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Electro Fenton oxidation for the removal of Rhodamine B from aqueous solution in a bubble column reactor under continuous mode

P.V. Nidheesh, R. Gandhimathi*

Department of Civil Engineering, National Institute of Technology, Tiruchirappalli 620 015, Tamilnadu, India,
Tel. +91 431 250 3171; Fax: +91 431 250 0133; email: rgmathii@nitt.edu

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ABSTRACT

Removal of hazardous dye, Rhodamine B, from aqueous solution using electrolytically generated Fenton technology in bubble column reactors (BCR) under continuous mode was investigated in the present study. BCR of capacity 3,000 mL was used for the electrolysis of 50 mg/L RhB solution. Ferric chloride was used as the Fenton catalyst and two graphite plates of effective area 100 cm^2 were used as the cathode. The effect of various operational parameters on dye removal behavior of the electro Fenton (EF) process was analyzed. Results after 8 hr of electrolysis showed that 98% of the dye was removed successfully at optimal conditions from the aqueous solution. The optimal solution pH, catalyst dosage, and applied voltage were obtained as 3, 5 mg/L, and 3.5 V, respectively. Experimental results demonstrated that EF process in BCR is effective for the removal of dyes from aqueous solution.

Keywords: Electro Fenton; Bubble column reactor; Dye removal; Rhodamine B; Advanced oxidation process

1. Introduction

Among all the electrochemical advanced oxidation processes, an electrolytic Fenton process known as electro Fenton (EF) process has recently emerged as a very promising technology for the mineralization of various organic pollutants. EF process has been very first reported by Oturan group and Brillas group [1–3]. EF process is an environmentally clean and compatible process having little sludge production with high mineralization efficiency in the presence of harmless chemicals [4–6]. In EF process, externally added catalytic amount of Fe^{2+} or Fe^{3+} reacts with H_2O_2 which is produced at the cathode surface as in Eq. (1) and generates hydroxyl radicals in the system as in conventional Fenton process (Eq. 2) [1,4]. This process is more powerful than the conventional Fenton process due to the continuous production of H_2O_2 and electro-regeneration of ferrous ion through the cathodic reduction of Fe^{3+} (Eq. 3) formed by Fenton's reaction [7]. This maintains the continuous production of hydroxyl radical in the electrolytic system and enhances the degradation of pollutants. Other important characteristics of the EF process are the maintenance of constant solution pH during the electrolysis. The protons consumed during the in situ production of H_2O_2 are counterbalanced by the oxidation of water at the anode as in Eq. (4) [8].

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*Corresponding author.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\cdot} \tag{2}$$

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

$$H_2O \rightarrow 0.5O_2 + 2H^+ + 2e^- \tag{4}$$

Carbonaceous materials are considered as the efficient cathode material suitable for the *in situ* electrolytic generation of H_2O_2 [6]. Various carbonaceous materials such as graphite, carbon sponge, activated carbon fiber, carbon PTFE, reticulated vitreous carbon, carbon felt, and so on were used for the abatement of various organic pollutants. H_2O_2 decomposition electrochemical activity of these materials is very low and the O_2 reduction activity is very high [9]. The pores in these materials can hold the oxygen molecules and enhance the *in situ* production rate of H_2O_2. Our previous work [10] demonstrated that the increase in depth of immersion of carbonaceous cathode increases the efficiency of EF process. This is mainly due to the increase in contact time between air bubbles and the cathode surface and an increase in contact with more amounts of finer bubbles than shallow electrodes.

By keeping the above point of view, bubble column reactor (BCR) is the better option for an EF process to get a higher amount of pollutant removal or mineralization efficiency. Bubble columns are the contactors in which a gas or a mixture of gases in the form of a dispersed phase of bubbles moves in a continuous liquid phase [11]. BCR belong to the general class of multiphase reactors which consist of three main categories, namely the trickle bed reactor (fixed or packed bed), fluidized bed reactor, and the BCR [12]. These reactors are used in industries due to its simple design, absence of mechanically moving parts, excellent heat and mass transfer properties, high thermal stability, good mixing, low power requirements, and hence low construction and operation costs [13,14]. These reactors are used in environmental field for the treatment of winery wastewater by ozone-based advanced oxidation processes [15], ultrasound-enhanced catalytic ozonation [16], lead and biological oxygen demand removal from wastewater using activated rice husk [17], ozonation of phenol and dye [18,19], etc.

