

Electrochemical degradation of scarlet red dye from aqueous environment by titanium-based dimensionally stable anodes with SS electrodes

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Abstract Textile effluents are toxic and carcinogenic materials that exist in the aquatic environment. In this study, the degradation efficiency of commercially available scarlet red dye investigated on TSA-SS Electro Fenton process (EFP) was reported. It is of great interest in the field of environmental engineering to remove dyes from aquatic environment. The influence of operating parameters such as pH (2–9), current density (0.1–0.5 mA/cm²), concentration of dye (0.1–0.5 g/L), H₂O₂ (0.1–0.5 g/L) concentration and Fe²⁺ concentration (0.01–0.03 g/L) were analyzed by batch system. The optimum degradation conditions were determined as pH—3, current density—0.4 mA/cm², concentration of dye—0.4 g/L, H₂O₂ concentration—0.5 g/L and Fe²⁺ concentration—0.025 g/L. These results indicated that the degradation efficiency of scarlet red dye by EFP depends on solution pH and Fenton reagent concentration and a low pH value was favorable for the dye degradation. It has been demonstrated that more than 94% dye removal was obtained at 50 min. Electro Fenton process was also investigated by cyclic voltammetry technologies.

Keywords Electro Fenton process · Dye degradation · TSA-SS electrode

Introduction

The pot ability of water is affected by various factors which include wastewater from industries. Various industries such as textiles, rubber, plastics, paper, cosmetics and tanneries use various dyeing process. They release waste water which contains dye effluents in a major proportion. Among them, textile industries generate large volume of effluents which contains organic dye effluents. Various processes were adopted to treat wastewater containing organic contaminants, particularly electrocoagulation, ultra-filtration, reverse osmosis (RO) and activated carbon adsorption. These treatment processes were not much effective to improve the quality of water with tolerable levels of effluents. To attain this objective, a treatment method is applied which entail the application of advanced oxidation process (AOP) [1, 2]. This method is recommended when wastewaters have high chemical stability, low biodegradability and this produces the complete mineralization of pollutants to CO₂, H₂O and inorganic compounds [3]. This AOP is attained when EFP is carried out. This EFP could be applied for various types of contaminants especially organic substances [4]. In EFP, H₂O₂ serves as the source of OH° radicals. So, with increase in H₂O₂ concentration degradation takes place effectively. These hydroxyl radicals act as redox agent with high redox potential. But if H₂O₂ concentration exceeds the limit, it will affect the process by production of per hydroxyl radicals [5] as shown in Eq. (1).



Also Fe²⁺ concentration helps in increase in efficiency by production of OH° radicals from H₂O₂. But after a particular concentration Fe²⁺ ions will have scavenging effect on OH° radicals [6] as shown in Eq. (2).

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This will reduce the efficiency of the process. So an optimum of Fe^{2+} concentration had to be maintained for effective degradation of the solution. The pH was considered to be one of the important factors which help in effective degradation [7]. At higher pH, complex formation of Fe^{2+} ions will take place thereby reducing the process efficiency. In this study, the influence of various parameters had studied.

Materials and methods

Physicochemical properties

In this work, commercially used dye scarlet red was purchased from Erode textile industry and the properties of scarlet red dye are given in Table 1. All chemicals like FeCl_3 , H_2O_2 , HCl and KCl of analytical grade purchased from merck. To test the removal efficiency UV–Vis spectroscopy (Model No. 3250, Agilent Technologies) is used for determination of dye concentration. The solution pH was measured with (Hanna instruments) pH meter.

Electrolysis was performed in a 1000-ml capacity cylindrical beaker with two electrodes. Titanium-based dimensionally stable anodes (DSA) and stainless steel (SS) were used as electrodes for anode and cathode, respectively. Area of each electrode was 50 cm^2 [8]. The synthetic dye solution of various concentrations was taken, and the pH was adjusted by adding 0.1 mM HCl solution. After that, various proportions of Fenton's reagents were added. The electrodes were partially immersed in a beaker that contains the synthetic solution 0.1 mM KCl chosen as the supporting electrolyte to maintain the current density [9]. The required electric power during the electrolysis process was provided by a laboratory DC power supply (Aplab 0.32 V, 0–10 A). The electrolytic cell was constantly

stirred with a magnetic stirrer in order to avoid the concentration gradient.

