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Electro-Fenton/peracetic acid process for the removal of Rhodamine B dye from aqueous media: effect of operational parameters and optimization with Taguchi method

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ABSTRACT

The growing population, the development of industry and agriculture and the shortage of safe water in the world have led to need for the treatment and recovery of wastewater. The textile industry is one of the most important industries in the world, which is a source of production of large amounts of colored and toxic wastewater. Conventional treatment methods, including physicochemical and biological methods, are not sufficient and efficient due to the stability of textile wastewater against degradation by light and biological agents, and some of these methods produce solid waste, which consequently causes other environmental problems. Therefore, the aim of this study was to investigate the efficiency of the electro-Fenton/peracetic acid process in removing Rhodamine B dye from aqueous media. The present study is an experimental study. In this experiment, synthetic solutions with a volume of 200 mL of the desired dye were made and the efficiency of the electro-Fenton/peracetic acid process, using the Taguchi method and determining the effect of operating parameters including contact time (10–90 min), pH initial solution (9–3), sodium chloride concentration (50–300 mg/L), peracetic acid concentration (5–100 ppm), and initial Rhodamine B dye concentration (25–500 ppm) and current density (6–14 mA), has been investigated in a batch reactor. The results of this study showed that the highest Rhodamine B dye removal efficiency B (99.9%) during electro-Fenton/peracetic acid process, was obtained in 90 min and under optimal conditions, that is, pH of 3, sodium chloride concentration of 200 mg/L, the peracetic acid concentration of 100 ppm, the Rhodamine B concentration of 100 ppm and the current density of 12 mA. Monitoring the changes in the desired dye showed that over time and decreasing the pH, the removal efficiency increases. On the other hand, the addition of sodium chloride, peracetic acid, the initial concentration of the dye and the amount of current density to a certain extent, increases the removal efficiency, and then by further increase in variables, the efficiency decreases. In addition, in this process, very little sludge is produced and the pollutant is converted into water, carbon dioxide and mineral compounds.

Keywords: Peracetic acid; Rhodamine B dye; Electro-Fenton; Aqueous media

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1. Introduction

In recent years, by the growing population, the expansion of industry, agriculture and the shortage of safe water in the world, the need for treatment and recovery of wastewater has become particularly important. Increased industrial activity leads to overproduction of various commercial chemicals, which eventually enter the water bodies in large quantities and in different ways. One of the biggest problems is the production of materials that are resistant to degradation, and dyes are also among these materials [1,2]. The textile industry is one of the most important industries in the world, which is a source of production of large amounts of colored and toxic wastewater due to the need for high volumes of water consumed in various sectors [3]. Wastewater treatment of the textile industry is an important issue because this wastewater contains harmful compounds and various types of dyes that reduce the process of self-purification in the environment and have carcinogenic effects for humans [4]. Rhodamine B dye is one of the dyes used in the textile industry that is toxic and if ingested by humans or animals, it irritates the skin, eyes, and respiratory tract. This dye is carcinogenic and destructive to the nerves and affects the reproductive system of humans and animals [5,6]. Therefore, due to environmental problems and maintaining the health of people in the community, treatment of this type of wastewater is of great importance. Numerous methods such as physical, chemical, and biological methods for the treatment of this type of wastewater have been studied [7]. Adsorption, coagulation/precipitation, membrane filtration, etc. are common methods for dye treatment. These methods, despite their advantages, also have major problems [8–11]. For example, adsorbent erosion, adverse reactions, low levels of some adsorbents, etc. are disadvantages of adsorption processes. In addition, the coagulation method is costly and produces a large volume of sludge [12]. Biological methods are also long and time-consuming or do not have high efficiency in removing these contaminants, so in recent decades, alternative methods such as chemical oxidation including ozonation, advanced oxidation processes, chlorination, etc. have been studied [13,14]. Advanced oxidation processes, based on the production of hydroxyl radicals due to their high oxidation power and conversion of many organic chemical compounds into minerals, water, and carbon dioxide, have been considered for water and wastewater treatment [15,16]. One of the methods of dye treatment is the electrochemical method. In this method, using current density, active agents are produced for treatment in the environment. This method is environmentally friendly and has advantages such as the need for simple equipment, high speed, short residence time to remove contaminants, easy operation, and low need for chemicals [17]. Organic peracids are among the oxidants used in water or wastewater treatment today. Organic acids are peroxide compounds having an organic chain and their structure is generally indicated by R-COOOH. These compounds are typically available as a solution of peracetic acid, hydrogen peroxide, carboxylic acid, and water. The most common industrial peracids are performic acid and peracetic acid. Eq. (1) shows the structural mechanism of organic peracids [18].

