Investigation of operational parameters influencing in treatment of dye from water by electro-Fenton process

Ali Reza Rahmani[a], Amir Shabanloo[b], Mehdi Fazlzadeh[c], Yousef Poureshgh[d,*]

[a]Faculty of Health and Research Center for Health Sciences, Department of Environmental Health Engineering, Hamadan University of Medical Sciences, Hamadan, IR Iran, Tel. +98 9181317314; email: rahmani@umsha.ac.ir
[b]Department of Environmental Health Engineering, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran, Tel. +98 9183786151; email: Shabanlo_a@yahoo.com
[c]Department of Environmental Health Engineering, School of Public Health, Ardabil University of Medical Sciences, Ardabil, Iran, Tel. +98 9148090705; email: m.fazlzadeh@gmail.com
[d]Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran, Tel. +98 9148092356; Fax: +98 4533512004; email: yusef.poureshg@gmail.com

ABSTRACT

In this paper, the degradation of Acid Black 1 (AB1) and Acid Blue 113 (AB113) of azo dyes was studied by electro-Fenton process using an iron electrode to generate Fe^{2+} ions in a batch reactor. In order to reach the maximum efficiency of the process, effective parameters such as: solution pH, operating time, current density, H_2O_2, and dye concentration were investigated. The experimental data indicated that pH, H_2O_2 and dye concentration played an important role in the process. The results showed that decolorization decreased with increasing pH; for instance, the maximum decolorization efficiencies 27 and 47% were obtained, respectively, for AB113 and AB1 at pH 11 and reaction time = 10 min. The best conditions for both dyes were obtained at reaction time of 10 min, pH 3.0, H_2O_2 concentration of 100 mg/L and current density of 5 mA/cm^2. In this case, COD removal rates were, respectively, 83.5 and 92.3% for AB113 and AB1 after 30 min.

*Keywords:* electro-Fenton; Degradation; Azo dye

1. Introduction

Synthetic dyes and pigments are one of the problematical classes of recalcitrant organic compounds discharged into the environment, especially water bodies [1–4]. These dyes are widely used in various industries such as dyestuff manufacturing, food processing, paper production, plastics, and printing industries [2,3]. it is estimated that about 10–15% of the total production of dyes is discharged into the environment without any treatment [2,5]. Azo dyes make up approximately 70% of the total production of dyes [6]. The chemical structure of these compounds has an azo group (−N=N−), as chromophore, and banded with aromatic rings and other groups such as −OH and −SO$_3$H [6–8]. Since these dyes are non-degradable, and have toxic, mutagenic, and carcinogenic properties, they are considered as major health hazards for human health and ecosystems [9]. There are various methods for dye-laden wastewater
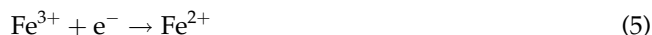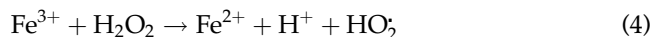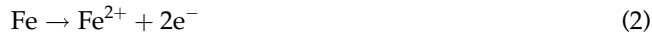
*Corresponding author.

treatment including combinations of biologic, chemical, and physical measures [1,10]. Adsorption on activated carbon, precipitation, chemical degradation, photo degradation, biodegradation, chemical coagulation, and electrocoagulation have successfully been used to remove dyes, but some of which have problems like high reaction time and being expensive. Chlorine and ozone have good efficiency, but these lead to toxic byproducts in water [10]. Some of the other physical methods such as flocculation and coagulation just transfer pollutants from liquid phase to solid phase [1]. Generally, the removal of dyestuff is very difficult by means of traditional processes because these compounds have high biochemical stability, high molecular weight and aromatic rings in structure [5]. The defects of these traditional process can be improved by the application of the advanced oxidation processes (AOPs) [9], which are hopeful technologies for dyes removal, and are based on the *in situ* production of oxidizing agents such as hydroxyl radicals (OH·) in solution. Hydroxyl radical can quickly and non-selectively oxidize various organic dyes, and have a powerful oxidative potential ($E^0 = 2.80$ V vs. NHE) [1,6,9]. Due to the volatility of this radical, it must be generated constantly "*in situ*" through chemical or photochemical reactions [11,12]. The synthetic dyes in wastewater are attacked by OH· and they are, in turn, oxidized to nontoxic and harmless species such as CO_2 and H_2O [1,11,13]. Conventional Fenton reaction (Fe^{2+}/H_2O_2) is one of the most widely used of AOPs for the degradation of a wide range of refractory organic compounds like dyes [14,15]. In this work, both H_2O_2 and Fe^{2+} are externally added to the solution; according to the Eq. (1) ferrous ion (Fe^{2+}) reacts with H_2O_2 and OH· is created [16].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^· \tag{1}$$
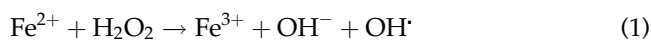
Although the Fenton reaction has a high efficiency, its large-scale usage is limited in wastewater treatment [17–19]. Recently, electrochemical AOPs (EAOPs), based on the Fenton's reaction chemistry, have received increasing attention for the remediation of acidic waters containing synthetic dyes [20]. A new AOP, which is induced by electrochemistry, the so-called electro-Fenton, has lately been applied to improve oxidation power [21,22]. In the electro-Fenton (EF) process, H_2O_2 is manually added and Fe^{2+} is generated from the sacrificial iron anode [21]. Nowadays, the EF process is divided into four approach: in first, approach Fe^{2+} and H_2O_2 are generated electrically on a sacrificial anode and a cathode, respectively [22,23].