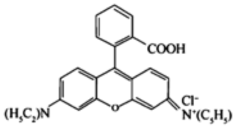
A few studies were conducted for the EF oxidation of organic pollutants in a continuous mode. Fered Fenton treatment of matured landfill leachate was carried out by Zhang et al. [20] using $Ti/RuO_2–IrO_2–SnO_2–TiO_2$ mesh anodes and Ti mesh cathodes in a continuous stirred tank reactor. Rosales et al. [21] carried out a continuous study on the decolorization of dyes via EF process using BCR and confirmed that the hydrodynamic behavior of BCR is similar to that of continuous stirred tank reactor. Rosales et al. [22] used BCR in continuous mode for the decolorization of dyes using Fe alginate gel beads as a Fenton catalyst. Our previous study [23] reported that the graphite–graphite EF system in a continuous stirred tank reactor has the ability to remove salicylic acid from aqueous solution. The present study focused on the EF removal of the hazardous dye, Rhodamine B (RhB), from aqueous solution in BCR. The properties of RhB are given in Table 1. RhB is widely used in paper, leather, paint industries, and textile industries. The release of RhB in water medium is harmful to both aquatic life and humans. RhB is hazardous, carcinogenic, toxic, and mutagenic, especially for pregnant women and children [24,25]. It is harmful if swallowed by human beings and animals, and causes irritation to the skin, eyes, and respiratory tract [26]. Therefore, treatment for this harmful pollutant is needed before entering into the natural water bodies. In the present study, RhB removal characteristics and its kinetic analysis by EF process in BCR was carried out. Influence of different operational parameters such as solution pH, applied voltage, catalyst concentration, and inlet flow rate on RhB removal was investigated.

2. Materials and methods

2.1. Chemicals

Analytical grade ferric chloride, supplied by Merck (CAS No. 7705-08-0), was used as the source of Fenton catalyst for all the experiments. RhB dye stuffs purchased from Loba Chemie (CAS No. 81-88-9) were used without further purification. Sulfuric acid of minimum assay 95–98% from Merck (CAS No. 7664-93-9) was used as the pH regulator.

Table 1
Properties of RhB

C.I. No.	45170
C.I. Name	Basic violet 10
Chemical formula	C28H31ClN2O3
Molecular weight	479.02 g/mol
λ_{max}	553.8 nm
Structural formula	

2.2. BCR and experimental procedure

BCR of diameter 10.4 cm and height 40 cm, which is made of glass, was used for all the electrolytic experiments. The height to diameter (H/D) ratio is an important parameter controlling the efficiency of BCR. If the value of H/D is very less, utilization rate of small bubbles becomes very less and it will cause a pressure drop in the system [13]. This will affect the RhB removal efficiency of the EF process. An outlet of 1 cm diameter was provided at 35.5 cm above the bottom of BCR. The hydrostatic pressure due to the 35.5 cm static liquid height is only less than 0.1 atm and the effect of this pressure on the bubble size and its rising velocity is negligible [13]. Thus, working volume for all the electrolytic experiments was considered as 3,000 mL.

Graphite plates obtained from Anabond Sainergy Fuel Cell India Private Limited, Chennai, Tamil Nadu, India, were used as both anode and cathode. The schematic diagram of the experimental set-up is shown in Fig. 1. Two cathodes and one anode were used for the electrolysis of dye solution. Cathodes of effective area 100 cm^2 and anode of effective area 80 cm^2 were used in all the electrolytic experiments. Anode was placed at the middle of cathodes. The depth of immersion of all the electrodes kept constant as 20 cm and placed vertically and parallel to each other with an effective inner electrode spacing of 1.75 cm. Constant power supply across the electrodes was ensured with a DC power supply (Make: Beetech, 0–5 A and 0–30 V). For all the experiments, 50 mg/L of RhB solution was used and the pH of this solution was adjusted to 3 using 4 M H_2SO_4. To the pH-adjusted dye solution, required amount of ferric chloride was added and mixed well. Air was purged in the solution using commercially available fish aerator and its diffusers were placed at the bottom of both cathodes. This will guarantee an oxygen-enriched solution and help for the cathodic *in situ* generation of H_2O_2. Inlet tank of capacity 20 L kept at 65 cm above the ground and the flow from tank was regulated to required level and monitored during the experiments. All the experiments were conducted at room temperature. Samples were withdrawn at regular intervals and residual concentration of RhB was analyzed using UV-Visible spectrometer (Lambda 25, PerkinElmer, USA). The color removal efficiency of the BCR in continuous mode was calculated using Eq. (5).

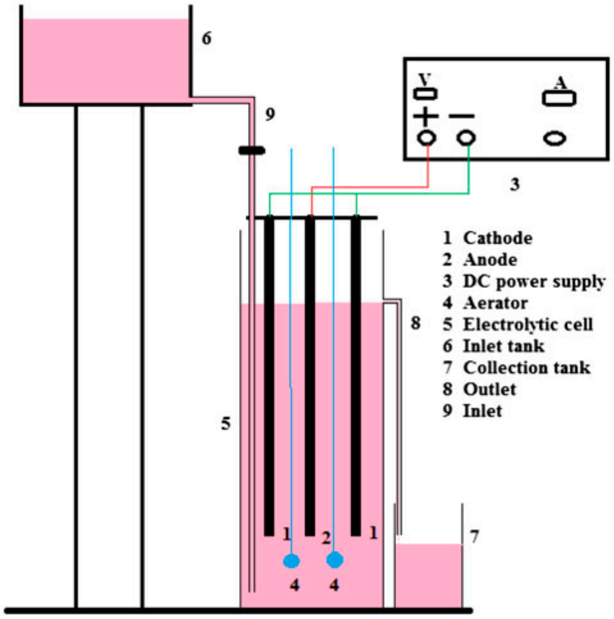


Fig. 1. Schematic diagram of experimental set-up.

$$\text{Removal efficiency (\%)} = \left(\frac{[\text{RhB}]_0 - [\text{RhB}]_t}{[\text{RhB}]_0}\right) \times 100 \quad (5)$$

where $[\text{RhB}]_t$ represents the concentration of RhB at time t; $[\text{RhB}]_0$ is the initial dye concentration.

