Decolorization of Crystal Violet from Aqueous Solution Using Electrofenton Process

Hadis Fattahi¹, Hazhir Karimi², Samira Amiri¹, Shohreh Heshmati¹, Fatemeh Hosseini¹, Hooshyar Hossini²*, Yaseen T Mustafa²,³

1. Students Research Committee, Kermanshah University of Medical Sciences, Kermanshah, Iran
2. Department of Environmental Science, Faculty of Science, University of Zakho, Kurdistan Region, Iraq
3. Center of Applied Remote Sensing & GIS, University of Zakho, Kurdistan Region, Iraq
4. Research Center for Environmental Determinants of Health (RCEDH), Health Institute, Kermanshah University of Medical Sciences, Kermanshah, Iran (corresponding author, H Hossini email: hoo.hosseini@gmail.com , tel: +988338273068)

Abstract: In recent years, advance oxidation processes (AOPs) have been widely interested for treatment of industrial wastewater and organic matter. Among, Electrofenton has been proposed as a strong oxidative method. So, the aim of this work was purification of colored aqueous containing crystal violet by electrofenton process and steel mesh electrodes. All regents and methods were prepared from analytical grad and standard methods. The amounts of crystal violet were determined by colorimetric using a spectrophotometer at a maximum wavelength about 586 nm. The main parameters such as pH, applied current, dye concentration, reaction time and supporting electrolyte dose were investigated. Experimental data analysis was also performed using excel software. The results of this study showed that the better dye degradation is occurred in acidic pH (pH3), contact time of 5 minutes, initial concentration of crystal violet 50 mg/l, applied current 0.8 A and an electrolyte level about 0.1 g/L of NaCl. Higher electrical current and lower pHs were caused to generate the higher amount of oxidative radical and regeneration of Fe²⁺. Under optimal condition, crystal violet was removed around 99.72%. Referring to the results, it can be concluded that the electrofenton is a suitable in situ hydrogen peroxide generation technology for treatment of colored wastewater.

Keywords: Electrofenton, crystal violet, Steel mesh electrodes, Decolorization
1. Introduction

Colored and textile wastewaters are significant and notable sources of environmental pollution [1] and they may also be caused to occurrence the phenomenon of eutrophication and interference in the quality of receiving waters. Moreover, the type of color and its concentration in wastewater is very important [2]. The studies have been shown that about 15 to 20% of the color used in the textile industry enters to the effluent [3]. Therefore, it is essential and inevitable that the color from effluents be removed. Crystal Violet (CV) is widely used in industries and enters to the environment in a large quantity [4]. CV is a water-soluble cationic dye which is used in dyeing industry, Microbial staining and veterinary medicine as an additive to chicken foods and preventing from the release of harmful bacteria. Today, the oxidation processes often is first suggestion of engineers to purify the colored wastewaters. Fenton-based process has been used extensively due to its high performance in producing hydroxyl free radicals and high oxidation power [5]. Free hydroxyl radicals effectively react with organic matter like dyes and can mineralize them directly [6]. Processes in which produce free hydroxyl radicals by electrical energy are called electrochemical advanced oxidation processes (EAOPs) [7]. In electro-Fenton (EF) processes, the free hydroxyl radical is generated in situ by electrochemical system. Free hydroxyl radicals have an unconnected pair electrons and short-life, and it is produced by means of electric force and in a mild acidic environment. In this way, the problems of the storage and transportation of H₂O₂ will be avoided, as result the overall costs will decrease significantly [8]. In recent years, EF process has been used to treat the wastewater as eco-friendly and clean technology [9], rapid reactions, small size of reactor, and high efficient to treat the industrial type of wastewaters [10]. In other hand, EF increases the biodegradability of wastewater and consequently better activates of biological systems [11]. Referring to the literatures, the EF process has been suggested to treat the various industrial wastewaters specially colored effluent. For example; Carlos et al. (2007) used the EF process to mineralize organic pollutants and they recommend the EF process as high efficient process (95% mineralization) [12]. In other study that conducted by Panizza et al. (2001), they reported that the color and COD were reduced to about 89% and 87%, respectively under optimal iron concentration, 3 mmol [13]. Kurt et al. (2007), was investigated the potential of EF for tannery wastewater and they reported about 95% removal of COD at pH=3, the flow of 15W and the oxidant content of 1.67 mg/L [14]. Lin et al. (2014) examined the removal of Orange 2 dye by EF process and they obtained about 94.3% [15].