In the second approach, H_2O_2 is manually added while a sacrificial iron anode is applied, as a source of Fe^{2+} electro-generation [24,25]. In the third approach, Fe^{2+} ion is manually added and H_2O_2 are generated electrically using an oxygen sparging on carbon-based cathode electrode or gas-diffusion cathode electrode [19,26]. In the fourth approach, Fenton's reagent is applied to generate OH· in an electrolytic cell and ferrous ion is regenerated via the reduction of ferric ion at the cathode [27].

In EF process, harmful and toxic materials are not used and, more importantly, it is an environment-friendly, low-cost method and does not result in secondary pollutants generation in water and wastewater [21,28,29]. The main reactions of the EF process have been explained in the following equations: sacrificial iron anode releases Fe^{2+} ions into the solution (Eq. (2)), simultaneously at the cathode; this makes water reduction (Eq. (3)). Then by adding H_2O_2 manually, the Fenton reactions (Eqs. (1) and (4)) occurs, continuously, regeneration of Fe^{2+} by continuous Fe^{3+} reduce at the cathode (Eq. (5)) [6,9,21]. Also, the production of OH· radicals with the electro-Fenton process has been presented in Fig. 1 [30].

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{2}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^· \tag{4}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{5}$$

However, some of hydroxyl radicals may react with Fe^{2+} and H_2O_2 and result in $HO_2^·$, which is not effective in oxidation process (Eqs. (6) and (7)) [9].

$$Fe^{2+} + OH^· \rightarrow Fe^{3+} + OH^- \tag{6}$$

$$H_2O_2 + OH^· \rightarrow HO_2^· + H_2O \tag{7}$$

The aim of the current study was to investigate the decolorization of Acid Black 1 and Acid Blue 113 azo dye by the electro-Fenton processes with iron electrodes in a batch reactor. Moreover, the effects of operating parameters: pH_i, current density, operating time, and H_2O_2 dosage and initial dyes concentration of were studied to determine optimum operating conditions. In addition, the removal efficiency of COD was measured at the optimum conditions.
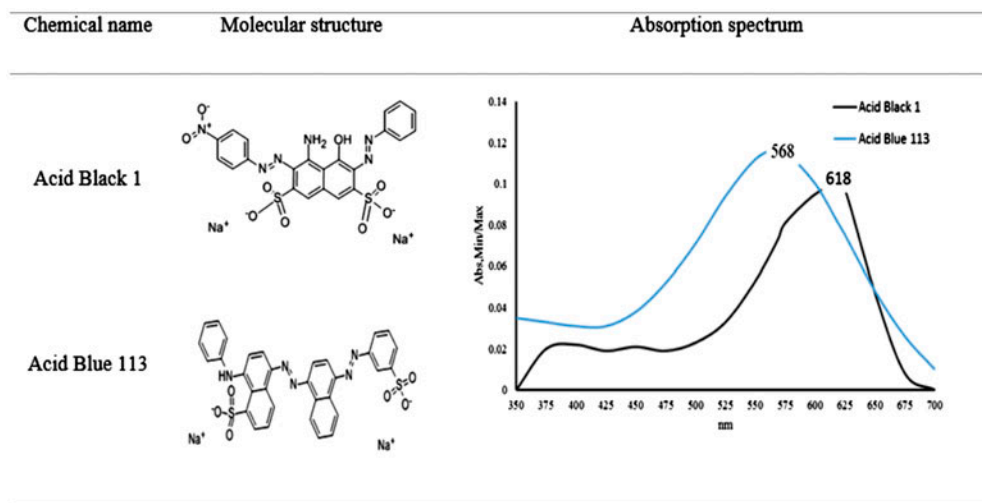
Fig. 1. Molecular structure and absorption spectrum of the Acid Black 1 and Acid Blue 113.