3. Results and discussion

3.1. Effect of applied voltage on RhB removal kinetics

Applied voltage is an important parameter affecting the efficiency of any electrolytic system. In EF process, the applied current is the driving force for the reduction of oxygen, leading to the generation of hydrogen peroxide at the cathode [27]. If the voltage is very less, the electrical force required for the chemical reaction will be less and results in lesser efficiency. On the other hand, if the applied voltage is very high, efficiency of the electrolytic system will increase, but the cost of the system also will get increased. Therefore, an optimal applied voltage is necessary for any electrolytic system with lesser operational cost and higher efficiency.

In order to find the effect of voltage on the RhB removal efficiency of EF process, experiments were carried out by changing the voltage from 2 to 4 V, with the increment of 0.5 V and the results obtained at regular interval are depicted in Fig. 2. It can be seen from Fig. 2 that the rate of RhB removal was increased by increasing applied voltage from 2 to 3.5 V. RhB removal efficiency values reached 45.5 and 87.3% after 1.5 hr of electrolysis for the applied voltages of 2 and 3.5 V, respectively. This faster RhB removal rate at higher voltage could be ascribed to the acceleration of

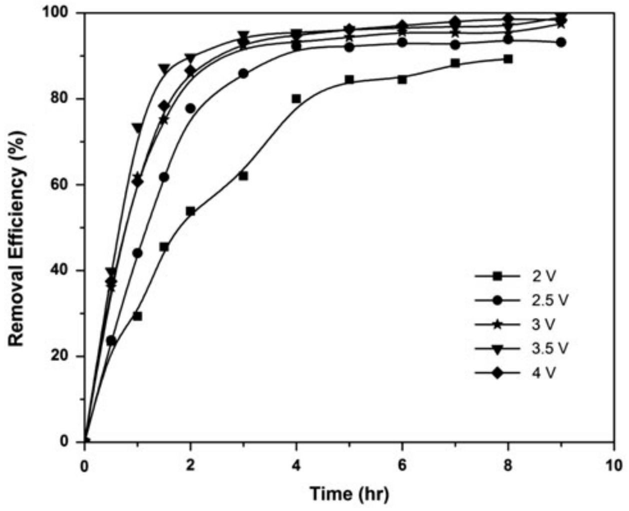


Fig. 2. RhB removal kinetics in BCR by EF process under various applied voltages.

H_2O_2 formation rate and also to the faster regeneration of Fe^{2+}, leading to the generation of higher amount of hydroxyl radicals from Fenton's reaction [28]. Özcan et al. [29] reported an increase in H_2O_2 production rate at carbon sponge cathode with an increase in applied current. Force of attraction of RhB toward the cathode, which is the working electrode of EF process, also increases with the increase in applied voltage. This will cause higher collision frequency between electrolytically produced hydroxyl radical and the dye molecules, leading to higher removal efficiency. But, further increase in the voltage from 3.5 to 4 V decreased the RhB removal efficiency of EF process. At the higher voltage values, formation of H_2O by $4e^-$ reduction of oxygen leads to the lesser formation of H_2O_2 [29]. Also, the increase in applied voltage increases the temperature of the solution, which will boost the decomposition rate of H_2O_2 and decreases the solubility of oxygen in the electrolytic system [29]. Hydrogen evolution at the cathode is also increases with the applied voltage. This will scarify the efficiency of EF process at higher voltages, even though ferrous ion regeneration rate is very high [30]. Ninety-eight percent of RhB was removed after 8 hr of electrolysis. Therefore, 3.5 V was considered as the optimal voltage required for the RhB removal in bubble reactor.

From Fig. 2, it can also be observed that the removal of RhB in the BCR follows an exponential decrease, which indicates that the removal kinetics follows pseudo-first-order kinetics. The rate of removal of RhB depends on the concentration of RhB and hydroxyl radicals, and in steady state this rate depends more on pollutant concentration than that of hydroxyl radical. Therefore, pseudo-first-order kinetic equation of RhB removal can be written as follows:

$$\frac{d[\mathrm{RhB}]_t}{dt} = -k_1[\mathrm{RhB}]_t \tag{6}$$

This results in a final expression of,

$$\ln\left(\frac{[\mathrm{RhB}]_0}{[\mathrm{RhB}]_t}\right) = -k_1 t \tag{7}$$

where $[\mathrm{RhB}]_t$ represents the concentration of RhB at time t (mg/L); $[\mathrm{RhB}]_0$ is the initial dye concentration (mg/L) and k_1 is the apparent pseudo-first-order kinetic rate constant (min^{-1}).

