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Use of Electrochemical Peroxidation to Degrade Reactive Blue 19: Application of a 2^3 Full Factorial Design

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A 5000 g/m^3 CI Reactive Blue 19 dye solution was treated using electrochemical peroxidation (ECP) process. This method involves the utilization of Fenton's reaction chemistry through the addition of hydrogen peroxide into the solution and the use of an iron anode as source of Fe(II) catalyst. The degradation of the dye was evaluated using a 2^3 full factorial design augmented with four centerpoints. The factors and levels of the experimental design were as follows: initial pH (2.2, 2.5, 2.8), initial H_2O_2 dosage (332 mol/m^3, 377 mol/m^3, 422 mol/m^3), and current density (164 A/m^2, 205 A/m^2, 246 A/m^2). Results of the study showed that initial pH-current density interaction significantly influenced the percent COD removal. Moreover, after 60 minutes of treatment, the percent absorbance reduction reached up to 99.98% and the percent COD removal reached up to 82.83%.

Keyword: Electrochemical peroxidation, Reactive Blue 19, Full factorial design, Decolorization, COD Removal, Fenton's reaction

INTRODUCTION

Most dyes are designed to withstand exposure to sunlight, heat, abrasion, and microbial attack (Brillas et al. 2009, Vlyssides et al. 2000). For these reasons, their accumulation in the aquatic environment and in living organisms has become a concern (Parac-Osterman et al. 2007, Slokar et al. 1998). Aesthetic problems also arise from the presence of dyes in wastewaters since even at very low concentrations these are visible to the naked eye (Barrera-Diaz et al. 2003, Modirshahla et al. 2007). Among the different dye groups, reactive dyes are most widely used in the textile industries (Kim et al. 2004) and it has a fixation range of only 60 to 90 percent causing most of it to end up in the wastewater (Tauber et al. 2005, US EPA 1997).

One of the reactive dyes used in textile manufacturing industries is Reactive Blue 19 (RB19), an anthraquinone-based dye with a fixation efficiency of around 75-80% (Pelegrini et al. 1999). Anthraquinone-based dyes are difficult to break down due to their complicated ring structures (Fu et al. 2001, Rezaee et al. 2008).

The present methods used for the color and COD removal of dye in wastewaters have major drawbacks. Physico-chemical methods require sludge disposal and cleaning maintenance (Lorimer 2001), chemical methods and advanced oxidation processes (AOPs) are costly (Martinez-Huitle 2008), and biological treatment methods are limited by the resistance of dyes to microbial degradation (US EPA 1996, Zollinger 1991). Among the current methods used, electrochemical (EC) methods have been proven effective and superior in the decolorization and mineralization of dyes. They are also preferred when limited space is available (Kobya et al. 2003).

THEORY

The specific EC method used in the study is the electrochemical peroxidation (ECP) process. This utilizes Fenton's reaction, Eq. (1), by adding hydrogen peroxide into the solution and by using a sacrificial anode as source of iron catalyst.

$$H_2O_2 + Fe^{2+} \rightarrow \bullet OH + OH^- + Fe^3 \quad (1)$$

Compared to other similar methods, ECP is considered to be practical since it makes use of a cheap and readily available material for its electrodes.

The aim of this work is to evaluate the efficiency of ECP process in removing the color and COD in RB19 dye-contaminated wastewater using a 2^3 full factorial design.

EXPERIMENT

The 5,000 g/m^3 dye solution with an average initial COD of 3,630 g/m^3 was placed in a 500 cm^3 glass reactor. The runs were conducted at room temperature with the mixing speed maintained at 5 Hz. Initial pH of the prepared dye solution was adjusted using H_2SO_4 and NaOH solutions. After which, a sample was collected for the initial absorbance and COD data of the synthetic wastewater. Hydrogen peroxide solution was then added and constant current was introduced. Throughout the process, samples were taken at specific time intervals. NaOH was added to each sample to stop further reaction of unreacted H_2O_2 and Fe^{2+}. For the details of the setup, see Figure 1.

