Reclamation of Model Wastewater Containing Rhodamine B by Electrochemical Fenton (ECF) process

N R Vaghela[1] and K Nath[2]*

[1]Department of Chemical Engineering Government Engineering College Bharuch – 392002, Gujarat, India

[*2]Department of Chemical Engineering, G H Patel College of Engineering & Technology [Affiliated to Gujarat Technological University, Ahmadabad], Vallabh Vidyanagar-388120, Gujarat, India

Treatment of the Synthetic Rhodamine B (RhB) wastewater by Electrochemical Fenton (ECF) processes for colour removal in batch mode using commercially available iron plates as electrodes was studied. Colour removal efficiency was determined for the ECF process by considering the effects of different variables such as pH, current density, RhB concentration and temperature. Improvement in colour removal efficiency was obtained when H_2O_2 was added as an oxidizing agent. The colour removal efficiency reached 94.89 % at the optimum experimental conditions (pH 3.0, 100 A/m^2, 50 mg/l RhB concentration, 5 minutes, 30°C and dosage of 0.2 M H_2O_2). Electrical energy consumption was calculated as 2.09 KWh/m^3. The ECF process was found capable to achieve the higher colour removal efficiencies with potential for wastewater treatment.

Keywords: Electrochemical Fenton; Wastewater, Rhodamine B, colour removal

Introduction

Rhodamine B (RhB) is a fluorescent basic dye, widely used in paper, paint, leather and textile industries. Roughly 1-2% of RhB loss occurs during production which comes ultimately in the effluent. RhB contaminated wastewater needs reclamation to reduce the environmental impact as a result of its carcinogenic and teratogenic effects[1]. Amongst several conventional treatment strategies adsorption[2], chemical and electro-coagulation[3] and biological processes are extensively reported in the literature. However, none of the aforementioned methods could offer a viable solution to the treatment of dye wastewater due to various reasons such as long treatment time, regeneration of spent adsorbents, sludge disposal, incomplete degradation of complex dye molecules etc. As an alternative strategy, electrochemical Fenton (ECF) process could be attractive due to its simple and cost effective operation without any need of addition of chemical reagents[4,5]. The effect of various operating parameters such as initial pH, current density, initial dye concentration, temperature was extensively studied using iron as electrodes in a monopolar configuration in an undivided electrochemical reactor and colour removal efficiency was calculated. In addition electrical energy consumption in the process was also evaluated.

Materials and methods

Rhodamine B (chemical formula $C_{28}H_{31}ClN_2O_3$) was collected from Kohinoor Group of Industries, Ankleshwar, India. It has molecular weight of 479.017 g/mol and maximum absorption wavelength (λ_{max}) 554 nm. A Synthetic solution was prepared by dissolving RhB dye in DI water and 1000 ppm stock solution was prepared. Subsequently, required concentration was prepared by diluting the stock solution. Analytical grade HCl, NaCl, NaOH, H_2O_2 was obtained from M/s Merck, India. In all experiments, double distilled water (conductivity: 1 μS/cm) was used to prepare the solutions. Commercially available iron plates were used as electrodes (150×50×2 mm).

Experimental Procedure

All the experiments were carried out in 250 ml cylindrical glass beaker in batch mode. Two plates of iron having a dimension of 150×50×2 mm were used

*Author for Correspondence
Email: kaushiknath@gcet.ac.in

as anode and cathode in a monopolar configuration and maintaining an interelectrode distance of 20 mm. The effective electrode area was 25 cm^2. 0.1 M HCl or 0.1 M NaOH was used to adjust the pH of the synthetic wastewater. A predetermined amount of H_2O_2 was added in the solution before the Direct current (DC) was applied. DC regulated power supply (Make: SIGMA, 0–30 V 0-5 A) was used for DC power input to the Electrochemical Cell. The desired current density (A/m^2) was set by changing the voltage of the DC power supply.

Determination of COD, TDS, pH & conductivity

Chemical oxygen demand (COD), total dissolved solid (TDS), pH and conductivity of the feed and permeate streams were measured using open reflux method, digital TDS meter (EI, Model No 651 E), digital pH meter (EI, Model No 112) and digital conductivity meter (EI, Model No 651) following standard methodologies (APHA 2005). Freshly prepared 1 M NaOH and HCl solutions were used for pH adjustment during pH study.

Estimation of RhB Concentration and colour removal efficiency

The concentration of RhB was determined by UV–Vis spectrophotometer (Systronics, model Model CL 335). The wave length of maximum absorption (λ_{max}) of the dye was determined to be 554 nm. The Concentration of unknown RhB solution was determined by a calibration curve. Colour removal efficiency was determined by measuring the light absorbance of a sample before and after the electrochemical process.