Apparent pseudo-first-order rate constants for the removal of RhB in the BCR were calculated for various applied voltage values by plotting $\ln([\mathrm{RhB}]_0/[\mathrm{RhB}]_t)$ against electrolysis time (Fig. 3) and the results are given in Table 2. The higher values of linear regression coefficient indicate that the RhB removal follows the pseudo-first-order kinetics. The dye removal rate constant increased with the increase in applied voltage up to 3.5 V and decreased thereafter. The apparent rate constant value increased 3.5 times with the increase of voltage from 2 to 3.5 V and this increment was linear with a linear regression coefficient of 0.98.

The RhB decolorization efficiency of the BCR was predicted using equation (Eq. 8) given by Rosales et al. [21].

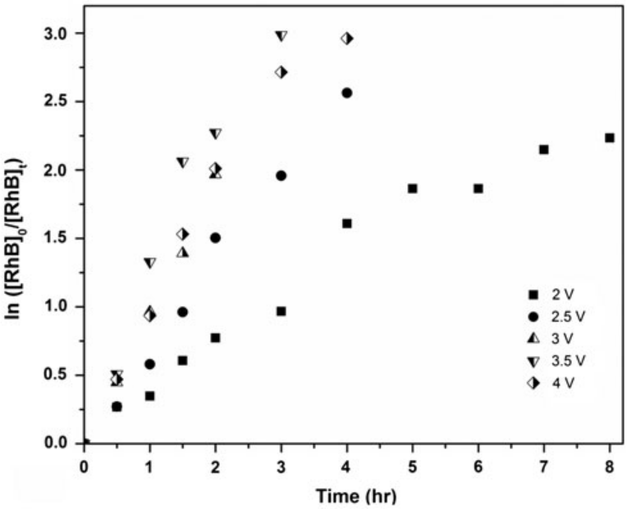


Fig. 3. Pseudo-first-order kinetic plots for RhB removal under various applied voltages.

Table 2
Pseudo-first-order kinetic coefficients for RhB removal under various applied voltages

Applied voltage (V)	Applied current (A)	k_1 (hr^{-1})	R^2	D	Operational cost (US$/g)
2	0.01	0.3182	0.95	76.08	0.43
2.5	0.03	0.6553	0.99	86.76	0.66
3	0.05	0.907	0.99	90.06	0.88
3.5	0.07	1.102	0.95	91.68	1.45
4	0.11	0.845	0.95	89.41	2.49

$$D = \frac{k_1 \tau}{1 + k_1 \tau} 100 \tag{8}$$

where D is the dye removal efficiency (%); τ is the residence time (min) and k_1 is the apparent pseudo-first-order kinetic coefficient (min^{-1}). The computed values of "D" at various applied voltage values are also given in Table 2 and it is compared with the experimental data. The model predicted removal efficiency of BCR is lesser than the values obtained from the experiments. The error between experimental data and model predicted data is maximum for 2 V and minimum for 3 V and the difference between both values is within 2.9 to 8.4%. This behavior is mainly due to the difference in mixing characteristics of fluid particles having the same residence time. The particles having the same residence time mix well in the reactor but it will not mix well in the presence of other particles having different residence time, until they go out from the reactor [31].

The specific energy conception (Q) of the continuous EF system at various voltages also calculated using Eq. (9).

$$Q = \frac{VIt}{m} \tag{9}$$

where V is the applied voltage (V), I is the current (A), t is the electrolysis time (hr), and m is the change in dye concentration during the electrolysis (g).

The change in specific energy consumption as a function of applied voltage and electrolysis time is given in Fig. 4. The value of Q increased with the increase in applied voltage and the electrolysis time. The rate of increase in Q is also a function of electrolysis time and applied voltage. This increase in specific energy consumption affects the cost of operation.

The operating cost for the electrolysis time of 3 hr including energy and material costs was calculated and the results are given in Table 2. Electrical energy price, graphite plate cost, and ferric chloride cost were considered as 0.06 US$/Wh, 0.07 US$/cm^2 and 0.008 US$/gm, respectively. From the table, it can be seen that the operating cost of BCR increases with an increase in applied voltage and the values are comparable with the operating cost of electrocoagulation [32].

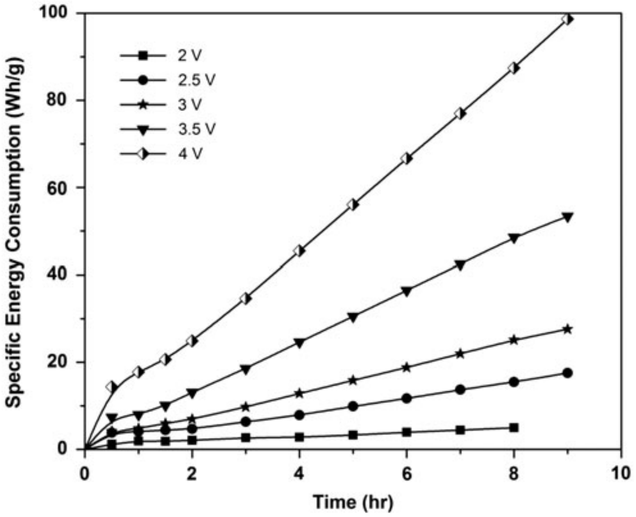


Fig. 4. Specific energy consumption as a function of electrolysis time and applied voltage.

