Performance Comparison of Fe^{2+} Activated Persulfate and Electro-Persulfate Process in Acid Blue 25 Removal from Aqueous Solution: Operating Conditions and Reaction Velocity

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ABSTRACT: The purpose of this study was to compare the performance of Fe^{2+} activated persulfate and electro-persulfate process in Acid Blue 25 removal from aqueous solution. For this reason, the effects of different parameters including pH, dye, sodium persulfate and ferrous sulfate concentrations were investigated. The removal efficiency of 92% at the time of 60 minute was obtained at pH= 3, dye concentration= 50 mg/L, sodium persulfate concentration= 500 mg/L and Fe (II) sulfate concentration= 100 mg/L for Fe^{2+} activated persulfate system and the removal efficiency of 95% at pH= 5, dye concentration = 200 mg/L, sodium persulfate concentration = 500 mg/L and ferrous sulfate concentration = 100 mg/L for electro-persulfate system by means of graphite materials as the neutral electrodes. COD removal efficiency in Fe^{2+} activated persulfate and electro-persulfate in the mentioned conditions were 90% and 89% in 180 minutes, respectively. Moreover, the result of process kinetics showed that using electrochemical process improved the reaction velocity from 0.0016 to 0.0487 mg/L/ min. The comparison between these two-process showed that using electrochemical process improved dye removal efficiency by 4 times.

1. INTRODUCTION

Dyes can be considered as common pollutants in the wastewater of textile industries. These compounds have adverse effects on the environment and ecosystem due to the resistance against the light, non-biodegradability, variable range of pH and toxicity. Up to now, the vast numbers of physical, chemical and biological methods have been used for dye removal which by-products and the cost of sludge disposal are some of the disadvantages of these methods [1].

Persulfate ($S_2O_8^{2-}$) has the second most reduction potential in advance oxidation processes after the ozone (O_3). The Sulfate radical ($SO_4^{•-}$) has unique characteristics such as high kinetic velocity and greater stability compared to hydroxyl radical ($OH^•$) [2]. However, due to its low rate of oxidation reaction at room temperature, various types of catalysts such as heat, UV radiation, alkalinity, activated carbon and metal ions can be used for the activation of persulfate and the production of $SO_4^{•-}$ with high capability of oxidation [3]; Nevertheless, using Fe^{2+} as a catalyst has the advantages of high removal efficiency and cost-effectiveness [4].

In recent years, electrochemical processes as an environmentally friendly technology have been widely used in the removal of various pollutants in the industrial wastewater. Compared with the conventional methods for the activation of persulfate, using of persulfate with electrolysis (electro-persulfate) improves the consumption of persulfates and

reduces Fe^{3+} to Fe^{2+}, as well as decreases sludge production and reactor volume, thereby reducing operating costs [5].

The main aim of this study was to compare the of Fe^{2+} activated persulfate process and electro-persulfate process in Acid Blue 25 removal by manual addition of FeSO$_4$ as a catalyst and evaluating the parameters by means of graphite electrodes.

2. MATERIALS AND METHODS

The dye used in this study was Acid Blue 25 ($C_{20}H_{13}N_2NaO_5S$, pH=8.2) which is widely used in textile, leather, pulp and paper industries. Sodium Hydroxide, Sulfuric Acid, sodium persulfate and iron (II) sulfate were the other ingredients which were used.

The electrochemical reactor used was a 500 mL Plexiglas. In each step of the study, the synthetic sewage was stirred up by magnetic stirrer at a speed of 100 rpm and sampling was carried out every 10 minutes. Before reading the samples and in order to eliminate the adverse effect of the produced sludge on the results, the samples were centrifuged at a speed of 3000 rpm for 1 minute and the absorbance of remained color in the samples was measured at the wavelength of 602 nm. Graphite electrodes used in electro-persulfate process were 120×60×10 mm, which were rinsed with acetone and distilled water to purify the contaminants.

