methyl orange degradation efficiency [15].

3.4. The effect of catalyst dosage and the initial methyl orange concentration

The experiment was conducted with catalyst concentrations ranging from 0.2 g/L to 1.0 g/L, an initial methyl orange concentration of 20 ppm, and a pH of 3. The results showed that the highest degradation efficiency (98.84%) was achieved after 60 minutes of reaction with a catalyst concentration of 0.8 g/L (figure 5b), and this efficiency remained nearly constant when the catalyst concentration was increased to 1.0 g/L. As the initial methyl orange concentration increased, the degradation efficiency correspondingly decreased due to the formation of various intermediate products during the degradation process, which disrupted the preferred pathway for breaking down the organic molecules, preventing the reaction from prioritizing the degradation of the initial methyl orange molecules [16].

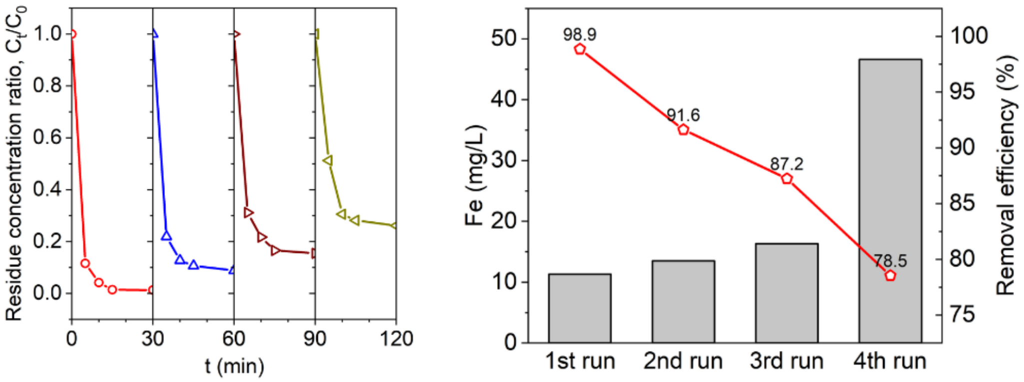


(a) (b)

Figure 5. *Effect of (a) initial concentration of methyl orange and (b) catalyst dosage m (g/L).*

3.5. The recovery and reusability of the synthesized material

The study on the reusability of the material was conducted under the optimal conditions identified in previous investigations, with a catalyst concentration of 0.8 g/L.



(a) (b)

Figure 6. *(a) The reusability of the material, (b) The amount of iron dissolved in the solution after the reaction.*

The results as present in figure 6 showed that after 4 cycles of material reuse, the degradation efficiency remained above 78%, compared to the initial cycle efficiency of 98.9%. Iron leaching gradually increased, particularly in the fourth reuse cycle, where it surged to over 46.6 mg/L. The iron leaching was due to the acidity of the solution when the reaction was carried out at pH = 3. The study also demonstrated the recovery and reusability of the Fe_3O_4/AC catalyst in the heterogeneous electro-Fenton.

4. CONCLUSIONS

The study results indicate that magnetic activated carbon (Fe_3O_4/AC) was successfully synthesized using the co-precipitation method. The degradation of methyl orange using the Electro-Fenton process with Fe_3O_4/AC material achieved a high efficiency of 98.86% under optimized conditions, including a solution pH of 3, potential 15 V, initial methyl orange concentration of 20 ppm with the catalyst concentration of 0.8 g/L. The material reusability was also examined, with a performance of 78.5% after 4 cycles. These findings highlight the potential of the heterogeneous Electro-Fenton process for treatment of persistent organic compounds such as methyl orange dye.

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TÓM TẮT

Phân hủy methyl orange bằng công nghệ Fenton điện hóa dị thể sử dụng vật liệu xúc tác dạng oxit sắt từ trên chất mang than hoạt tính

Trong nghiên cứu này, methyl orange đã được xử lý bằng phương pháp Fenton điện hóa dị thể với sự có mặt của chất xúc tác Fe_3O_4*/AC và các tấm điện cực với diện tích 100 cm*^{2}*. Kết quả mang lại hiệu suất loại bỏ methyl orange bằng 98,86 % với các điều kiện tối ưu đã được nghiên cứu bao gồm: pH của dung dịch bằng 3, hiệu điện thế giữa các cặp điện cực bằng 15 V, nồng độ ban đầu của methyl orange bằng 20 ppm và hàm lượng vật liệu được sử dụng là 0,8 g/L. Vật liệu tổng hợp được có khả năng tái sử dụng đạt hiệu suất phân hủy sau 4 lần tái sử dụng bằng 78,5%. Từ đó có thể thấy hiệu quả xử lý ô nhiễm bởi nguồn methyl orange trong nước của phương pháp Fenton điện hóa với chất xúc tác oxit sắt từ trên chất mang than hoạt tính.*

Từ khóa: Fenton điện hóa dị thể; Methyl orange; Than hoạt tính từ tính.