Bipolar Electro-Fenton System for Textile Dye Removal From Aqueous Solution

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ABSTRACT
The main goal of this article is to study a bipolar electro-Fenton process using stainless steel mesh for removal of methylene blue (MB) as a model of textile dye from aqueous solution. The effect of operating parameters such as the applied current, supporting electrolyte, the type of electrode, H_2O_2 concentrations (1-10 mmol/L) and hydraulic retention time (5-60min) on the proposed electro-Fenton efficacy was evaluated. The optimum condition was obtained as follows: initial pH 3, the current density 1.4 mA/cm^2, H_2O_2 10 mmol/L, Na_2SO_4 concentration 0.4 g/L as supporting electrolyte. The results show that the MB removal and COD reduction could be achieved 92% and 70%, respectively. The experimental results indicate that the bipolar electro-Fenton process using stainless steel mesh electrode is a promising wastewater treatment technique for removal of dye from aqueous solutions.
Key words: Electro-Fenton; Electrochemistry; Pollution; Dye; Wastewater

INTRODUCTION
Synthetic dyes are widely utilized in various industries such as textile, leather tanning, pulp and paper [1-3]. According to the scientific reports, 700000 tons of dye products are made in the world every year [2]. MB is one of the common dyes in the textile industries. It is a basic, cationic dye which has been widely used in coloring paper, hair colorant, dyeing cotton and paper [4]. Synthetic dyes have wide applications, but it can cause some adverse effects in humans [5]. The discharge of dyes from textile industries can lead to adverse effects on the environment and change biological life in receiving water sources. On the other hand, international environmental standards have been presented more stringent and colored wastewaters require treatment before discharge into the environment [6]. Problems related to dye pollution could be decreased by physical, chemical and biological treatments such as biodegradation, chemical oxidation, coagulation and filtration [1-3]. Due to the low biodegradability of some synthetic dyes, chemical treatment processes are more effective compared to conventional biological wastewater treatments. Advanced oxidation processes have presented as a promising method for effective removal of synthetic organic materials from the water and wastewater [7]. Electro-Fenton process is a proposed technique between these processes and it has been extensively used for organic pollutant degradation in environment [8]. The process is based on the catalytic electrogeneration of Fenton's reagent to produce hydroxyl radicals and degrade organic pollutants in aqueous solutions. It has some advantages such as compatibility with the various environments, versatility and high efficiency for pollutants removal, mater kinetic reaction and the possibility of complete mineralization in the optimum conditions [9]. Electrode surface is one of the important factors in the electrochemical oxidation process. In this aspect, a stainless steel mesh electrode could be attractive in experimental applications, because its large surface and higher mass transfer. To the best of our knowledge and based on the literature review, there is no report on the utilization of bipolar electro-Fenton process using stainless steel mesh electrodes for degradation of synthetic dye from aqueous solutions. The novel additional data on the removal efficiency of bipolar electro-Fenton would contribute to an improved understanding of organic material degradation.

MATERIALS AND METHODS
Materials
MB was obtained from Merck company and used as a synthetic textile dye in this study. The molecular structure of MB is illustrated in Fig. 1. A flexible woven mesh of stainless steel was used as electrode. Hydrogen peroxide solution (30% w/w), KCL, Na_2SO_4, NaCl, Na_2CO_3, $K_2Cr_2O_7$, $HgSO_4$, Ag_2SO_4 and potassium hydrogen phethalate were purchased

from Merck. All chemicals used were of analytical grade. The HCl and NaOH were used to adjust the pH of the electrolyte.

Electrocatalysis experiments

The experiments were performed using a plexiglas reactor with a volume of 250ml, supplied with a magnetic stirrer. A pair of stainless steel mesh was used as the anode and cathode electrodes. Two iron electrodes were installed between anode and cathode. The batch experimental setup is shown in Fig. 2. The electrodes were connected to a digital DC power supply (Atten APS3005-3D). As showed in Fig. 2, there is no electrical connection between inner electrodes. The electrochemical reactor was inoculated with synthetic wastewater containing 100 mgL^{-1}MB. The effect of different operating parameters including current density (0.3 - 2.75 mA/cm^2), supporting electrolyte type (KCl, Na_2SO_4, NaCl, Na_2CO_3) and dosage (100, 200, 400mgL^{-1}), electrode material (steel mesh, stainless steel and iron plate) and hydraulic retention time (5- 60 min) were evaluated in the bipolar electro-Fenton reactor. In order to achieve high removal efficiency, the electro-Fenton process was conducted by adding various concentrations of H_2O_2 (1-10mmol/L). The experiments were utilized according to "one factor at a time" method (OFAT). All experiments were carried out at room temperature (25±1 $^{\circ}C$).