Experiments related to both processes were conducted in the current of 0.5 A, electrolyte concentration of 1600 mg/L,

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Table 1. the amount of assessed parameters

Parameter	amount
pH	3, 5, 8.2, 9
Dye Concentration (mg/L)	50, 75, 100, 150, 200, 250
Fe^{2+} Concentration (mg/L)	50, 75, 100, 150, 200
$S_2O_8^{2-}$ Concentration (mg/L)	300, 400, 500, 600

(a)

(b)

Fig. 1. the changes in dye concentration based on time in different amounts of Fe^{2+} (a) Fe^{2+} activated persulfate (pH=3, [Dye]=50 mg/L, [$Na_2S_2O_8$] =500 mg/L), (b) electro-persulfate (pH=5, [Dye] = 200 mg/L, [$Na_2S_2O_8$] = 500 mg/L)

the effective cross section of graphite electrodes of 30 cm², the space between electrodes of 3 cm and the stirrer velocity of 100 rpm and the parameters were measured based on Table 1. It should be noted that all experiments were carried out at a temperature of (25±1) ºC by OFAT method, with 3 times repetitions and with a maximum error of 5%.

3. RESULTS AND DISCUSSION

In advanced oxidation processes, in which Fe^{2+} is used to activate and produce $SO_4^{•-}$, pH affects either the species and state of iron existed in the solution and the reactions of $S_2O_8^{2-}$ with pollutants. According to reactions 1 and 2, by the gradual increase of pH from acidic to alkaline levels, most of the iron converts to Fe^{3+} and since only Fe^{2+} is capable of activating $S_2O_8^{2-}$, by decreasing the Fe^{2+} to Fe^{3+} ratio, the efficiency decreases Significantly. Moreover, at the amounts of pH more than 4, the solubility of Fe^{2+} decreases and the iron becomes colloid which leads to the decrease of efficiency [6].

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{•-} + SO_4^{2-} \quad (1)$$

$$Fe^{2+} + SO_4^{•-} \rightarrow Fe^{3+} + SO_4^{2-} \quad (2)$$
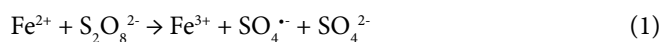
According to the above description and considering the economic issues (reducing the amount of chemicals used to adjust the pH), the pH values of 3 and 5 were selected for the Fe^{2+} activated persulfate and electro-persulfate systems as optimal pH, respectively. Also, due to the fact that the dye removal efficiency in both systems is not significantly different at 60 minutes and 90 minutes, the time of 60 minutes was chosen as the optimal time of the experiment.

Moreover, according to the obtained results and considering economic issues, the initial optimal initial concentration of dyes for Fe^{2+} activated persulfate and electro-persulfate processes was chosen 50 and 150 mg/L, respectively. Because in high concentrations of dye, the removal efficiency decreases due to the reduction of production of oxidizing radicals on the catalyst surface and the stability of the number of oxidizing radicals [7]. Additionally, by-products compete with dye molecules to achieve active Fe^{2+} sites. Thus, the reaction between the catalyst and the oxidizing agent is disrupted and the removal efficiency is reduced [8]. Considering economic issues and results, the persulfate concentration of 500 mg/L was chosen as the optimum amount in both systems. The amount of oxidant that is responsible for producing reactive radicals is an important factor in improving the efficiency of the oxidation process. Increasing the removal efficiency of dyes by increasing the initial concentration of sodium persulfate is due to the production of more amount of $SO_4^{•-}$. The sulfate radicals form a double bond, transport electrons
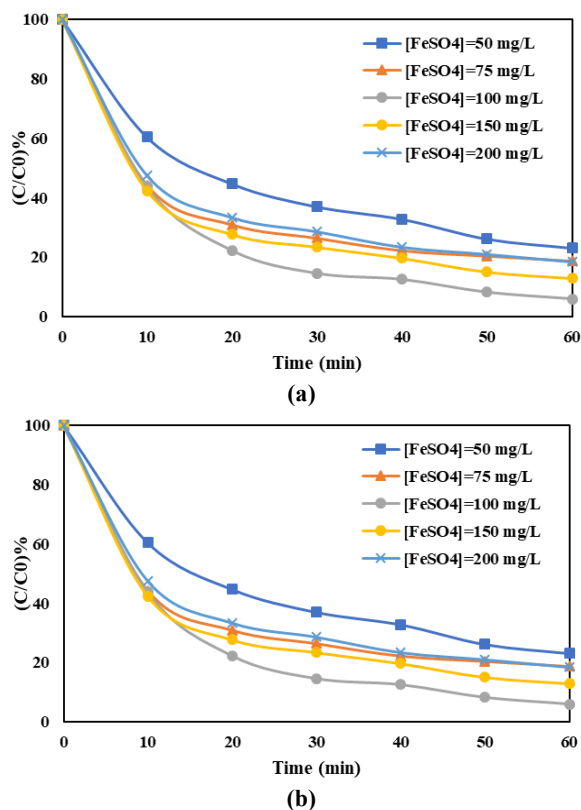
and, as a result, decompose the pollutant. Also, according to reaction 3, persulfate ions converts to radical sulfate by using electron released in the electro-persulfate system, which increases the system's ability to remove higher concentrations of dyes [9].