Electrochemical measurements

Cyclic voltammetry (CV) measurements were carried out using a potentiostat/galvanostat EG&G Model 263A and a frequency response detector FRD 100 of Princeton Applied Research. The working electrode was the glassy carbon, the counter electrode was a platinum, and a reference electrode was silver electrode. All the experiments were carried out at room temperature.

Results and discussion

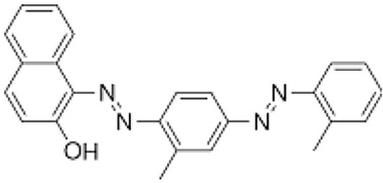
Influence of pH

In this process, pH is an important parameter and it affects the hydroxyl radical mechanism of EFP. The pH was varied within the range of 2–9. The maximum degradation efficiency was obtained at pH 3 as illustrated in Fig. 1. Therefore, acidic pH favors the degradation when compared to the basic pH levels [10]. Because when the pH is increased Fe^{2+} ions form insoluble complexes which cannot activate H_2O_2 to produce OH° radicals. They finally precipitate as $\text{Fe}(\text{OH})_3$ which cannot act as catalyst [11]. So degradation efficiency decreases with increase in pH. The previous results obtained [12] were well matched with the current data.

Influence of Fe^{2+} concentration

Fe^{2+} ions added as catalyst play an important role in EFP process in which degradation takes place efficiently. Figure 2 illustrates the effect of Fe^{2+} concentration on degradation of dye during EFP process. These ions help in the activation of H_2O_2 and in turn help in the production of OH° radicals leading to the degradation efficiency

Table 1 Physicochemical properties of scarlet red

Chemical name	(1Z)-1-[[2-methyl-4-[(2-methylphenyl)diazenyl]phenyl]hydrazinylidene]naphthalen-2-one
Chemical formula	$\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}$
Chemical structure	
Molecular weight	380.451 g/mol
Class	Sudan IV
Color index	85,836

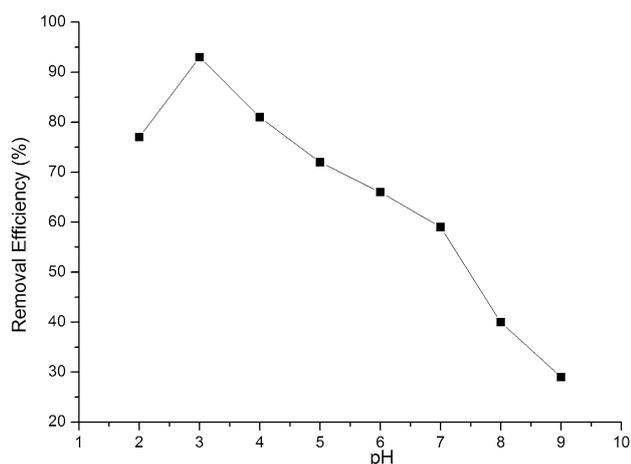


Fig. 1 Influence of pH on degradation of scarlet red dye in EFP processes (dye = 0.1 g/L, H_2O_2 = 0.1 g/L, Fe^{2+} = 0.01 g/L and $\text{CD} = 0.1 \text{ mA cm}^{-2}$)