Result & Discussions
Effect of initial dye concentration

The effect of the initial concentration of RhB on the dye decolorization by electrochemical Fenton process was investigated in the range from 50 to 125 mg/l at a constant current density of 100 A/m^2, pH 3.0, 30°C temperature and 0.2 M H_2O_2. The results are presented in Figure 1. A perusal of Figure 2 indicates that the colour removal efficiency decreased from 97.33% to 48.6% for 30 minutes with the increase in initial dye concentration from 50 to 125 mg/l. At higher concentration, the insufficient amount of hydroxyl radicals were produced to degrade the dye molecules at constant current density for the same process time[6]. The high concentration of

RhB would consume more hydroxyl radicals, so the effect would be reduced with the increase of the initial RhB concentration.Therefore, 50 mg/l could be considered to be suitable concentration value for further experiments.

Effect of initial pH

The effect of the initial pH on the decolorization of RhB is an important parameter in ECF process[7]. Effect of the initial pH of the feed solution on the colour removal efficiency was studied in the range of 3.0–11.0 for a constant initial concentration of 50 ppm at 100 A/m^2 current density, 30°C temperature and 0.2 M H_2O_2. It reveals that the colour removal efficiency decreased from 97.33% to 48.91% when initial pH increased from 3.0 to 11.0. It is reported in
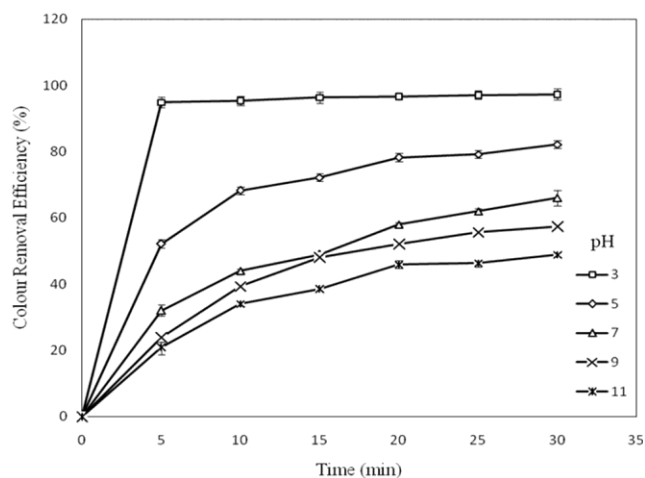

Fig. 1 — Colour removal efficiency as a function of time at different initial pH during treatment of the Synthetic Rhodamine B (RhB) wastewater by Electrochemical Fenton (ECF) process
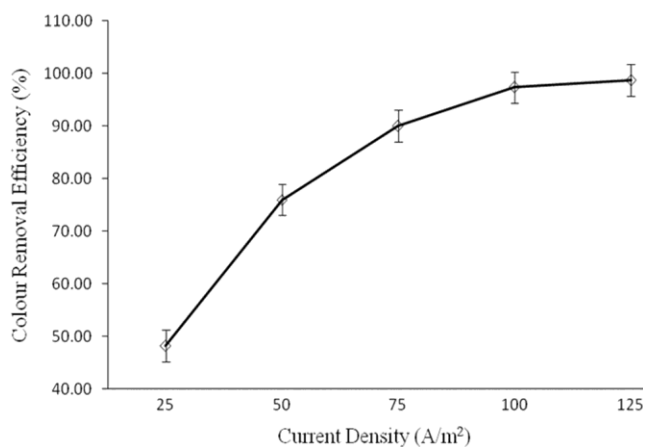

Fig. 2 — Colour removal efficiency as a function of current density during treatment of the Synthetic Rhodamine B (RhB) wastewater by Electrochemical Fenton (ECF) process

the literature that the acidic medium provides conducive condition for Fenton process[8]. In Fenton related processes, at low pH values iron species tend to form stable complexes with H_2O_2. On the other hand, at higher pH, iron species form ferric hydroxides and start to precipitate[8]. In addition high pH in the solution often leads to the creation of more free radical scavengers (i.e. CO_3^{2-}, HCO_3^-, etc.) derived from mineralization of organic material, resulting in a decrease in the concentration of HO· radical. At low pH (below 3.0), H_2O_2 remains steady in the solution due to the formation of oxonium ion[8]. At higher pH, especially above 5.0, H_2O_2 becomes unstable in basic medium. Beyond pH 7.0, H_2O_2 decomposes into H_2O and O_2[9]. From experimental results, it is validated that the maximum removal efficiency could be achieved at pH 3.0[8]. Thus, it was prudent to consider pH 3.0 to be the optimum experimental value for the ECF process. Changes in solution pH during the experiments were found to be in the range of 4.9 to 8.7. These observations are in agreement with similar experimental work reported by Nandi et al.[7].