Analysis

Samples of MB dye were examined according to standard methods for the examination of water and wastewater [10]. In order to remove sludge suspended particles, all samples were centrifuged at 5000 rpm for 5min. Residual MB dye was determined at its maximum absorbance wavelength of 488nm by UV–Visible Spectrophotometer (Ray Leigh UV-9200). The pH values were adjusted by a portable pH meter (Sension 378, HACH), and the chemical oxygen demand (COD) was measured using COD reactor CR-2200 WTW.

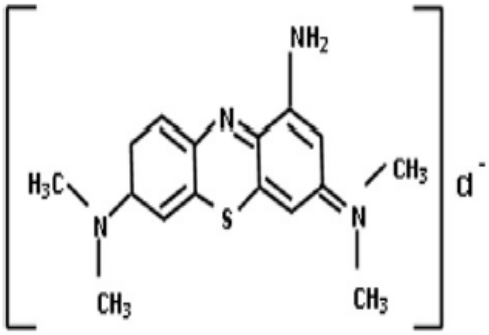

Fig. 1: The chemical structure of MB

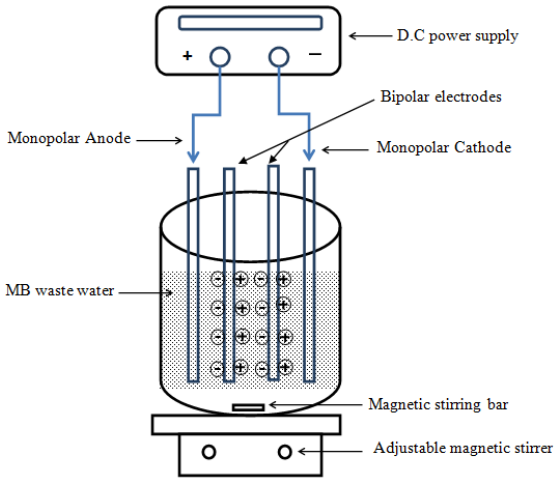

Fig.2: Schematic of electro-Fenton reactor with bipolar electrodes

RESULTS AND DISCUSSION

Effect of electrode material

In various electrochemical process, electrodes have a remarkable effect on the treatment efficiency. Hence, selection of suitable electrode materials and their arrangements is important at the treatment efficiencies [11]. To investigate the effect of electrode materials on the MB removal efficiency, bipolar electro-Fenton process was carried out using steel mesh and stainless steel as sacrificial electrodes. The experimental results show that, stainless steel mesh electrodes were more effective than a stainless steel plate (Fig. 3). The higher MB dye removal was obtained in shorter reaction time. Application of steel mesh in bipolar electro-Fenton reactor could produce more ferrous ions (Fe^{+2}) in electrolyte and consequently lead to hydroxyl radicals ($OH^{\bullet}$) generation from hydrogen peroxide (H_2O_2) as an oxidizing agent [12, 13]. Steel mesh electrodes could produce Fe^{+3} ions will undergo further spontaneous reactions to generate hydroxides and/or polyhydroxides [14]. Thus, the reasons have presented for higher dye removal efficiency by steel mesh in comparison with the other electrodes could be explained considering the sufficient ability of hydrous ferric oxide to adsorb dye molecules [15]. In fact, the process with ferrous ion production in solution is a combination process that has the advantages of both electrocoagulation and Fenton oxidation [11]. Regarding the obtained results it was observed that using iron plate as the electrodes; higher amounts of sludge were generated. Dry weight of sludge produced using iron sheet, steel mesh and stainless steel plates were achieved 1.02, 0.35 and 0.78g, respectively. The electrocoagulation process with iron electrodes and the electrooxidation process with Ti/Pt electrodes have showed that decolorization

of aqueous indigo carmine solutions obtained 100% color removal in 35 and 20min of reaction at the applied current densities of 5 and 10mA cm^{-2} [16].