2. Materials and methods

2.1. Materials

Acid Black 1 and Acid Blue 113 azo dye were purchased from the Aldrich Chemical Company (Milwaukee, Wisconsin). Molecular structure of the dyes is given in Fig. 1. Fig. 1 compares the absorption spectrum of Acid Blue 113 and Acid Black 1 an aqueous solution. Sodium hydroxide, sulfuric acid, sodium sulfate, H_2O_2 (30 wt.%), and all other reagents were purchased from Merck (Darmstadt, Germany), and the arrangements and experiments were realized at room temperature.

2.2. Experimental apparatus and analytical methods

The samples containing different concentrations of the dyes (50, 100, 150, and 200 mg/L) were prepared by dissolving 1 g of each dye in 1,000 ml of double distilled water as the stock solution. The EF batch reactor was made of cylindrical glass cell (1,250 mL) and filled with 1,000 mL of the samples with required concentrations of dye standards. Four plate iron electrodes (two anodes and two cathodes) with the dimensions of (2 mm × 20 mm × 100 mm) immersed into the solution were operated. The spacing between the electrodes was set at 20 mm. The electrodes were connected for monopolar operation to a digital DC Power Supply (Aram Tronik Co., Iran). Initial pH of the solutions was adjusted with sulfuric acid and NaOH (0.1 N). In order to improve the conductivity and ionic strength, 100 mg/L of Na_2SO_4 was added, as a supporting electrolyte in all experiments. The required concentrations of H_2O_2 (25, 50, 75, and 100 mg/l) were manually added to the electrolytic reactor. The mixture was agitated using a magnetic stirrer at 200 rpm. The duration of the experiment was 30 min and the samples were taken at regular time intervals. Before each run, the samples were centrifuged for 3 min at 4,000 rpm. The effect of H_2O_2 concentration (25–100 mg/L), initial pH (3–11), initial dyes concentration (50–200 mg/L) and current density (0–10 mA/cm^2) were studied. And, final pH values were measured for all samples. The decolorization of the AB113 and AB1 solutions were followed from the absorbance at the maximum wavelength of the dyes (λ_{max} = 568 nm) and (λ_{max} = 618 nm), respectively. The schema of the experimental design has been shown in Fig. 2. COD determination was done according to the titrimetric method (method 5220 C) of Standard Methods for the Examination of Water and Wastewater [31].

3. Results and discussion

3.1. Effect of pH

The effect of solution pH (3–11) on dye degradation in EF process was studied and the results are shown in Fig. 3. This step of the experiments was performed using under the following conditions: initial dye concentration of 100 mg/L, H_2O_2 concentration of 100 mg/L, current density of 5 mA/cm^2, and Na_2SO_4 concentration of 100 mg/L. The results illustrated that the impact of solution pH on dye degradation was meaningful. After 10 min of the reaction, the maximum dye decolorization was obtained at 99.4% for AB1 and 98.2%, respectively, for AB113 at pH 3. With
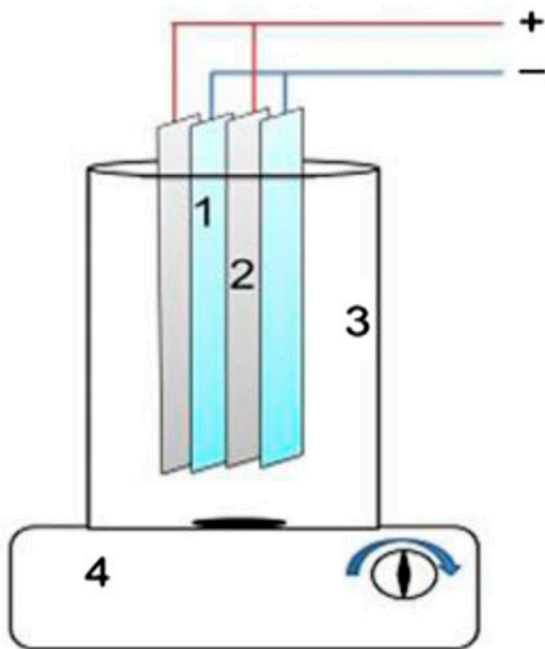
Fig. 2. Schema of the experimental apparatus in EF process.
Notes: (1) Cathode electrode, (2) Anode electrode, (3) Electrochemical cell and (4) Magnetic stirrer.
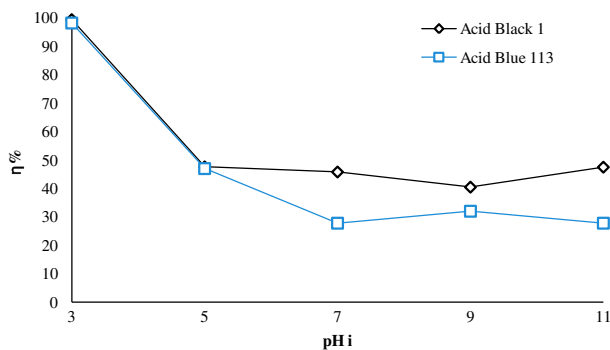