Effect of current density

Among the variables that are usually studied in ECF process, the current density is one of the most frequently referenced terms since it affects the rate of reactions. Current density is also another significant process parameter for the ECF processes. Effect of current density on the colour removal efficiency for synthetic RhB wastewater using ECF processes was studied in the range of 25–125 A/m^2 at a constant initial pH of 3.0, temperature of 30°C and 0.2 M H_2O_2. Fig. 2 represents the colour removal efficiency as a function of current density. There is the significant improvement in colour removal efficiency within 5 minutes at 25–100 A/m^2. The colour removal efficiencies improved from 22% to 96.6% within 5 minutes and from 48.22% to 98.7% in 30 minutes. As the current density increased, more amount of Fe^{2+} ions leached to the solution leading to the production of a higher concentration of radicals in less time. The increase in current density resulted in the electro-regeneration of the ferrous ion from ferric ion which in turn enhanced the Fenton chain reaction efficiency[5]. However, it is noteworthy to mention that beyond 100 A/m^2, no significant increase could be observed in the colour removal. As current density increases, the discharge potential of Cl_2 increases. Thereafter, simultaneously Cl_2 and O_2 evolution takes place[4]. Thus, 100 A/m^2 current density could be considered as the optimum experimental condition for further experiments.

Effect of dosage of H_2O_2

From the economic point of view, optimum dosage of H_2O_2 is required to study. To determine the effect of dosage of H_2O_2 on the colour removal efficiency by ECF process, experiments were carried out with synthetic RhB wastewater for 0.01, 0.2 and 0.8 M dosage of H_2O_2 for 0 to 30 minutes by maintaining the constant current density of 100 A/m^2, pH 3.0 and temperature of 30°C. The result shows that colour removal efficiency increased from 90.11 to 94.89% when dosage of H_2O_2 increased from 0.01 to 0.2 M in 5 minutes due to increment in the degradation rate of RhB when H_2O_2 dosage increases[10] and colour removal efficiency reached to 97.33 % at 30 minutes for 0.2 M. But colour removal efficiency decreased to 96.66 % at 0.8 M dosage of H_2O_2 due to undesirable hydroxyl radical scavenging reactions[10]. Thus, the optimum dosage of H_2O_2 was selected as 0.2 M for further experiments.

Effect of temperature and thermodynamic analysis

Effect of temperature for 50 ppm synthetic RhB wastewater on colour removal were studied in the range of 30 to 60°C for 0 to 30 minutes with constant current density of 100 A/m^2, pH$_i$ 3.0, 0.2 M H_2O_2. The study of temperature effect of the colour removal efficiency indicates that increasing temperature resulted in a positive effect on the colour removal efficiency in Fenton related processes. The colour removal efficiency increased by 97.33% to 100% when the temperature increases from 30°C to 60°C. This happened because of formation of the rate of oxidizing species (such as °OH radical or high-valence iron species) which increases as a rate of reaction increases between H_2O_2 and ferrous/ferric iron when the temperature increases. 30°C was considered as an optimum experimental condition for the ECF process. The kinetic parameter for ECF process was calculated by using the well-known Arrhenius equation. The RhB removal rate depends on the RhB concentration and OH radical concentrations ($dC_t/dt = -kC_tC_{OH}$)[11]. Where, C_t represented RhB concentration and C_{OH} represented the OH radical concentration at time t. Assuming C_{OH} reached equilibrium instantaneously with excess H_2O_2, then C_{OH} could be treated as a constant. The rate expression equation was simplified into a pseudo

first order kinetic model. As a result, pseudo first order kinetics is considered to calculate the rate constant using Eq. 1 .

$$\ln (c_t/c_o) = -k_a t \qquad \qquad ... (1)$$

Where C_t is the dye concentration at time t, C_o is the initial dye concentration; k_a is pseudo first order rate constant. k_a is obtaining from plot $\ln (C_t/C_0)$ versus t (Figure. 3). The activation energy (E_a) and Arrhenius constant (A) value were calculated to be 20.76 KJ/mol and 627.66, respectively. It indicates that colour removal efficiency of RhB from synthetic wastewater by ECF process required low activation energy[11].

Electrical energy consumption and electrode consumption

The electrical energy consumption (C_{energy}, kWh/m³) were determined according to Eq. 2

$$C_{energy} = U\, i\, t_{EC}/v \qquad \qquad ... (2)$$

where U is the average cell voltage (V), i is the current (A), t_{EC} is the process time (h) and υ is the volume of the solution taken for the experiment (m³).