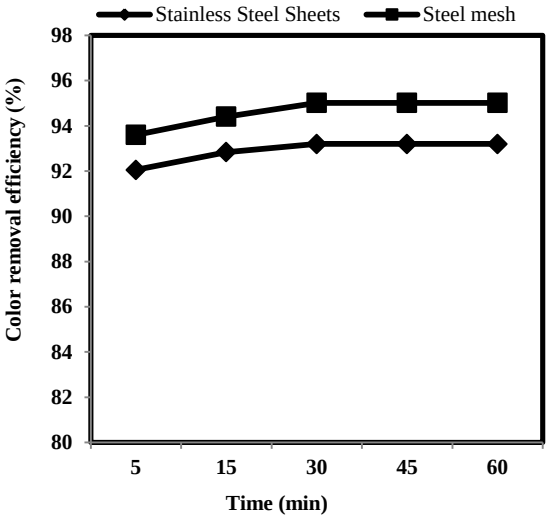

Fig. 3: Effect of electrode materials on the MB removal efficiency: C_0 = 100mg/L; pH = 3; applied current density= 1.4 mA/cm^2

Effect of current density

In order to evaluate the effect of applied current density on MB dye removal, the efficiency of bipolar electro-Fenton process was evaluated at various currents. It was observed that, with increasing applied current density from 0.3 to 2.75mA/cm^2, the degradation rate of MB dye was increased from 30% up to 92% and the time required to obtain further removal efficiency decreased. Applied current is a motive force for the reduction of oxygen and it is a reason for production of hydrogen peroxide (H_2O_2) at the cathode. High applied current could increase the generation of hydrogen peroxide. The number of hydroxyl radicals ($^{\bullet}OH$) in the supporting electrolyte is increased, which are highly reactive and responsible for decomposition [17]. With increasing current the efficiency of Fenton chain reactions improved due to the higher electro-regeneration of Fe^{+2} ion from Fe^{+3}[18]. However, higher applied current is favorable for dye degradation, but high current need more applied voltage in the electrochemical system and consequently the increase of the energy cost, sludge generation and electrodes consumption. In this study the optimum current density was determined in 1.4mA/cm^2. Decolorization of C.I. Acid Yellow 23 solution by electrocoagulation process showed that almost 98% color and 69% COD were removed, when the current density was approximately 112.5A/m^2 [19]. Aoudj *et al.* reported that increasing current density led to increasing dye removal efficiency from 52.34% (at 0.125mA/cm^2) to 98.15% (at 1.875 mA/cm^2). It was stated that more aluminium ions are produced in the reaction solution at higher current density and formation rate of $Al(OH)_3$ increased. Further current density had no significant improvement in removal efficiency. Considering the electrical energy consumption for higher densities, the value of 1.875mA/cm^2 was considered as optimal [20].

Effect of H_2O_2

Fig 4 shows the relationship between MB removal efficiency and H_2O_2 concentration at various reaction times. As shown, the H_2O_2 concentration had direct impact on dye removal efficiency, but higher concentration of H_2O_2 (higher than the optimum value), did not markedly increase bipolar electro-Fenton process performance. Initial concentration of H_2O_2 has great effect in electro-Fenton process [18] due to the increment of •OH concentration following the addition of H_2O_2 [21]. Zhang *et al.*[15] investigated the degradation of organic materials in the leachate by electro-Fenton technique and showed that performance of hydrogen peroxide declined with the increase of Fenton's reagent dosage. Decrease in removal efficiency at high concentration of H_2O_2, could be due to the $^{\bullet}OH$ scavenging impact of H_2O_2 and the recombination of the hydroxyl radical (Eqs. 1-3) [11]. In this study, significant correlation was obtained between the concentration of H_2O_2 and sludge generated in the process. By improving the H_2O_2, the amount of sediments reduced. The results show that using 340mg/L H_2O_2 leads to 1.32g sediment. Reduction in sludge generation by increasing the H_2O_2 dosage could be due to decline of efficiency that represents the MB degradation.

$$\mathbf{HO^{\bullet} + H_2O_2 \rightarrow HO^{\bullet 2} + H_2O} \quad (1)$$
$$\mathbf{HO^{\bullet}_2 + HO^{\bullet} \rightarrow H_2O + O2} \quad (2)$$
$$\mathbf{2HO^{\bullet} \rightarrow H_2O_2} \quad (3)$$

The highest dye removal efficiency in Fenton and modified Fenton process were obtained at the optimum H_2O_2/Fe^{2+} and H_2O_2/Fe^{3+} concentrations of 11.3 and 5.1mM. In the modified Fenton method, the maximum removal efficiency was 94.8% and 99.43%, for reactive red 198 and reactive blue 19. In the Fenton method, the maximum removal was achieved at 94.70% and 99.31% for reactive red 198 and reactive blue 19, respectively [22]. Ozgen *et al.* also reported that the degradation dye solution efficiency, enhanced with increasing H_2O_2 concentration. The removal efficiency could be reached up to 95% with 0.1 mL 30% H_2O_2 for RB19, RR21, and the mixture. This is explained by the amount of $^{\bullet}OH$ radicals involved in the degradation process [23].