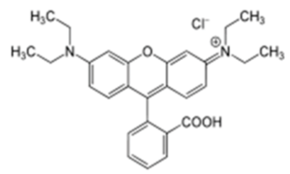
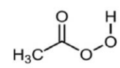
$$\text{R-COOOH}(\text{aq}) + \text{H}_2\text{O}_2(l) \quad (1)$$

$$\text{R-COOH}(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \quad (2)$$

PAA or proxy acetic acid (Table 1) is a clear, colorless liquid that does not produce foam and has a pungent odor related to acetic acid. This chemical is very corrosive and is a strong oxidizing agent that has a higher oxidation power than chlorine or chlorine dioxide [19]. One of the desirable properties of peracetic acid is that it has a weak O–OH bond, which can lead to the production of large amounts of hydroxyl radicals, which attack the target pollutant. The only by-product reported due to the use of peracetic acid is harmless carboxylic acid [20]. The two theories that have been proposed regarding the mechanism of disinfection and oxidation of this chemical are as follows: (1) The release of activated oxygen, which destroys the sulfhydryl (–SH) and sulfur (S–S) bonds of enzymes in the cell membrane, affects the translocation across the cell membrane, and, as a result, cell tissue activity stops, and (2) the second mechanism described for the efficiency of peracetic acid is the production of hydroxyl radicals [21,22]. The addition of metals such as silver, iron(III), manganese(II), and copper(II), can activate peracetic acid and increase the removal efficiency [23]. Hou et al. [24] entitled "Decomposition of Rhodamine B by the Fenton process based on zero-valent iron using H_2O_2" and achieved high removal efficiencies. Rahmani et al. [25] conducted a study entitled "Evaluation of the efficiency of parameters affecting the removal of dye from water using the electro-Fenton process" and obtained similar results.

Therefore, according to the above, it can be said that the presence of dye in the receiving waters prevents the penetration of light, causes the occurrence of eutrophication, disrupts photosynthetic activity and inhibits the growth of living organisms. Moreover, the dyes used in the textile industry have various health effects such as carcinogenicity, mutagenicity and allergenicity, and conventional wastewater treatment cannot remove these dyes. Among the various treatment methods, the electrochemical method

Table 1
Physical and chemical characteristics of Rhodamine B dye and peracetic acid [22]

Name	Rhodamine B	Peracetic acid
Chemical formula	$C_{28}H_{31}N_2O_3Cl$	CH_3CO_3H
Molecular structure		
Molecular weight	479.02 (g/mol)	76
Family	–	Peracids
Max. landa	564	–
Oxidizing power	–	Ev81/1

has attracted much attention in the field of removal of various pollutants. In recent years, the use of optimization methods such as the Taguchi method has attracted the attention of researchers in various disciplines to obtain the best answer. In this method, reducing the number of experiments compared to the classical method reduces the cost and time required. Taguchi method is a method for experimental analysis that allows determining the effect of factors and levels of experimental and laboratory studies with a certain number of experiments and based on specific and predetermined levels of compounds. The advantages of the Taguchi method are simplicity, speeding up the testing process, low cost and reducing the number of samples [26,27]. Seid-Mohammadi et al. conducted a study entitled "Degradation of cephalexin antibiotics in aqueous solutions using the hybrid process of ultrasonic waves/hydrogen peroxide/nickel oxide nanoparticles (US/H_2O_2/NiO)" using the Taguchi scheme and examined five parameters. The results showed that the pH of the solution had the greatest role in the removal rate of contaminants [27]. Therefore, according to the above, the purpose of this study is to use the electro-Fenton/peracetic acid process to remove Rhodamine B dye from aqueous media.

2. Materials and methods

2.1. Materials

Peracetic acid, sodium hydroxide, sulfuric acid were purchased from the German Merck Company and Rhodamine B dye was purchased from Alvan Sabet Company, Hamedan. Table 1 shows the physical and chemical characteristics of Rhodamine B dye and peracetic acid (Table 1).

2.1.1. Laboratory scale reactor

This study was performed in a 250 cc glass reactor. Fig. 1 shows the electro-Fenton/peracetic acid system. The electrodes used were 2 electrodes made of iron, which were cost-effective and available, and were placed next to each other at a distance of 2 cm.