Fig. 3. Effect of pH in decolorization of AB 1 and AB 113 by electro-Fenton process.

increasing the pH value from 3 to 11, the decolorization efficiency dramatically decreased. The amounts of decolorization were, respectively, 47.4 and 27.8% for AB1 and AB113 at pH 11 after 10 min. During the electro-Fenton process, the pH of the solutions was almost unchanged for both dyes. The observed change was as an increase in final pH. Fig. 4 describes different pH trends for solution pH.

In the EF process, the solution pH was basic parameter; it has a strong influence on H_2O_2 electro
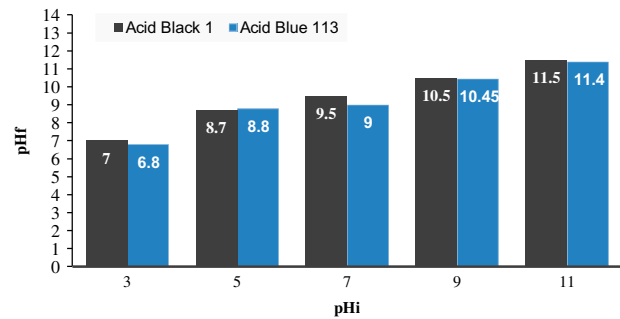

Fig. 4. pH variation of during EF process.

generation, stability of hydroxyl radical and prevents the precipitation of iron ions and oxidation efficiency [11]. Generally, the Fenton and EF process are managed and operated in acidic solution at pH values around 2–4 [19,32–35]. At higher pH, especially pH > 5, the efficiency of the EF process decreases quickly; therefore, H_2O_2 is rapidly converted to O_2 and H_2O increasing pH value and, in turn, it leads to a decrease in oxidation ability of OH· [27,34,36]. Furthermore, Fe^{2+} ions are unstable especially at pH > 4 and rapidly converted into ferric ions (Eq. (6)), which can form ferric oxyhydroxides ($FeOOH^{2+}$) (Eq. (8)) or Fe (OH)$_3$; these compounds can, in turn, be precipitated at higher pH [35]. By contrast, at lower pH values, iron species form stable complexes with H_2O_2 [11,34,35].

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^+ + H^+ \qquad (8)$$
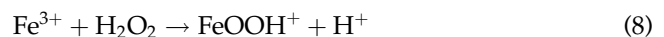
When the pH of the solution was further raised (<9), the coagulation process and the EF oxidation simultaneously occurred, and consequently the efficiency decreased (Fig. 4) [33]. Generally, according to the reports by most researches, the optimum pH in EF process is between 2 and 4 [22]. The result of this research is also consistent with those of previous reports. In our study, the optimal pH for decolorization and COD removal was obtained at 3. Also, the results showed that the pH of the solution during the EF process increased. Due to reduction of water at the cathode (Eq. (3)) resulting in hydroxyl radicals formation in solution (Eq. (1)), the final pH (pH$_f$) of the solutions increased. The increase in pH during the EF process because of the conversion of Fe^{2+} and Fe^{3+} to Fe (OH)$_n$, leads to a decrease in electrocoagulation and pollutants by electrostatic attraction of reactions [37]. It can be concluded that at high pHs, removal efficiency is owing to the electrocoagulation process.