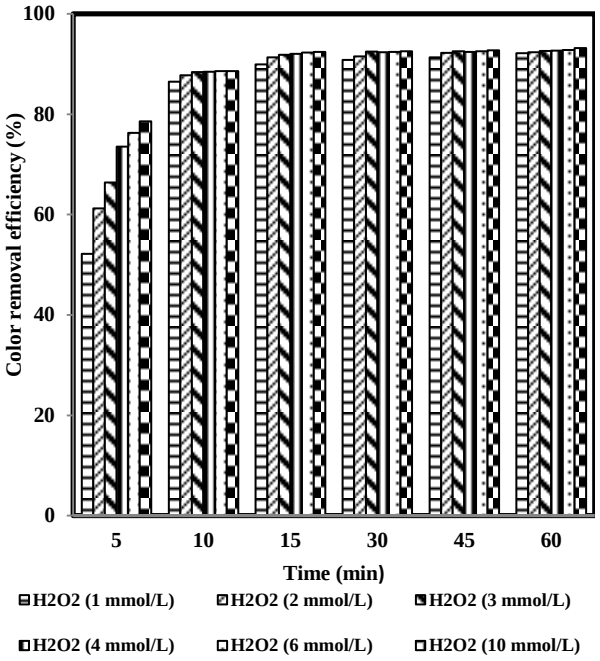

Fig. 4: Effect of H_2O_2 concentration on the MB removal in the electro-Fenton process (experimental conditions: C_0=100mg/L; pH= 3; applied current density= 1.4mA/cm^2)

Effect of reaction time

The effect of time of experiments on the dye removal electro-Fenton efficiency depends directly on the amount of ions produced by the electrodes. In higher electrolysis period, the ions concentration and hydroxide flocs increase. Accordingly, as indicated in Fig. 5a, b, an increase in treatment time to 60 min could cause an increase in the COD and MB removal efficiency. Over time, the color intencity of solution was reduced. The main color changes occurred quickly in the initial times, and then it was gradually declined. It was reported that the time required to complete the oxidation process depends significantly on the H_2O_2 dosage and the point of H_2O_2 utilization in the oxidation process or point of oxidation termination [21]. In this study, 60 min was selected as optimum oxidation time. Results from decolorization of C.I. Acid Yellow 23 solution by electrocoagulation process were indicated that increasing the time of electrolysis from 2 to 6 min yields an increase in the color removal (15.53% to 98.98%). In the present study, the COD removal efficiency during 15-60 min reaction time was obtained about 62.26% - 69.2 %. The MB dye was degraded rapidly in the first 15 min of reaction time and later the rate of decomposition gradually slowed down. Initial rapid decomposition is greatly due to the easily degradable organic materials[21].

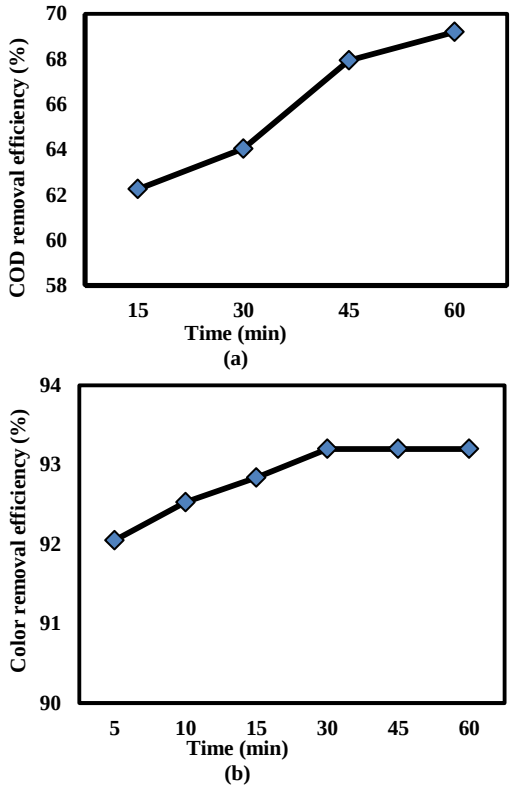

Fig. 5: Effect of reaction time on the (a) COD and (b) MB removal efficiency (experimental condition: C_0 = 100 mg/L; pH = 3; applied current density= 1.4 mA/cm^2