2.2. Methods

Optimization table related to variables and test steps. (To increase the accuracy, all experiments were performed with 3 replications). A total of 75 experiments were performed. The order of the experiments was random. Descriptive methods and graphs were used to display the information, and multiple regression was used to analyze the information. The findings of the model were analyzed based on diagrams. The significance level of the tests was considered to be 5%. In this experiment, samples with a volume of 250 mL were prepared and the following parameters were examined: pH (3, 4, 5, 7, and 9), contact time (5, 10, 20, 30, 60, and 90 min), Rhodamine B dye concentration (25, 50, 100, 200, and 300 mg/L), concentration of peracetic acid (5, 10, 25, 50, and100 mg/L), amount of NaCl electrolyte (50, 100, 150, 200, and 300 mg/L) and the amount of current density (0.06, 0.08, 0.1, 0.12, and 0.14 amps). The order of the experiments was as follows: 5 experiments per day were randomly selected based on the Taguchi method, and by considering the mentioned values, for each parameter, the removal efficiency was obtained. At the end of all experiments, the average of the results obtained from each experiment was considered as the final answer. At each stage, samples with a volume of 250 mL and the desired concentration of stock solution were taken and after adjusting the current density and other desired factors in the experiment, the efficiency of the reaction at the mentioned times was evaluated. After the reaction, the samples were poured into the tube and after centrifugation, the absorbance value was read by DR-5000 spectrophotometer (Hach, UV-VIS) at 564 nm wavelength and finally, the optimal values for each variable were obtained. A high-performance liquid chromatography (HPLC) was used to measure the dye concentration in textile industry wastewater. HPLC Agilent 1260 Infinity (Agilent Technologies Co., Ltd., USA) equipped with a Shimadzu LC-20 AB pump: 140 mm × 260 mm × 420 mm, operating temperature range: 4°C–35°C, power requirements: 100 VAC, 150 VA, 50/60 Hz, maximum discharge pressure: 40 MPa, flow-rate setting range: 0.0001–10 mL/min, solvent delivery method: parallel-type double plunger,

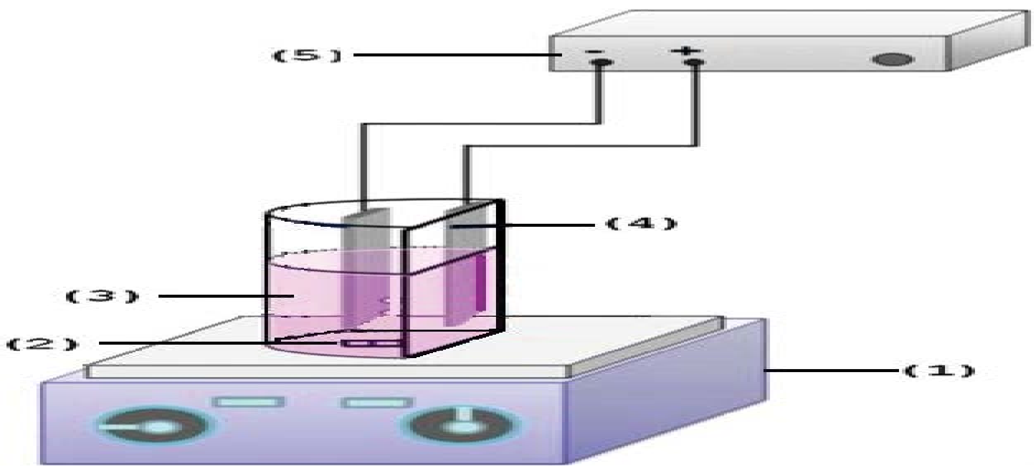


Fig. 1. Schematic of the electro-Fenton/peracetic acid system. (1) Mixer, (2) magnet, (3) electrochemical cell, (4) electrodes, (5) DC power.

plunger capacity: 10 μL), A C18 column (250 mm × 4.6 mm, with 5 μm particle size, pore size: 12 nm) was used as the stationary phase, and a UV-Vis spectrophotometer (Shimadzu UV-1600 (Japan)), dimensions: 380 mm (200 mm at closing LCD unit) × 550 mm × 470 mm, power consumption: 160 VA, frequency: 50/60 Hz, wavelength range: 190–1,100 nm, wavelength accuracy: ±0.5 nm, wavelength repeatability: ±0.1 nm. A 20 μL of Rhodamine B dye solution was injected into the column at a retention time of 3.5–3.8 min and then measured at a fixed wavelength of 564 nm.

2.2.1. Laboratory and statistical analysis methods

In order to analyze the data and draw graphs, Excel software was used and in order to calculate the removal efficiency of the desired pollutants, Eq. (3) was used:

$$\text{RE}(\%) = \frac{C_i - C_t}{C_i} \times 100 \quad (3)$$

where C_i and C_t indicates the primary and secondary concentrations of dyes at times zero and t, respectively and RE indicates removal efficiency.

3. Results

The results of experiments performed to determine the efficiency of the electro-Fenton/peracetic acid system for the removal of Rhodamine B dye from aqueous solutions were calculated, and the results of analysis of variance are shown in Table 2 and the results of the experiments are shown in Table 3. In this study, time is investigated as the first parameter.