3.2. Effect of solution pH

Solution pH plays an important role in the efficient performance of EF process. This is mainly due to the solubility behavior of iron species at the different pH values. At pH less than 3.5, solution contains higher concentrations of Fe^{3+}, $Fe(OH)_2^+$, and $Fe_2(OH)_2^{4+}$ than other iron species. Therefore, EF process works effectively at pH less than 3.5. Solution pH higher than 3.5 contains more amount of hydroxide complex than Fe^{3+}. At these pH values, electrocoagulation or sorption of pollutants on the iron hydroxides occurs. Moreover, the pH 3 is widely accepted as the optimum value for EF process. From the point of H_2O_2 production at cathode, low solution pH is required for the generation of H_2O_2 on the cathode surface, due to the utilization of protons in the solution. Fig. 5 depicted the RhB

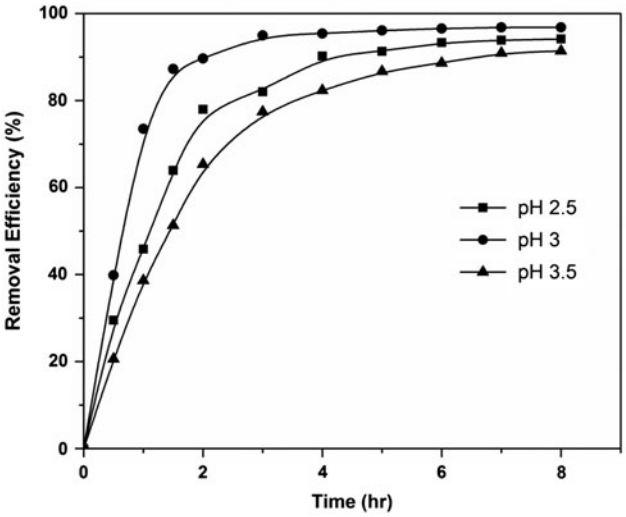


Fig. 5. Time course RhB concentration at various solution pH values.

removal kinetics at different solution pH values of 2.5, 3 and 3.5 in BCR under continuous mode. The obtained results also verified that the optimal pH of EF process is 3. Increase and decrease in solution pH from 3 decreased the dye removal efficiency of EF process. RhB removal efficiencies of EF process after 90 min of electrolysis at solution pHs of 2.5, 3, and 3.5 were 63.9, 87.3, and 51.3%, respectively. Lesser dye removal efficiency of EF process at pH of 2.5 is mainly due to the evolution of hydrogen gas and the production of oxonium ion and water. At lower pH values, electrolytically *in situ* generated hydrogen peroxide reacts with excess protons in the solution, forms oxonium ions as in Eq. (10) [33]. Oxonium ions are electrophilic and cause retardation in the reaction rate between H_2O_2 and Fe^{2+} [34]. At the same time, hydrogen gases are evolved at the cathode surface as in Eq. (11) which leads to the decrease in H_2O_2 production rate [29]. Water formation at lower pH will occur in two ways—reduction of hydrogen peroxide as in Eq. (12) and the reaction of protons with oxygen as in Eq. (13) [29,35]. Also, at lower pH values, iron forms stable complexes with hydrogen peroxides [36]. These reactions reduce the effective quantity of hydroxyl radicals, resulting in the efficiency reduction of the EF system.

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{10}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{11}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{12}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{13}$$

3.3. Effect of catalyst concentration

Concentration of Fenton catalyst is an important parameter affecting the production of hydroxyl radical and, thus, efficiency of the EF process. In conventional Fenton process, the ratio: concentration of Fe^{2+} to H_2O_2 controls the overall efficiency of the system. But, in EF process, the effect of concentration of iron species is more than the concentration of H_2O_2 on the pollutant oxidation efficiency, as H_2O_2 is continuously produced at the cathode surface and depends on the concentration of oxygen in the solution. In the overall reactions, 0.5 moles of oxygen produces 2 moles of hydroxyl radical [1], which indicates that the oxygen required for the EF process is also very less. Therefore, the production rate of H_2O_2 is a constant for the same operating conditions.