1.1. Objective

The purpose of this study was to investigate the removal of crystal violet by EF and mesh-type of stainless steel electrodes. This arrangement was chosen by reduction the cost of electrode material consuming and better operating. For this purpose, the influence of main effective parameters including initial pH, applied current, dye matter concentration, reaction time and supporting electrolyte were investigated.

2. Material and Methods

This study was conducted in a laboratory scale and in a batch reactor. To perform the electrochemical tests, a cylindrical glass with a useful volume of 500 ml was used. The system was operated in a monopolar mood using mesh-type stainless steel electrodes (0.1×3×15 cm). Scheme 1, illustrates the electrochemical reactor with its accessories. The distance between the two electrodes was 2 cm. The electrical force was provided by a DC power supply (Iran). Violet crystal, FeSO₄·7H₂O, KCl, H₂SO₄, HCL, NaOH and other required chemicals were purchased from the Merck Company (Germany). Magnetic starrier (Germany IKAMAG), Magnet and Centrifuge (CE.148, Finon) were used for mixing and separation. To determine the amounts of violet crystal, Spectrophotometer uv-vis (Jenway 6305 model) was used. The pH of samples was adjusted by 1M H₂SO₄ and NaOH.
3. Results and discussion

3.1. The effect of pH

The effect of different solution pH on the efficiency of EF process under certain condition (CV 50 mg/L, Current density 0.2 A, 0.1 KCl, and 1mmol iron sulfate and 60 minutes of reaction time) are shown in Fig. 1. Generally, pH has a direct effect on the chemical reaction, and this can affect on the amount of *OH production, and also affect on species and state of iron ions in the solution [16]. At high pHs, the efficiency of EF declines sharply, because H2O2 decomposes rapidly into water and oxygen due to chemical instability [17]. Also, increasing pH reduces the oxidation potential of *OH [17]. At higher pH (pH > 3), the ferric ions are transformed into a ferric. Ferric iron does not have the ability to react with H2O2 and does not produce *OH, so, lose in efficiency is concluded. At higher pHs with the increase in ferric ions (in the form of ferric hydroxide (Fe(OH)₃)) and ferric oxyhydroxide (FeOOH)) produces a lot of sludge [18]. By increasing the pH to 7 to 9, the electrocoagulation process replaces with EF, as a result the efficacy of dye removal increase again [19]. At pH 5, the removal efficiency was 17%, and in pH 7 and pH 9, the removal efficiency was 30.39% and 37.81%, respectively. In order to investigate the effect of other parameters, optimum pH was considered equal to 3.

![Scheme 1. Electrochemical system](image1)

![Figure 1. The effect of pH on the efficacy of EF](image2)
3.2. The effect of current

To determine the effect of current on the removal rate of crystal violet, this phase of the experiments was designed. Fig. 2 shows the effect of different current (0.1 to 0.8 A) on the EF efficiency. The result was obtained under CV concentration 50 mg/L, pH 3, electrolyte dosage 0.1 g/L NaCl, iron sulfate 1 mmol and reaction time of 60 min. The decolorization rate at different current 0.1, 0.2, 0.4, 0.6 and 0.8 A was determined 16.17%, 41.56%, 64.71%, 90.70% and 97.71%, respectively. Referring to the result, the highest removal rate was seen at 0.8 A. It can be observed that the removal efficiency is directly proportional to passing current via electrolyte. In electrochemical processes, increasing in passing current leads to a further reduction of anode material and generates more oxidative species. This fact is caused to increase the decolorization rate of dye and, consequently, an increase in efficiency. Panizza, and Cerisola (2009) believed that the enhancement oxidation of dye can be related to the excessive formation of \( \text{H}_2\text{O}_2 \) and \( \bullet \text{OH} \) \[20\]. Under higher current, upper oxidation rate could be resulted to acceleration of \( \text{H}_2\text{O}_2 \) formation rate (equation 1) and also to the faster regeneration of \( \text{Fe}^{2+} \) (equation 2). This fact can lead to the generation of higher amount of \( \bullet \text{OH} \) from Fentons reaction (equation 3) \[21\].