Effect of supporting electrolyte

Electrolyte would be helpful in an electrochemical reaction due to improving the solution conductivity and speed up the electron transfer. Hence, it is required, particularly in the solution without sufficient conductivity. To investigate the effect of supporting electrolyte dosage and species on MB removal in the bipolar electro-Fenton process, experiments were performed using KCL, Na_2SO_4, NaCl, and Na_2CO_3 (Fig. 6). The obtained results reveal that, Na_2SO_4 had better performance than the other compounds in MB removal efficiency. It could be due to higher electrogenerated H_2O_2 in Na_2SO_4 solution. In other words, the accumulation of H_2O_2 in the presence of Na_2SO_4 is more than other supporting electrolytes [24]. Zhou *et al.* reported that higher amounts of Na_2SO_4 make higher current density, which leads to producing more and faster hydrogen peroxide and increases the electro-Fenton efficiency [13, 24]. But, significant decrement in efficiency of the system was reported at 0.2M Na_2SO_4 dosage. It was attributed to the

consumption of the produced hydroxyl radical by high SO_4^{2-} concentration as in Eq. 4 [13].

$$HO^{\bullet} + SO_4^{-2} \rightarrow HO^{-} + SO_4^{\bullet-} \quad (4)$$

Ghoneim *et al.* compared the efficiency of 0.05M Na_2SO_4, 0.05M NaCl and 0.05M KCl as supporting electrolyte [14]. The time required for dye removal was achieved 120, 180 and 180 min, respectively, for 0.05 M Na_2SO_4, 0.05 M NaCl and 0.05 M KCl solution[14]. The produced HOCl within the electrolysis of NaCl solution has oxidative capability to organic compounds, but its function is too lower than that of the $HO^{\bullet}$ formed in the process [25]. The results show that using various concentrations of Na_2SO_4 concentration, the performance had no considerable changes. Similarly, Daneshvar *et al.* reported that increasing of $NaClO_4$ concentration from 0.05 to 0.1M had not remarkable impact in dye degradation[17].

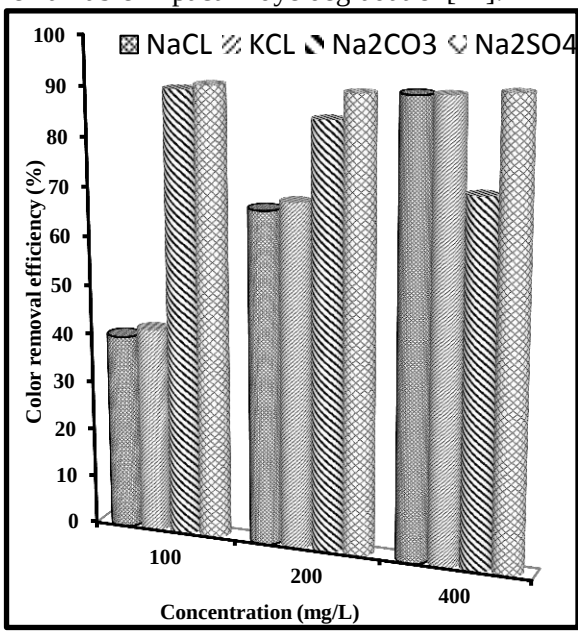

Fig. 6: Effect of supporting electrolyte species and concentration on the MB removal efficiency (experimental condition: C_0 = 100 mg/L; pH = 3; applied current density= 1.4mA/cm^2)

CONCLUSION

In this study, the performance of bipolar electro-Fenton process was investigated for MB degradation and COD reduction in an aqueous solution. Effective operating parameters on process efficiency were pH, applied current density, reaction time, supporting electrolyte, the concentration of H_2O_2, and electrodes. Optimum operating condition was as follows: initial pH 3, the applied current density 1.4 mA/cm^2, 10mmol/L H_2O_2, 60 min reaction time, Na_2SO_4 as supporting electrolyte, stainless steel mesh electrodes as anode/cathode and iron sheets as bipolar electrodes. The electro-Fenton process was able to decolorize wastewater containing MB up to 93.2%. The COD reduction was obtained about 70%. It can be concluded that the process does not require the addition of chemical compounds and Fenton's reagent can electrochemically generate. The proposed technique is an environmental friendly method utilizing simple reactor with easy operation.

ETHICAL ISSUES

Ethical issues such as plagiarism have been observed by the authors.

CONFLICT OF INTEREST

Authors have no conflict of interests.

AUTHORS' CONTRIBUTION

All authors equally help to write this manuscript.

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