To optimize the catalyst concentration of EF process, the removal of 50 mg/L RhB solution was carried out in the presence of various Fe^{3+} concentrations at constant solution pH 3, inlet flow rate of 5 mL/min and applied voltage of 3.5 V. When the Fe^{3+} concentration increased from 2.5 to 5 mg/L, the RhB removal efficiency of EF process under the continuous mode of operation also increased from 53.5 to 73.5%. Further increase in the catalyst concentration decreased the dye removal efficiency of EF system. This indicates that the optimal iron species molar concentration required for the Fenton reaction in the presence of electrolytic H_2O_2 is 5 mg/L. The increase in efficiency of this electrolytic system with the increase in Fe^{3+} concentration from 2.5 to 5 mg/L is mainly due to the increase in hydroxyl radical production. At lower Fe^{3+} concentration, the amount of Fe^{2+} in the solution by the cathodic regeneration is also less. This indicates that the concentration of H_2O_2 is very high at lower catalyst concentration, since the production rate of H_2O_2 is constant and independent of iron species concentration. These excess H_2O_2 reacts with the hydroxyl radicals produced in the system as in Eq. (14) [37] and reduce the efficiency of EF system since, the organic compound oxidation ability of hydroperoxyl radical is lesser than that of hydroxyl radicals [38].

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{14}$$

But, further increase in the catalyst concentration from 5 to 7.5 mg/L decreased the efficiency of the system to 65.7%. The negative effect at 7.5 mg/L of catalyst concentration is mainly due to the scavenging reactions (Eqs. 15–17) occurred between hydroxyl radicals and iron species in the electrolytic system during electrolysis [39]. With the increase in concentration of Fe^{3+} at solution pH 3, the concentration of hydroxide complexes of iron such as $Fe(OH)_2^+$ and $Fe_2(OH)_2^{4+}$ also increases. These complexes attract towards the cathode, leading to the formation a yellowish layer on cathode surface. This reduces the effective pore volume required for the H_2O_2 production and hence reduces the efficiency of the system.

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^- \tag{15}$$

$$Fe^{3+} + H_2O_2 \rightarrow FeO - OH^{2+} + H^+ \tag{16}$$

$$FeO - OH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \tag{17}$$

3.4. Effect of inlet flow rate

Inlet flow rate of pollutant is an important parameter considered for the design of reactors for industrial applications. It determines the capacity required for the reactor for a specific volume of pollutant. With the increase in inlet flow rate, the retention time of the reactor decreases, this reduces the residence time and results in efficiency reduction. To analyze the effect of inlet flow rate on the efficiency of EF process in BCR reactor, electrolysis were carried out at different flow rates of 5, 10, and 15 mL/min and the obtained results are depicted in Fig. 6. As can be seen from Fig. 6, the dye removal efficiency of the EF process increased at initial stages (up to 2 hr) of electrolysis with the increase in flow rate from 5 to 10 mL/min. These results are in contrary with the above described concepts. This behavior of EF process in BCR is mainly due to the increase in collision between hydroxyl radicals and RhB molecules. H_2O_2 production in the EF system is very high at the initial stages of electrolysis and it will come to equilibrium in later stages [29]. This indicates that the production of hydroxyl radical also follows the same. Also, the life time of the hydroxyl radical is very short and it will react spontaneously at the point of formation. From Fig. 6, it can also be seen that the rate of removal of dye was decreasing with an increase in the electrolysis time. This result verifies the H_2O_2 and hydroxyl radical formation profiles with electrolysis time. At the initial stages of electrolysis, the concentration of pollutant is very high and hydroxyl radical formed near cathode can oxidize the pollutant easily. As the time passes, the concentration of the contaminants decreases, resulting in the reduction of collision rate between the organic compound and hydroxyl radical, which will decrease the removal rate with electrolysis time. With the increase in the flow rate from 5 to 10 mL/min, the pollutant concentration in the solution increases, leading to an increase in the rate of collision between dye molecules and hydroxyl radicals, thus, the removal efficiency of the system will improve. This result also indicates that the production of H_2O_2 in the EF system is higher than that required for the flow rate of 5 mL/min. But, further increase in flow rate from 10 to 15 mL/min reduced the dye removal rate and efficiency of the electrolytic system. The rate of RhB removal at an inlet flow rate of 15 mL/min follows the same trend as that of 5 mL/min up to 1 hr of electrolysis. This also indicates that the pollutant removal efficiency at 15 mL/min flow rate is higher than that at 5 mL/min. The lesser efficiency at 15 mL/min than 10 mL/min flow rate is mainly due to the insufficient production of hydroxyl radical. Further results shows that the removal efficiency remains constant with electrolysis time. During these stages, the concentration of the byproducts produced during the oxidation of RhB is higher than that of dye molecule concentration. This results in higher collision rate of hydroxyl radicals with the byproducts than the dye molecules, leading to lesser dye removal at later stages of the electrolysis.