The rate of ferrous ions released ($C_{electrode}$, g) from the anode follows the Faraday's law (Eq. 3).

$$C_{electrode} = i\, t_{EC}\, M/zF \qquad \qquad ... (3)$$

where M is molecular weight of iron (g/mol), z is the number of electron involved in the redox reaction and F is the Faraday's constant (F = 96487 C/mol).
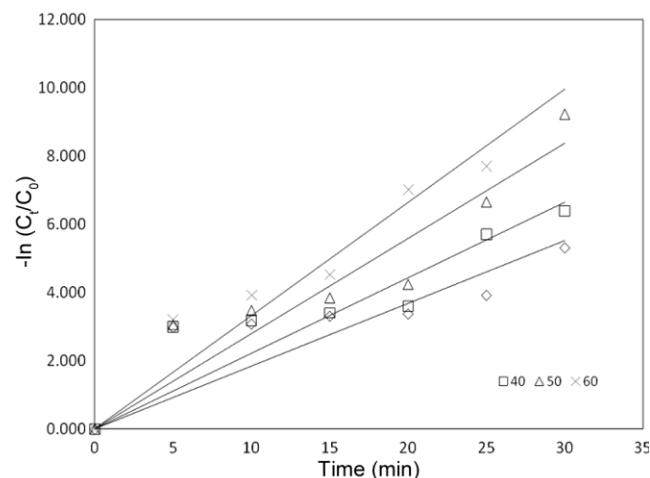

Fig. 3 — Kinetics of RhB removal from model wastewater by Electrochemical Fenton (ECF) process following Pseudo first order model at three different initial concentrations

Electrical energy consumption for ECF process was estimated to be 2.09 KWh/m³ at the optimum experimental conditions (pH$_i$ 3.0, 100 A/m², 50 ppm RhB concentration, 5 minutes, 30°C and dosage of 0.2 M H$_2$O$_2$). This result shows that the ECF process consumed less energy at optimum experimental conditions. Electrode consumption was calculated 0.5 mg at optimum experimental conditions. Moreover, the sludge generation by ECF process at optimum experimental conditions was 0.48 kg/m³. COD reduction was observed 60% by ECF processes.

Conclusion

In this study, the effects of different experimental parameters on the ECF processes were studied based on colour removal efficiency of synthetic RhB wastewater and electrical energy consumption. The optimum experimental conditions for synthetic RhB wastewater were determined as 50 ppm initial dye concentration, 100 A/m² current density, pH$_i$ 3, 0.2 M dosage of H$_2$O$_2$, 30°C and 5 minutes process time. The ECF process resulted in higher removal efficiency of 94.89 %. The sludge generated by the ECF process is 0.48 kg/m³ and the electrical energy consumption was 2.09 KWh/m³ for ECF process. It was clearly observed that ECF processes were very effective for the colour removal of synthetic RhB wastewater. Overall, the ECF process was found more capable to achieve the higher colour removal efficiencies and shows more potential for wastewater treatment.

References
1   Rosales E, Iglesias O, Pazos M, & Sanromán M A, Decolourisation of dyes under electro-Fenton process using Fe alginate gel beads, *J Hazard Mater,* **213–214** (2012) 369–377.
2   Thakur A, & Kaur H, Response surface optimization of Rhodamine B dye removal using paper industry waste as adsorbent, *Int J Ind Chem,* **8** (2017) 175–186.
3   Yuksel E, Gurbulak E, & Murat E, Degradation of Alizarin Yellow R using UV/H$_2$O$_2$ Advanced Oxidation Process. Environ Sci Technol, 33 (2014) 482–489.
4   Rathinam R, Govindaraj M, Vijayakumar K, & Pattabhi S, Decolourization of Rhodamine B from aqueous solution by electrochemical oxidation using graphite electrodes, Desalin Water Treat, **52** (2016) 16995–17001.
5   Nidheesh P V, & Gandhimathi R, Electrolytic removal of Rhodamine B from aqueous solution by peroxicoagulation process, *Environ Sci Pollut Res,* **21** (2014) 8585.
6   Nidheesh P V, & Gandhimathi R, Removal of Rhodamine B from aqueous solution using graphite–graphite electro-Fenton system, *Desalin Water Treat,* **52** (2014) 1872–1877.
7   Kumar B N, & Patel S, Effects of operational parameters on the removal of brilliant green dye from aqueous solutions by electrocoagulation, *Arab J Chem,* **10** (2017) S2961–S2968.

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

9   Sandhwar V K, & Prasad B, Comparative study of electrocoagulation and electrochemical Fenton treatment of aqueous solution of benzoic acid (BA): Optimization of process and sludge analysis, *Korean J Chem Eng,* **34** (2017) 1062–1072.

10 Ghime D, & Ghosh P, Kinetic Model for the Oxidative Degradation of Aqueous p-Nitrophenol by Fenton's Reagent, *J Sci Ind Res,* **77** (2018) 208–212.

11 Korbahti B K, & Demirbuken P, Electrochemical Oxidation of Resorcinol in Aqueous Medium Using Boron-Doped Diamond Anode: Reaction Kinetics and Process Optimization with Response Surface Methodology, *Front Chem,* **5** (2017) 75.