In this table, we can find the effect of factors. By looking at the level of significance and if it was zero, it shows that the parameter has an effect on the removal efficiency. In this study, all parameters have a significance level of zero. Therefore, it can be said that all variables have an effect on the removal efficiency. In the following, we show the effect of each of the factors.

3.1. Effect of contact time

According to Taguchi design, we select a time of 90 min as a reference and measure the rest of the time relative to it. Based on this and according to Fig. 2, the time of 90 min has the highest removal efficiency and the rest of the times from maximum to minimum removal time were 60, 30, 20 and 10 min, respectively. Therefore, there is a significant difference between the removal time at reference time (90 min) and other times, and this shows that the effect of different times on removal is different.

3.2. Investigating the effect of pH

According to Taguchi design, we did choose a pH of 9 as a reference and measure the other pHs relative to it. According to this design, the highest removal efficiency is obtained at pH equal to 3 and the lowest at pH equal to 9. Fig. 3 shows the removal efficiency of the electro-Fenton/peracetic acid process at different pHs. According to the figure, there is a significant difference between the reference pH (9) and pH values of 3, 4, and 5. This means that their removal efficiency is different; however, at pH 7, there is no significant difference. This means that the removal efficiencies of the two are close to each other and do not differ much. Therefore, the removal efficiency from the highest to the lowest value is 3 > 4 > 5 > 7 > 9.

3.3. Investigation of the effect of initial concentration of sodium chloride electrolyte

In this section, we selected the concentration of 300 mg/L as a reference and measured the other concentrations relative to it. As shown in Fig. 4, all concentrations have higher removal efficiencies than the reference concentration (300 mg/L). Accordingly, the lowest removal rate

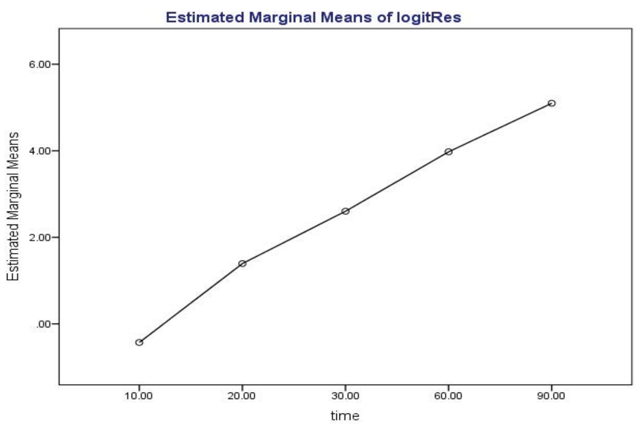


Fig. 2. Effect of contact time on Rhodamine B dye removal efficiency by electro-Fenton/peracetic acid process.

Table 2
Results of analysis of variance of parameters affecting dye removal

Parameters	Degrees of freedom	Average of squares	Significance level	Percentage of participation (%)
Time	4	70.326	0.000	85.118
pH	4	7.775	0.000	9.410
Electrolyte	4	12.912	0.000	15.628
Peracetic acid	4	29.310	0.000	35.475
Dye concentration	4	61.703	0.000	74.688
Current density	4	32.139	0.000	38.898

Table 3
Results of color removal by electro-Fenton/peracetic acid process

Raw	Current density (A)	Initial dye concentration (mg/L)	Peracetic acid (mg/L)	Electrolyte (mg/L)	pH	Time (min)	Efficiency A (%)	Efficiency B (%)	Efficiency C (%)	Average (%)
1	0.06	25	5	50	3	10	77.02	64.32	62.68	68.01
2	0.08	50	10	100	4	10	53.13	46.97	33.8	44.63
3	0.1	100	25	150	5	10	14.14	17.97	19.22	17.11
4	0.12	200	50	200	7	10	46.84	46.04	46.97	46.61
5	0.14	300	100	300	9	10	30.03	25.14	26.59	27.25
6	0.14	200	25	100	3	20	59.05	62.15	62.7	61.3
7	0.08	300	50	150	4	20	45.64	44.64	40.2	43.49
8	0.08	25	100	200	5	20	99.98	99.97	99.98	99.97
9	0.1	50	5	300	7	20	14.63	17.62	26.06	19.43
10	0.12	100	10	50	9	20	46.47	46.28	44.61	45.78
11	0.12	50	100	150	3	30	99.99	99.99	99.98	99.98
12	0.14	100	5	200	4	30	99.76	96.54	99.46	98.58
13	0.06	200	10	300	5	30	15.53	17.96	15.16	16.22
14	0.06	300	25	50	7	30	27.46	31.28	23.64	27.46
15	0.1	25	50	100	9	30	87.48	85.54	83.99	85.67
16	0.1	300	10	200	3	60	43.02	46.18	40.62	43.27
17	0.12	25	25	300	4	60	99.96	99.98	99.58	99.84
18	0.14	50	50	50	5	60	99.99	98.99	99.47	99.48
19	0.06	100	100	100	7	60	99.48	98.32	91.72	96.5
20	0.08	200	5	150	9	60	92.54	93.54	93.67	93.25
21	0.08	100	50	300	3	90	99.85	99.8	98.6	99.41
22	0.1	200	100	50	4	90	98.37	96.84	97.63	97.61
23	0.12	300	5	100	5	90	96.66	96.42	95.95	96.34
24	0.14	25	10	150	7	90	99.98	99.48	99.99	99.82
25	0.06	50	25	200	9	90	99.81	98.84	99.14	99.26