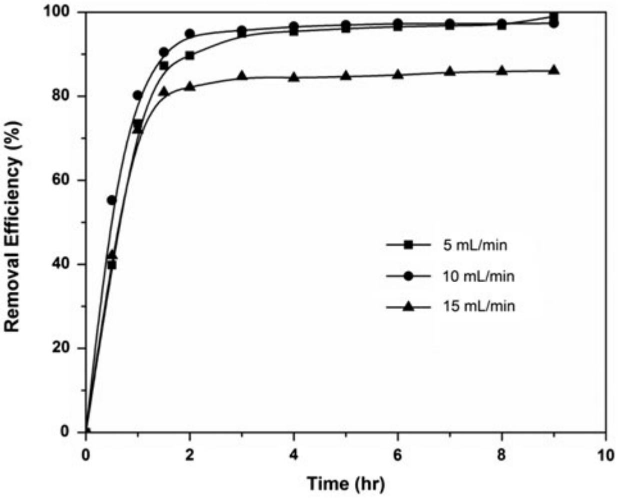


Fig. 6. RhB removal kinetics by EF process as a function of inlet flow rate.

4. Conclusions

EF treatment for 50 mg/L RhB solution at acidic condition was carried out in a 3,000 mL BCR to investigate the effects of operational parameters on the system performance. RhB removal rate was increased with the increase in voltage up to 3.5 V and then decreased. The rate of RhB removal followed pseudo-first-order kinetics. Optimum solution pH and catalyst dosage for the dye removal was found as 3 and 5 mg/L, respectively. At the optimal conditions, 98% of the RhB was effectively removed from the aqueous solution. The dye removal efficiency of this system increased with the increase in flow rate from 5 to 10 mL/min and then decreased. Overall, EF process in BCR under continuous mode was found to be an effective way for the removal of dyes from aqueous solution.

References

[1] M.A. Oturan, An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for *in situ* destruction of organic pollutants: Application to herbicide 2,4-D, J. Appl. Electrochem. 30 (2000) 475–482.

[2] M.A. Oturan, J. Peiroten, P. Chartrin, A.J. Acher, Complete destruction of p-Nitrophenol in aqueous medium by electro-Fenton method, Environ. Sci. Technol. 34 (16) (2000) 3474–3479.

[3] E. Brillas, E. Mur, J. Casado, Iron(II) catalysis of the mineralization of aniline using a carbon–PTFE O_2-fed cathode, J. Electrochem. Soc. 143 (1996) L49–L53.

[4] E. Brillas, I. Sirés, M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry, Chem. Rev. 109 (2009) 6570–6631.

[5] P.V. Nidheesh, R. Gandhimathi, S.T. Ramesh, Degradation of dyes from aqueous solution by Fenton processes: A review, Environ. Sci. Pollut. Res. 20 (2013) 2099–2132.

[6] P.V. Nidheesh, R. Gandhimathi, Trends in electro-Fenton process for water and wastewater treatment: An overview, Desalination 299 (2012) 1–15.

[7] M. Zhou, Q. Tan, Q. Wang, Y. Jiao, N. Oturan, M.A. Oturan, Degradation of organics in reverse osmosis concentrate by electro-Fenton process, J. Hazard. Mater. 215–216 (2012) 287–293.

[8] H.S. El-Desoky, M.M. Ghoneim, R. El-Sheikh, N.M. Zidan, Oxidation of Levafix CA reactive azo-dyes in industrial wastewater of textile dyeing by electro-generated Fenton's reagent, J. Hazard. Mater. 175 (2010) 858–865.

[9] M. Panizza, G. Cerisola, Removal of organic pollutants from industrial wastewater by electrogenerated Fenton's reagent, Water Res. 35 (2001) 3987–3992.

[10] P.V. Nidheesh, R. Gandhimathi, Removal of Rhodamine B from aqueous solution using graphite–graphite electro-Fenton system, Desali. Water Treat. 52 (2014) 1872–1877.

[11] P. Mena, A. Ferreira, J.A. Teixeira, F. Rocha, Effect of some solid properties on gas–liquid mass transfer in a bubble column, Chem. Eng. Process. 50 (2011) 181–188.

[12] N. Kantarci, F. Borak, K.O. Ulgen, Bubble column reactors, Process Biochem. 40 (2005) 2263–2283.

[13] R. Lau, R. Mo, W.S.B. Beverly Sim, Bubble characteristics in shallow bubble column reactors, Chem. Eng. Res. Des. 88 (2010) 197–203.

[14] W.-D. Deckwer, Bubble column reactors, Wiley, Chichester, 1992.

[15] M.S. Lucas, J.A. Peres, G. Li Puma, Treatment of winery wastewater by ozone-based advanced oxidation processes (O_3, O_3/UV and O_3/UV/H_2O_2) in a pilot-scale bubble column reactor and process economics, Sep. Puri. Technol. 72 (2010) 235–241.

[16] Y. Wang, H. Zhang, L. Chen, Ultrasound enhanced catalytic ozonation of tetracycline in a rectangular air-lift reactor, Catal. Today 175 (2011) 283–292.

[17] J.N. Sahu, S. Agarwal, B.C. Meikap, M.N. Biswas, Performance of a modified multi-stage bubble column reactor for lead(II) and biological oxygen demand removal from wastewater using activated rice husk, J. Hazard. Mater. 161 (2009) 317–324.