3.2. Effect of current density

The impact of current density (0–10 mA/cm^2) on the dye degradation was studied. The experiments were performed using the following conditions: initial dye concentration 100 mg/L, pH 3, H$_2$O$_2$ concentration 100 mg/L, and Na$_2$SO$_4$ 100 mg/L. The findings have been shown in Fig. 5. When electrical current was off, the decolorization efficiencies were 14.5 and 10% for AB1 and AB113, respectively. Increasing current density from 0 to 5, the efficiency increased meaningfully up to 99% for both dyes. However, when current density was raised from 5 to 10 mA/cm^2, the efficiency decreased to 70.11 and 55.45% for AB1 and AB113, respectively.

This parameter is another principal operational factor in the EF process. Fe^{2+} ions are released into the solution from the iron anode; reduction of oxygen at the cathode surface and electro generation of hydrogen peroxide, regeneration of ferrous ions from ferric ions and electro generation of OH· were controlled by applied current in the electrochemical reactor [32,38,39]. The removal efficiency increases with increasing applied current density because increasing the applied current density can enhance the concentration of hydrogen peroxide via the reduction of O$_2$ [6]. Increasing applied voltage on the electrochemical reactor leads to an increase in applied current density [32].

The efficiency of the EF process will decrease because of interference and side reactions occurring in electrochemical cell, like the separation of oxygen at anode (Eq. (9)) and the formation of hydrogen at cathode (Eq. (10)). All these reactions happen at a higher current density [34,35].
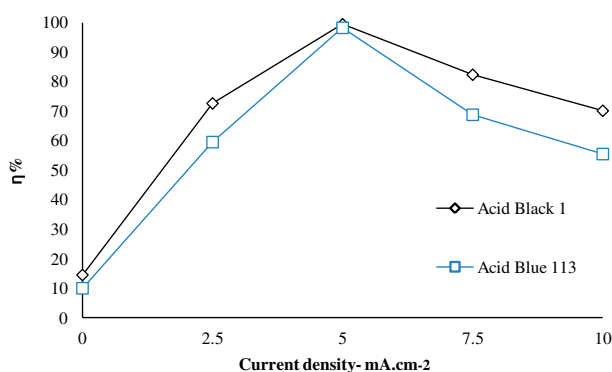
$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{9}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{10}$$

Also, in this study, when the applied current density exceeded 5 mA/cm^2, the efficiency decreased. The following intervention reaction (Eq. (11)) occurs at higher current density [34].

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \tag{11}$$

3.3. Effect of H$_2$O$_2$ concentration

In this work, H$_2$O$_2$ was manually added and the effect of its concentration on the decolorization efficiency was studied at the fixed conditions as follows: dye concentration 100 mg/l, pH 3, and current density 5 mA/cm^2 and Na$_2$SO$_4$ 100 mg/L. The results obtained have been shown in Fig. 6. When H$_2$O$_2$ concentration was 0, the maximum dye removal efficiencies were obtained 7.3% for AB1 and 5.12% for AB113 after 10 min of the reaction. When H$_2$O$_2$ concentration increased from 0 to 100 mg/l, the efficiency increased significantly to approximately 98% for both dyes.

H$_2$O$_2$ plays an important in Fenton reaction and Fenton related process. An increasing in initial H$_2$O$_2$ concentration would also lead to an increase in the production of hydroxyl radicals, which could react with organic pollutants in the solution; thus, it can be said that removal of pollutants increases by increasing H$_2$O$_2$ concentration [35,40]. When there are large quantities of hydrogen peroxide, removal efficiency decreases due to hydroxyl radical scavenging activity by hydrogen peroxide (Eqs. (7) and (12)) leading to the formation of hydroperoxyl radicals (HO$_2$·) [35].
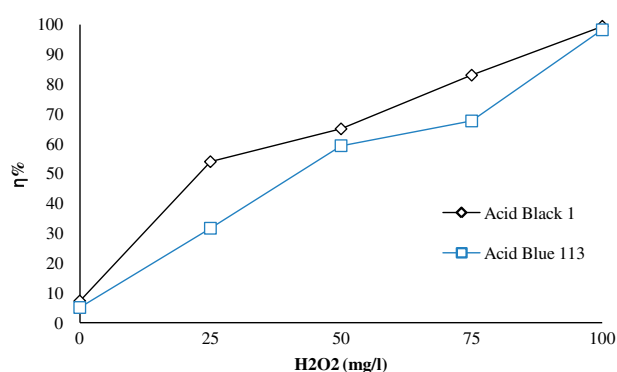
$$HO_2^· + HO^· \rightarrow H_2O + O_2 \tag{12}$$

Fig. 5. Effect of Current density in decolorization of AB 1 and AB 113 by electro-Fenton process.