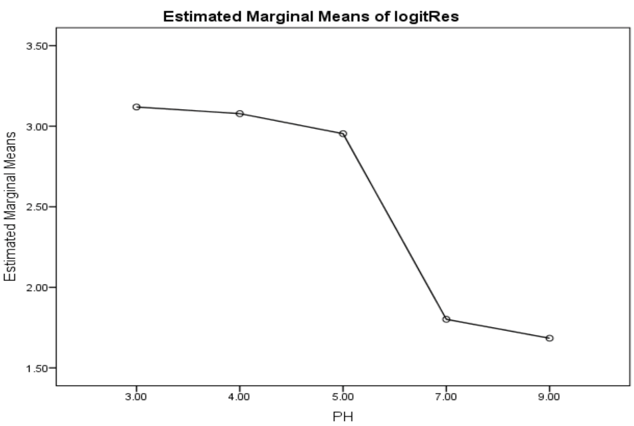


Fig. 3. Effect of pH on Rhodamine B dye removal efficiency by electro-Fenton/peracetic acid process.

was related to the concentration of 300 mg/L and the highest was related to the concentration of 200 mg/L; order of maximum to minimum removal efficiency were as follows: 200 > 150 > 100 > 50 > 300 mg/L. There is no significant difference between reference concentration and concentrations of 50 and 100 mg/L; it means that they have close removal efficiencies, while there is a significant difference between reference concentration with concentrations of 150 and 200 mg/L. This indicates that it has a different removal rate than these two concentrations.

3.4. Investigation of the effect of initial concentration of peracetic acid

According to the Taguchi design, a concentration of 100 mg/L was selected as the reference. According to Fig. 5, all concentrations have a significant difference relative to the reference concentration; it indicates their removal efficiency is different from the reference. Therefore, the highest removal rate was related to the concentration of 100 mg/L and the lowest was related to the concentration of 5 mg/L. The lowest to highest the removal efficiency was obtained for current values in order of 5 > 10 > 25 > 50 > 100 mg/L.

3.5. Investigation of the effect of Rhodamine B dye concentration

The concentration of 25 mg/L was selected as a reference and we compare the other concentrations with it. As shown in Fig. 6, all concentrations have lower removal efficiencies than the reference. In other words, there is a significant difference between them. The highest removal efficiency is related to the concentration of 25 mg/L and the lowest is related to the concentration of 300 mg/L. The highest to the

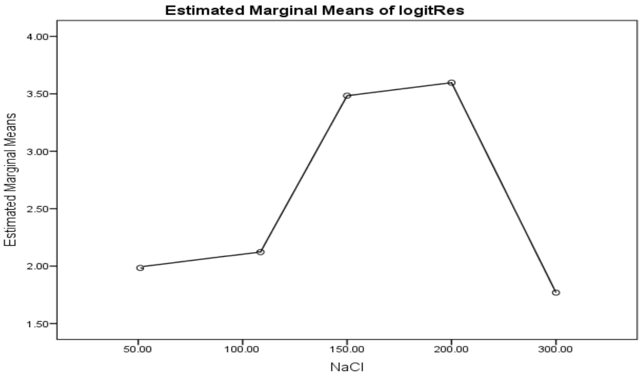


Fig. 4. Effect of sodium chloride electrolyte on Rhodamine B dye removal efficiency by electro-Fenton/peracetic acid process.

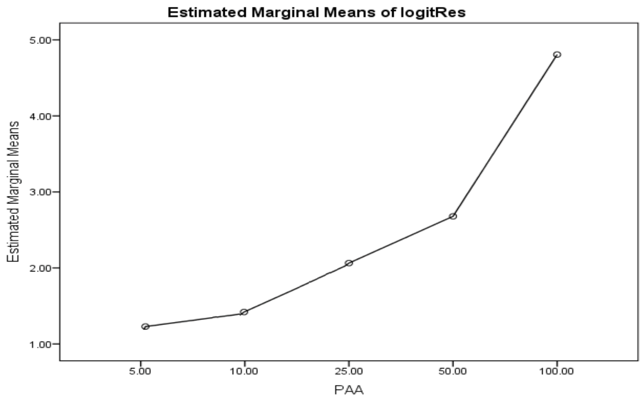


Fig. 5. Effect of peracetic acid on Rhodamine B dye removal efficiency by electro-Fenton/peracetic acid process.