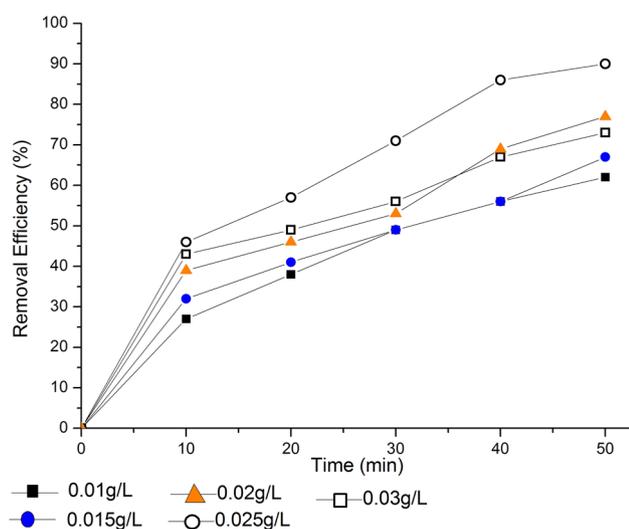
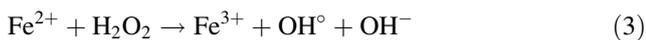


Fig. 2 Influence of Fe^{2+} on degradation of scarlet red dye in EFP processes (dye = 0.4 g/L, H_2O_2 = 0.5 g/L, pH = 3 and $\text{CD} = 0.4 \text{ mA cm}^{-2}$)

improvement as shown in Eq. (3) [13]. The Fe^{2+} concentration was varied between 0.01 and 0.03 g/L in the interval of 0.05 g/L.



The optimum Fe^{2+} dosage with maximum degradation efficiency was found to be 0.025 g/L. After that point degradation efficiency starts to decrease. This was because of the scavenging effect of Fe^{2+} ions which convert OH° radicals to OH^- ions [14].

Influence of H_2O_2 concentration

H_2O_2 reagent provides the hydroxyl radicals for carrying out the mineralization mechanism that produces the sludge

[8, 15]. The concentration of hydroxyl radicals was dependent on the addition of H_2O_2 concentration [16], and it influences the decomposition of complex organic compounds by Fenton's reaction. Due to the high cost of H_2O_2 selection of an optimum H_2O_2 concentration by Fenton's reagent is important for dye degradation [17]. The degradation increases with increase in H_2O_2 concentration varied at a range of 0.1–0.5 g/L and was the maximum efficiency obtained at 0.5 g/L illustrated in Fig. 3. However, the increase of H_2O_2 further results in the decrease in dye removal process because surplus H_2O_2 molecules act as a scavenger of hydroxyl radical to formation of perhydroxyl radical with low oxidation potential [15].

Influence of dye concentration

Dye concentration was varied over the range of 0.1–0.5 g/L. The optimum dye concentration was found to be 0.4 g/L for which maximum degradation was obtained. Figure 4 illustrates the influence of dye concentration in EFP process at lower concentration, the lesser degradation of dye was related to the low frequency of effective collisions between molecules and surplus Fe^{2+} molecules causing scavenging effect [18]. But also with higher concentration of dye, efficiency of the process decreases due to the intermediate components that react with hydroxyl radicals instead of dye components [19]. Also, the reactive species produced was not enough for effective degradation of dyes at higher concentration. So when the concentration of dye increases, the amount of Fenton's reagent added to the solution had to be increased. Figure 4 illustrates the