\[
\begin{align*}
\text{O}_2 + 2\text{H}^+ +2\text{e}^- & \rightarrow \text{H}_2\text{O}_2 & (1) \\
\text{Fe}^{3+} +\text{e}^- & \rightarrow \text{Fe}^{2+} & (2) \\
\text{Fe}^{2+} +\text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \bullet \text{OH} & (3)
\end{align*}
\]

3.3. Supporting electrolyte

The results of added salts, 100 mg/L of \( \text{Na}_2\text{SO}_4 \), KCl and NaCl, as supporting electrolyte on prepress of EF process are represented in Fig. 3. At 60 min of contact time, samples were taken from the reactors and finally the residual color was determined. As can be seen in the plot, the most efficient supporting electrolyte that could facilitate the removal of CV is KCl salt. Decolorization rate was 99.86% for KCl. Removal percentage for \( \text{Na}_2\text{SO}_4 \) and NaCl salts were 99.72% and 90.19%, respectively.
3.4. The effect of CV concentration

Fig. 4 illustrates the effect of initial CV concentrations on the decolorization rate under optimum condition (contact time 60 min, electrical current 0.8 A, 0.1 g/L KCl salt, pH 3 and 1 mmol/L of iron sulfate). The results show that an increasing in dye concentration in the range of 20 to 200 mg/L leads to lose in decolorization rate. Previously the researches have been implied that increasing in concentration of pollutants has been accompanied by a reduction in the process efficiency [22]. Increasing the color concentration in constant operating conditions reduces the efficiency for two main reasons; first constant amounts of hydroxyl radical, [23] and second, higher concentrations of pollutants can produce more oxidation-by-products, which will consume more amounts of radical hydroxyl [24]. The 50 mg/L of CV was chosen for next step.
3.5. The effect of electrolyte dosage

To determine the optimum dosage of KCl, different dosages, 0.05, 0.1 and 0.15 g/L were tested. The results of electrolyte dosage are displayed in Fig. 5 under optimum condition, CV 50 mg/L, electrical current 0.8 A, pH 3, and reaction time of 60 minutes. It is clear that the increasing in electrolyte dose leads to increase the electrical conductivity of the solution. Also, preventing the inactivation of the electrodes can be occurred. As the amount of salt in the solution increases, more removal efficiency occurs. The maximum efficiency was for both 100 and 150 mg/L of KCl (99.86%).

![Figure 5. The effect of KCl dose on the EF process](image)

3.6. Contact time

Finally, the effect of time (zero to 60 min) on the efficiency of the process was studied. This experiment was performed under optimal conditions (CV concentration 150 mg/L, pH 3, electrical current 0.8 A, 0.1 g KCl salt, 1 mmol of iron sulfate). The results of this experiment are shown in Fig. 6. Accordingly, EF was able to decolorize the CV at lower time about 5 min. The time is one of the influencing factors on the progress of chemical process. In the electrochemical processes, the relationship between removal rate and time is related to provide the enough contact between pollutants and generated oxidant agents.

![Figure 6. The effect of time on the efficiency of the EF](image)
4. Conclusion

The results of this research indicate that the EF process is a suitable technology for treatment of colored wastewater like textile industrial effluent. Under optimal conditions, pH 3, contact time 5 min, initial dye concentration 50 mg/L, electrical current 0.8 A, 0.1 g/L of KCl salt, the removal efficiency about more than 99% was achieved. So, it can be concluded that the electrofenton is a suitable technology for treatment of colored wastewater like textile industrial effluent. Also, the result revealed that the in situ hydrogen peroxide generation is effective to pollutant oxidative like dyes and pigments.

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6. Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this article.

7. Reference

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