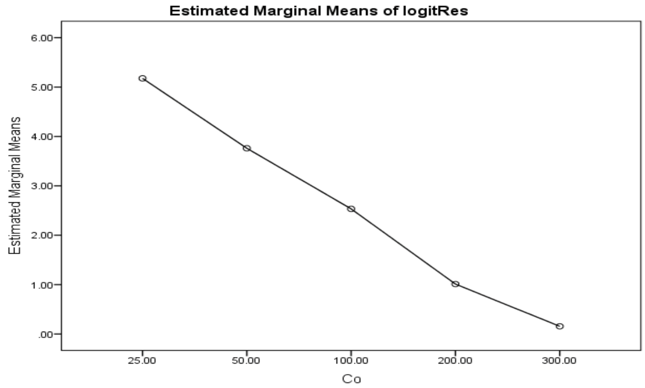


Fig. 6. Effect of Rhodamine B dye concentration on removal efficiency by electro-Fenton/peracetic acid process.

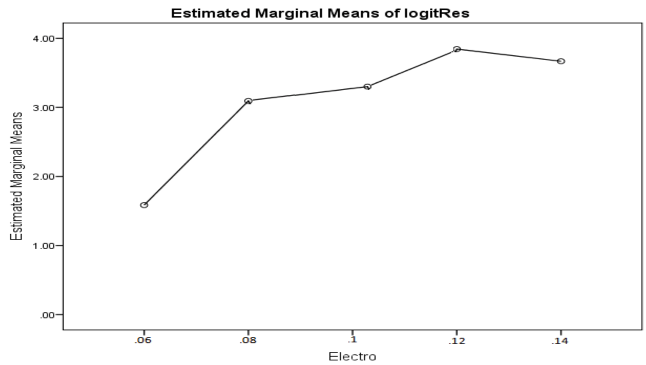


Fig. 7. Effect of current density on Rhodamine B dye removal efficiency by electro-Fenton/peracetic acid process.

lowest removal efficiency was obtained for current values in order of 25 > 50 > 100 > 200 > 300 mg/L.

3.6. Investigating the effect of current density

A current of 12 mA is selected as the reference. There is no significant difference between the reference current density removal efficiency (12 mA) and the 10 mA current density. However, there is a significant difference between the removal efficiency at reference current density and 6, 8 and 10 mA current density; it means that their removal efficiency is different. According to Fig. 7, the highest removal rate is related to current density of 12 mA and the lowest is related to current density of 6 mA; the highest to the lowest removal efficiency was obtained for current density values in order of 12 > 14 > 10 > 8 > 6 mA.

4. Discussion

4.1. Effect of contact time

Contact time is one of the important parameters in chemical reactions. The results of experiments to determine the effect of time on the removal efficiency of Rhodamine B dye by the electro/peracetic acid system presented in Fig. 2, indicate that contact time and removal efficiency are directly related to each other and with increasing contact time, removal efficiency increases.

The reason for the increase in removal efficiency can be explained by the fact that peracetic acid has a weak O–OH bond which can lead to the production of large amounts of hydroxyl radicals and these radicals attack the target contaminant [28]. Among oxidizing agents, hydrogen peroxide is widely used and the presence of iron ions increases the oxidation power of hydrogen peroxide. In fact, it can be said that iron ions act as a catalyst for the decomposition of hydrogen peroxide into two different types of oxygen radicals ($HOO^{\bullet}$ and $OH^{\bullet}$) and therefore, over time, the dye degradation rate increases [29]. Ma et al. [30] performed a study to examine the removal of methylene blue dye in electro-Fenton process at various times of 10–120 min. They also concluded that the removal efficiency increases with increasing reaction time, and under optimal conditions, for example, pH of 3, time of 120 min, current of 50 mA and 120 min, the maximum removal efficiency is obtained 99%.