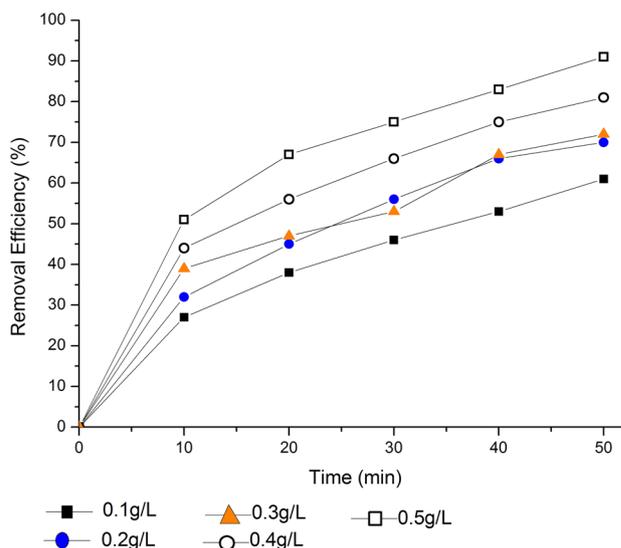


Fig. 3 Influence of H_2O_2 on degradation of scarlet red dye in EFP processes (dye = 0.4 g/L, pH = 3, Fe^{2+} = 0.025 g/L and $\text{CD} = 0.4 \text{ mA cm}^{-2}$)

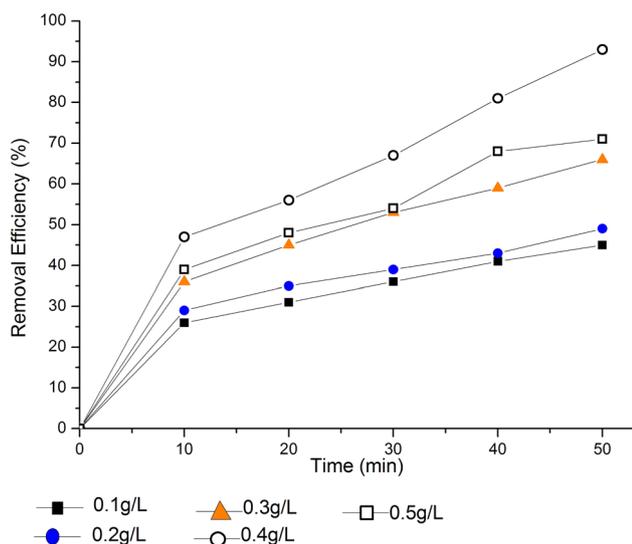


Fig. 4 Influence of dye concentration on degradation of scarlet red in EFP processes (pH = 3, $\text{H}_2\text{O}_2 = 0.5 \text{ g/L}$, $\text{Fe}^{2+} = 0.025 \text{ g/L}$ and $\text{CD} = 0.4 \text{ mA cm}^{-2}$)

variation of degradation efficiency on the basis of dye concentration.

Influence of current density

In all oxidation mechanism of electrochemical method current density was considered to be the important parameter. The influence of current density had been examined in the range of $0.1\text{--}0.5 \text{ mA/cm}^2$ optimum of 0.4 mA/cm^2 , and the results are illustrated in Fig. 5. The data from the graph show that there is a gradual increase in the degradation rate with increase in current. The increase

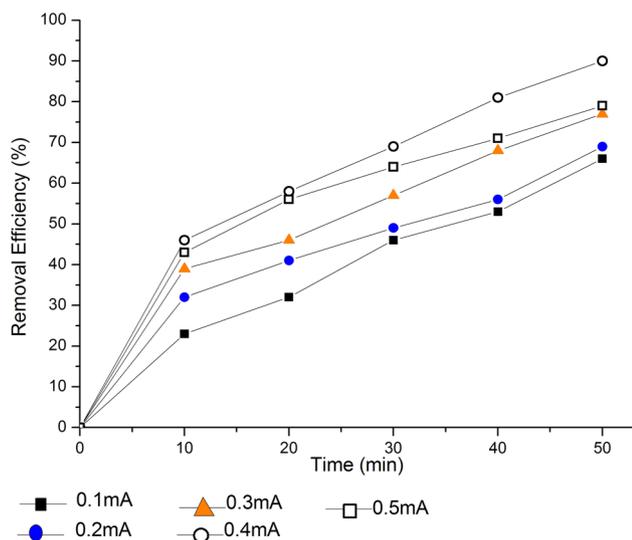


Fig. 5 Influence of current density on degradation of scarlet red dye in EFP processes (dye = 0.4 g/L , $\text{H}_2\text{O}_2 = 0.5 \text{ g/L}$, $\text{Fe}^{2+} = 0.025 \text{ g/L}$ and pH = 3)

in current density enhances the oxidation power which in turn helps in the greater production of H_2O_2 and leads to the generation of more amounts of hydroxyl radicals from Fenton's reagent [20]. At higher current density, the degradation efficiency was attained almost constant due to the formation of intermediates as complexes of Fe^{2+} with carboxylic acids that were more difficult to destroy during electrolysis [21].