[18] M. Matheswaran, Il Shik Moon, Influence parameters in the ozonation of phenol wastewater treatment using bubble column reactor under continuous circulation, J. Ind. Eng. Chem. 15 (2009) 287–292.

[19] S. Palit, Studies on ozone-oxidation of dye in a bubble column reactor at different pH and different oxidation-reduction potential, Int. J. Environ. Sci. Develop. 1 (2010) 341–346.

[20] H. Zhang, X. Ran, X. Wu, Electro-Fenton treatment of mature landfill leachate in a continuous flow reactor, J. Hazard. Mater. 241–242 (2012) 259–266.

[21] E. Rosales, M. Pazos, M.A. Longo, M.A. Sanromán, Electro-Fenton decoloration of dyes in a continuous reactor: A promising technology in colored wastewater treatment, Chem. Eng. J. 155 (2009) 62–67.

[22] E. Rosales, O. Iglesias, M. Pazos, M.A. Sanromán, Decolourisation of dyes under electro-Fenton process using Fe alginate gel beads, J. Hazard. Mater. 213–214 (2012) 369–377.

[23] S.J. George, R. Gandhimathi, P.V. Nidheesh, S.T. Ramesh, Electro-Fenton method oxidation of salicylic acid in aqueous solution with graphite electrodes, Environ. Eng. Sci. 30 (2013) 750–756.

[24] V.K. Gupta, Application of low-cost adsorbents for dye removal—A review, J. Environ. Manage. 90 (2009) 2313–2342.

[25] K.P. Mishra, P.R. Gogate, Intensification of degradation of aqueous solutions of Rhodamine B using sonochemical reactors at operating capacity of 7 L, J. Environ. Manage. 92(8) (2011) 1972–1977.

[26] J. Rochat, P. Demenge, J.C. Rerat, Toxicologic study of a fluorescent tracer: Rhodamine B, Toxicol. Eur. Res. 1 (1978) 23–26.

[27] T.S.N. Sankara Narayanan, G. Magesh, N. Rajendran, Degradation of Ochlorophenol from aqueous solution by electro-Fenton process, Fresenius Environ. Bull. 12 (7) (2003) 776–780.

[28] M. Panizza, M.A. Oturan, Degradation of Alizarin Red by electro-Fenton process using a graphite-felt cathode, Electrochim. Acta 56 (2011) 7084–7087.

[29] A. Özcan, Y. Şahin, A. Savas Koparal, M.A. Oturan, Carbon sponge as a new cathode material for the electro-Fenton process: Comparison with carbon felt cathode and application to degradation of synthetic dye basic blue 3 in aqueous medium, J. Electroanal. Chem. 616 (2008) 71–78.

[30] Z. Qiang, J-H. Chang, C-P. Huang, Electrochemical regeneration of Fe^{2+} in Fenton oxidation processes, Water Res. 37 (2003) 1308–1319.

[31] J.H. Ramirez, F.M. Duarte, F.G. Martins, C.A. Costa, L.M. Madeira, Modelling of the synthetic dye Orange II degradation using Fenton's reagent: From batch to continuous reactor operation, Chem. Eng. J. 148 (2008) 394–404.

[32] P. Maha Lakshmi, P. Sivashanmugam, Treatment of Oil tanning effluent by electrocoagulation: Influence of ultrasound and hybrid electrode on COD removal, Sep. Purif. Technol. 116 (2013) 378–384.

[33] M. Zhou, Q. Yu, L. Lei, G. Barton, Electro-Fenton method for the removal of methyl red in an efficient electrochemical system, Sep. Purif. Technol. 57 (2007) 380–387.

[34] C.-C. Jiang, J.-F. Zhang, Progress and prospect in electro-Fenton process for wastewater treatment, J. Zhejiang Univ. Sci. A 8 (2007) 1118–1125.

[35] A.A. Alvarez-Gallegos, D. Pletcher, The removal of low level organics via hydrogen peroxide formed in a reticulated vitreous carbon cathode cell, Part 1. The electrosynthesis of hydrogen peroxide in aqueous acidic solutions, Electrochim. Acta 44 (1998) 853–861.

[36] C.-T. Wang, W.-L. Chou, M.-H. Chung, Y.-M. Kuo, COD removal from real dyeing wastewater by electro-Fenton technology using an activated carbon fiber cathode, Desalination 253 (2010) 129–134.

[37] K. Dutta, S. Mukhopadhyay, S. Bhattacharjee, B. Chaudhuri, Chemical oxidation of methylene blue using a Fenton-like reaction, J. Hazard. Mater. B84 (2001) 57–71.

[38] I. Arslan-Alaton, G. Tureli, T. Olmez-Hanci, Treatment of azo dye production wastewaters using Photo-Fenton like advanced oxidation processes: Optimization by response surface methodology, J. Photochem. Photobiol. A 202 (2009) 142–153.

[39] A. Özcan, M.A. Oturan, N. Oturan, Y. Şahin, Removal of Acid Orange 7 from water by electrochemically generated Fenton's reagent, J. Hazard. Mater. 163 (2009) 1213–1220.