4.2. Effect of pH

Ambient pH is one of the most key and effective factors in electro-Fenton reactions and its effects are clearly seen [31]. This process is effective in the acidic range and the ability to oxidize hydroxyl radicals in these conditions is very high. Many studies have reported the highest removal efficiency at pH of 3 [24]. As shown in Fig. 3, the desired maximum dye removal efficiency takes place at pH equal to 3. These results indicate that the pH of the reaction medium has a great effect on the reaction rate and the decomposition of the dye. The reason for the increase in decomposition at acidic pH is the lower number of low reactivity species such as perhydroxy (•OOH) radical than hydroxyl radical [32]. With increasing pH more than 5, the rate of degradation decreases. The main reason for this decrease is that: in an alkaline environment, iron begins to precipitate and takes the form of iron hydroxide. In fact, high pH causes the formation of iron hydrates and the production of ferric species, which in turn causes the rapid decomposition of H_2O_2 into water and oxygen, as a result, no hydroxyl radical is formed [33]. In addition, the high pH in the solution leads to the formation of large amounts of scavengers or hydroxyl radical scavenging agents (such as carbonates, bicarbonates, etc.) which are the result of mineralization of organic matter and thus reduce the concentration of hydroxyl radicals [34]. In other words, increasing the pH reduces the amount of decolorization. Because in this case, the reaction between iron ions and hydrogen peroxide and as a result the production of hydroxyl radical is affected. The formation of ferrous and ferric iron oxide hydroxides at pH above 4 prevents the reaction between iron ions and hydrogen peroxide. As a result, a small amount of hydroxyl radical can be produced.

Zhou et al. [35] entitled "Using the electro-Fenton method to remove methyl red dye", the results showed that the removal efficiency of this contaminant at pH = 3 was the highest and close to 80%. And the lowest removal value is at pH = 5 and about 50%. The results of studies conducted by Maezono et al. [36], which has been obtained the best dye removal efficiency at an acidic pH, also confirm our results.

4.3. Effect of initial concentration of sodium chloride electrolyte

Sodium chloride electrolyte concentration plays a very important role in the electro-Fenton system, because it improves electrical conductivity and intensifies the transfer of electrons in the environment. According to the results obtained from Fig. 4, the decomposition of the dye increases the decomposition efficiency by increasing the electrolyte concentration to a certain extent, but adding more sodium chloride is useless and reduces the decomposition. The main reason for this decrease could be the reaction between hydroxyl radicals and chlorine ions [Eq. (4)], which leads to the production of ClOH–. In addition, during the electro-Fenton process, Cl_2 and HOCl are formed [Eqs. (5) and (6)], which HOCl power to oxidize organic matter is less than hydroxyl radicals. Therefore, with increasing electrolyte concentration, the removal efficiency decreases [37].

$$OH^{\circ} + Cl^{-} \qquad ClOH^{-} \tag{4}$$

$$2Cl^{-} \qquad Cl_2 + 2e^{-} \tag{5}$$

$$Cl_2 + H_2O \qquad HOCl + Cl^{-} + H^{+} \tag{6}$$

Özcan et al. [38] conducted a study entitled "Study of mineralization and removal of norfloxacin from water by the electro-Fenton process" and showed that with increasing the amount of sodium chloride electrolyte, the removal rate decreases; they have stated that reason for this is the production of Cl_2 and HOCl, which have less oxidizing power than hydroxyl radicals.

4.4. Effect of initial concentration of peracetic acid

Peracetic acid concentrations of 5–100 mg/L were investigated to remove Rhodamine B dye. According to Fig. 5, the highest Rhodamine B dye removal efficiency is at a peracetic acid concentration of 100 mg/L.

As the initial concentration of the desired dye increases, the removal efficiency also increases. The reason for this increase in removal can be explained by the fact that peracetic acid has a weak O–OH bond, which can lead to the production of large amounts of hydroxyl radicals, and these radicals attack the target pollutant [28]. In addition, the iron ion in solution forms a complex with Rhodamine B dye, which then reacts with the iron-dye complex with peracetic acid, increasing the rate of decomposition.

One of the constituents of peracetic acid is hydrogen peroxide. The initial concentration of hydrogen peroxide plays an important role in electro-Fenton processes. In fact, it can be said that increasing the dose of hydrogen peroxide leads to the production of larger amounts of hydroxyl radicals, and these radicals attack the dye molecules, and as a result, the rate of decomposition increases [39]. Rahmani et al. [25] conducted a study entitled "Degradation of phenol in aqueous solutions using the electro-Fenton process" and found the same result, so that, in a time of 60 min, with increasing the concentration of hydrogen peroxide from 25 to 100 mg/L, the removal efficiency increases from 55% to about 99.9%.

4.5. Effect of initial Rhodamine B dye concentration

According to Fig. 6, as the dye concentration increases, the removal efficiency decreases. The main reason for the reduction of degradation is that the high concentration of dye requires more oxidants for complete degradation and the amount of radical produced is too low to completely remove the dye, so as the amount of dye increases, more peracetic acid should be used to produce more hydroxyl radicals. The results of similar research also show that in advanced oxidation processes, the ratio of the hydroxyl radical produced to the amount of pollutant is very important, and more oxidizing substances should be consumed to increase the amount of pollutant [40,41]. In addition, at high dye concentrations, there is a competition between the hydroxyl radicals in the electrolyte, which produces intermediates in the solution [42]. In fact, at low concentrations, the reaction occurs faster and a large amount of dye is transferred to the surface of the electrodes and removed. Rahmani et al. [43] achieved a similar result in a study entitled "Degradation of azo acid red 18 dye using electrochemical processes". According to their findings, with increasing dye concentration, the removal efficiency decreases, which said it is due to the decrease in the ratio of hydroxyl radical concentration to the desired dye.