Mechanism of degradation of azo dyes

In EFP the degradation of o'scarlet red dye was investigated in acidic pH of 3. Fe^{2+} ions were used as catalyst, and H_2O_2 acts as a reagent. As the current density was intensified the degradation of dye also progressed gradually. The hydroxyl radicals produced by H_2O_2 help in this process. As the color loss becomes visible it could be explained by reaction of OH^\bullet radicals with azo bonds ($-\text{N}=\text{N}-$) [22]. They break the azo bond which causes the decolorization due to change in absorption properties. From the removal efficiency curves, we can infer that color intensity decreases as time increases during the reaction. The reaction between hydroxyl radicals and azo bonds produces hydroxylated derivatives [23]. The scarlet dye compound disappeared by producing intermediates like hydroxyl derivatives and other iron complexes.

Figure 6 illustrates the cyclic voltammetry (CV) scan 0.4 g/L dye solution at pH 3.0; scan rate was 30 mV/s . It was clearly visible that the Oxygen Reduction Reaction (ORR) currents at the cathode potential higher than -0.9 V . As the operating cathode potential of H_2O_2 -producing dye solution was changed from -0.9 to -0.7 V and cathode potentials appeared almost the same over the whole testing period, it was concluded that the presence of scarlet red dye had a slight impact on the ORR process

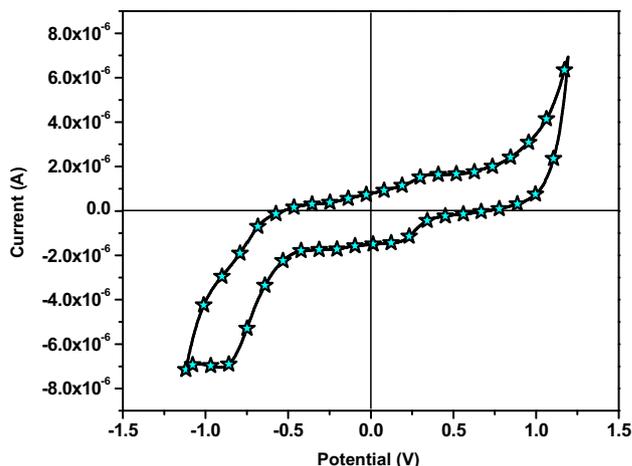


Fig. 6 Cyclic voltammetry scan of 0.4 g/L dye solution at pH 3.0, scan rate 30 mV/s

occurring on the surface of the TSA-SS Electro Fenton process.

Discussion

Electro Fenton processes have been proved to be a feasible technology for the treatment of dyes from synthetic solutions. In this study, the degradation of scarlet red dye was investigated by EFP using TSA-SS electrodes. The influence of operating parameters such as pH (2–9), current density (0.1–0.5 mA/cm²), concentration of dye (0.1–0.5 g/L), concentration of H₂O₂ (0.1–0.5 g/L) and concentration of Fe²⁺ (0.01–0.03 g/L) was analyzed in a batch system. The optimum solution pH for EFP for the scarlet red dye was obtained at 3. The optimum concentration of H₂O₂, Fe²⁺ and dye concentration was 0.5, 0.025 and 0.4 g/L with the current density of 0.4 mA/cm², respectively. At the optimal conditions, 94% of scarlet red was degraded from the solution at 50 min. The conducted cyclic voltammetry studies confirm that, an impact was occurred over the surface of TSA-SS Electro Fenton process by the presence of scarlet red dye.

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