Fig. 6. Effect of H$_2$O$_2$ concentration in decolorization of AB 1 and AB 113 by electro-Fenton process.

3.4. Effect of initial dye concentration

The effect of initial dye concentration (50–200 mg/L) on the efficiency has been shown in Fig. 7. This step of experiments was performed using 100 mg/L of H_2O_2, current density of 5 mA/cm^2, Na_2SO_4 of 100 mg/L and pH of 3. The results showed that with increasing dye content from 50 to 200 mg/L after 10 min of electrochemical reaction, the decolorization efficiency decreased from 100 to 32% for AB1 and 99.3–22% for AB113; This might be due to the fact that at a constant current density, the same number of iron ions and hydroxyl radical are enter the solution at different phenol concentrations [41]. Also, at high initial dye concentration, competitive destruction of OH· takes place by the generated intermediates [33].

3.5. Effect of time on COD removal and dye concentration

The reaction time is entirely effective in removal efficiency [42]. The effect of various retention times on decolorization and COD removal has been shown in Fig. 8. At the fixed conditions: dye concentration 100 mg/l, pH 3 and applied current density 5 mA/cm^2, and Na_2SO_4 100 mg/L, the findings illustrated that an increase in retention time led to an increase in removal efficiency. After 10 min, the decolorization leveled off, but COD removal continued to rise steadily from 0 to 120 min.

As can be seen from Fig. 1, the highest pick, which was related to azo group (−N=N−), occurred at 568 and 618 nm for acid black 113 and acid black 1, respectively. In oxidation processes, azo groups rapidly decompose and the solution becomes colorless. Naturally, longer time is required for the removal of aromatic rings. Therefore, in studies on dye compound oxidation, COD removal is done in longer time compared with decolorization [43].
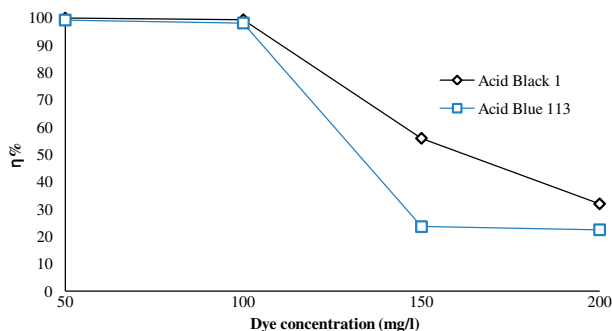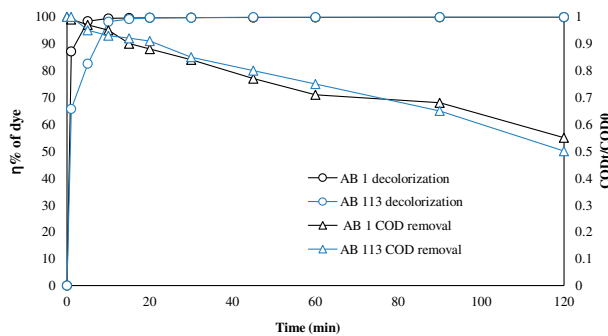

Fig. 8. Effect of detention time in dye decolorization and COD reduction by electro-Fenton process.

4. Conclusion

In this paper, the degradation of Acid Black 1 (AB1) and Acid Blue 113 (AB113) of azo dyes were studied by the EF process based an iron electrodes for electro-generation of Fe^{2+}. The experimental data indicated that pH, H_2O_2 concentration and dye concentration were effective in the process. The results showed that decolorization declined with increasing pH, which reached 47.4 and 27.8%, respectively, for AB1 and AB113 at pH 11 after 10 min. The removal efficiency increased dramatically to nearly 98% for both dyes with increasing H_2O_2 concentration from 0 to 100 mg/L. At optimum conditions: reaction time 10 min, pH 3.0 and H_2O_2 concentration 100 mg/L and current density 5 mA/cm^2 98–99% of both dyes was removed. According to the results obtained, it can be concluded that the EF process using iron electrodes for dye degradation and remediation of wastewater can be a promising process in terms of environmental and economical features.

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Fig. 7. Effect of AB 1 and AB 113 concentration in electro-Fenton process efficiency.

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