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{•-} + SO_4^{2-} \quad (3)$$

The results of tests performed to determine the optimal concentration of Fe^{2+} are presented in Fig. 1.

As shown in Fig. 1 (a), the dye removal efficiency in Fe^{2+} activated persulfate system after 60 minutes at concentrations of 50, 75, 100, 150, and 200 mg/L was 77, 81, 92, 87 and 81.5%, respectively. Also, according to Fig. 1 (b), the dye removal efficiency in electro-persulfate system after 60 is 86, 95, 93 and 92%, respectively. Because, despite the fact that Fe^{2+} can effectively activate persulfate (reaction 1) [10], Fe^{3+} exhibits inappropriate performance in activation. Regarding reaction 4, Fe^{3+} is converted to Fe^{2+} by releasing electron in the electro-persulfate system, which results in the reduction of Fe^{2+} and increasing dye removal efficiency compared with the Fe^{2+} activated persulfate system [11].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} (Cathode) \quad (4)$$

By adding Fe^{2+} to the reactor, the process will be effective in the first few minutes, and will continue to result in the conversion of Fe^{2+} into Fe^{3+} the process will stop. Therefore,

a high concentration of Fe^{2+} should be added to the solution, which would produce high volumes of sludge. Another problem with the addition of excess Fe^{2+} was that it led to the production of other sulfate species that had less oxidation power (Reaction 2) [12].

Therefore, considering the above reasons and economic issues, concentration of 100 mg/L was selected as the optimum concentration for both systems.

According to the results of the COD test in the Fe^{2+} activated persulfate system after 180 minutes, 90% of the initial COD and in the electro-persulfate system, with dye concentration and initial COD of 128 mg/L and 200 mg/L respectively a similar elimination percentage (89%) was obtained in the same period, indicating the proper function of the electro-persulfate system.

In the kinetics of processes, Fe^{2+} activated persulfate process second-order kinetics and the electro-persulfate process followed the first-order kinetics. Also, due to the speed constants, the use of the electro-persulfate system caused a significant increase in reaction speed from 0.0016 to 0.0487 mg/L/min.

4. CONCLUSION

In this study, the efficiency of Fe^{2+} activated persulfate and electro-persulfate processes in Acid Blue 25 removal was compared. According to the results, using the electro-persulfate system in addition to having a higher reaction rate compared to Fe^{2+} activated persulfate, due to improving the consumption of persulfate, eliminates 4 times as much dye with a constant amount of sodium persulfate and iron sulfate (II) and the less need to chemicals to reach the optimum pH. Also, in electro-persulfate process, the production of sludge due to the reduction of Fe^{2+} was lower which resulted in lower operating cost.

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