4.6. Effect of current density

According to Fig. 7, with increasing current density to a certain extent (12 mA), the removal efficiency increases. But after that and with increasing current (14 mA), the removal efficiency decreases. In the electro-Fenton process, the production of hydrogen peroxide at the electrode depends on the intensity of the current. Increasing the amount of current increases the amount of H_2O_2 produced and thus increases the production of very strong hydroxyl radicals that are responsible for the degradation of pollutants in the electrolyte [44].

In addition, increasing the current rate converts ferric iron to ferrous iron. Also, at higher currents, hydrogen and oxygen are produced [Eq. (7)], and this factor prevents the main reactions from taking place, thus reducing the efficiency of the electro-Fenton process [45].

$$2H_2O \leftrightarrow 4H^+ + O_2 + 4e^- \tag{7}$$

Guo et al. [31] entitled "Effectiveness of the electro-Fenton process in the decomposition of organic pollutants", the removal of methylene blue dye was examined at different currents of 30–90 mA. They also found that the removal efficiency increased with increasing current to a certain extent (50 mA), and then with increasing current, the removal rate decreased. Under optimal conditions including pH of 3, time of 120 min, and current of 50 mA, the maximum removal efficiency was achieved and was 99%. Rahmani et al. [25] entitled "Evaluation of the efficiency of parameters affecting the removal of dye from water using the electro-Fenton process", they concluded that under optimal conditions, that is, pH of 3, the dye concentration of 100 mg/L, hydrogen peroxide concentration of 100 mg/L, etc., with increasing the current from 0 to 5 mA, the removal efficiency increases and reach to about 99%; however, with a further increase in current from 5 to 10 mA, removal efficiency was reduced and reached about 55%.

4.7. Identification of by-products in degradation of Rhodamine B using electro-Fenton/peracetic acid process

The Rhodamine B degradation by-products analysis carried out using the liquid chromatography–mass spectrometry (LC/MS) (Shimadzu LCMS-2010A) system equipped with C18 column (100 mm × 2.1 mm) and an electron spray ionization source. To detect the by-products in the degradation of Rhodamine B using electro-Fenton/peracetic acid process, a series of experiments were carried out at optimal condition (dye concentration = 50 mg/L, pH = 3; PAA concentration = 100 mg/L, contact time = 90 min, and NaCl = 200 mg/L, current density = 12 mA) by LC-MS. Identified main intermediates and Rhodamine B (m/z = 443) degradation pathways by LC/MS were N,N-diethyl-N′-ethylrhodamine (m/z = 414.5), N,N-diethyl-N′-ethylrhodamine (m/z = 415.0), N,N-diethylrhodamine (m/z = 388.0), N,N′-diethylrhodamine (m/z = 386.4), N-ethylrhodamine (m/z = 360.0), rhodamine (m/z = 332.0), amino rhodamine (m/z = 317.0), 9-phenyl-3H-xanthene (m/z = 257.0), 2-(2,5-dihydroxypheny) acetic acid (m/z = 168.0), phthalic acid (m/z = 166.0), terephthalic acid (m/z = 166.0), 2,4-dihydroxybenzoic acid (m/z = 154.0), adipic acid (m/z = 146), 3-hydroxybenzoic acid (m/z = 138.0), 2-hydroxypentanedioic acid (m/z = 132.0), benzoic acid (m/z = 122.0), succinic acid (m/z = 118.0), diphenol (m/z = 110.0), N-ethylethylenediamine (m/z = 88.15), formic acid (m/z = 46.0). Finally, all the low molecular weight substances could be oxidized and mineralized into carbon dioxide (CO_2), water (H_2O) and inorganic oxidized N.

5. Conclusion

In this study, the efficiency of the electro-Fenton/peracetic acid system in removing Rhodamine B dye was investigated. The results show that this system is very effective for removing Rhodamine B dye; the highest removal rate in optimal conditions, including contact time of 90 min, pH of 3, sodium chloride electrolyte concentration of 200 mg/L, peracetic acid concentration of 100 mg/L, the amount of current density of 12 mA, and the Rhodamine B of 25 mg/L concentration, was 99.9%. In addition, in this process, very little sludge is produced and the pollutant is converted into water, carbon dioxide, and mineral compounds.

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