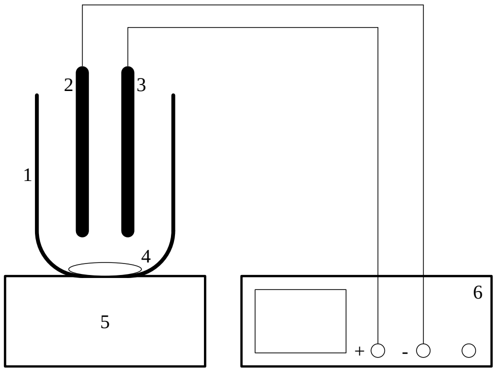

Figure 1. Batch Reactor System
(1 glass reactor, 2 cathode, 3 iron anode, 4 stir bar, 5 stirrer, 6 power supply)

Using a UVmini-1240 Shimadzu UV-Vis spectrophotometer, the absorbance measurements of the dye solutions were determined at the maximum absorbance wavelength of 590 nm (Pelegrini et al. 1999). On the other hand, COD removal measurements were determined using a LaMotte SMARTSpectro spectrophotometer (photometric accuracy: ± 0.005AU to 1.0AU) with the wavelength set at 600 nm.

As shown in Table 1, a 2^3 full factorial design augmented with four centerpoints was used to determine the efficiency of the ECP process in degrading RB19 dye. Using this type of design will be useful in determining not only the main effects of the factors but also the effect of their interactions to the removal of color and COD.

RESULTS AND DISCUSSIONS

Color removal

After 60 minutes of reaction, the dark blue solution turned colorless. The removal of color was further confirmed by the data on percent reduction in absorbance shown in Figure 2. It can be seen in the plot that all runs resulted to almost 100% color removal.

The percent reduction in absorbance was calculated using Eq. (2):

$$Y_{\substack{Absorbance\\Reduction}} = \frac{ABS_i - ABS_t}{ABS_i} \times 100 \qquad (2)$$

where $Y_{\text{Absorbance Reduction}}$ is the percent reduction in absorbance, ABS_i is the initial absorbance of the solution, and ABS_t is the absorbance of the solution at time t.

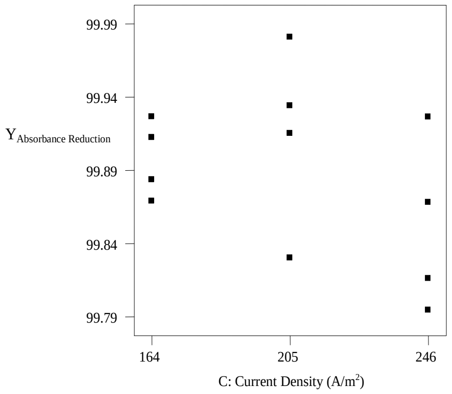

Figure 2. Reduction in absorbance

The removal of the color indicated thatRB19 was degraded. However, this does not necessarily mean that the dye was completely converted into inorganic substances. To evaluate the mineralization of RB19, the COD values at different time intervals were monitored.

COD removal

Eq. (3) was used to calculate for the percent COD removal:

$$Y_{CODRemoval} = \frac{COD_i - COD_t}{COD_i} \times 100 \qquad (3)$$

Table 1. Factors and levels used in the 2^3 full factorial design experiment

Factors	Unit	Levels (-)	Levels 0	Levels (+)
A = initial pH		2.2	2.5	2.8
B = initial H_2O_2 dosage	mol/m^3	332	377	422
C = current density	A/m^2	164	205	246

2^3 **Factorial Design + 4 Centerpoints**

Responses

$Y_{\text{Absorbance Reduction}}$ = % Absorbance Reduction

$Y_{\text{COD Removal}}$ = % COD Removal where $Y_{COD\ Removal}$ is the percent COD removal, COD_i is the initial COD of the dye solution, and COD_t is the COD of the dye solution at time t.

Using Design Expert 7.0.3, the p-values for the different system parameters were determined. The factors and interactions with p-values less than 0.0500 are considered significant. Based on the data, interaction AC (p-value = 0.0307) is significant. The 3FI (3-factor interactions) model is also found to be significant which means that the data closely fits the model and it has only 2.65% chance of being affected by noise. Meanwhile, the curvature effect (p-value = 0.2008) is insignificant which means that there is no need to proceed to a quadratic experimental design.

Since AC (initial pH – current density) interaction is significant, AC interaction plots were evaluated. The AC interaction plot at initial H_2O_2 dosage equal to 332 mol/m^3 is shown in Figure 3. Increasing the current density from 164 A/m^2 to 246 A/m^2 had a slightly stronger effect on the percent COD removal when the pH is at 2.8. Though the percent COD removals at pH = 2.2 were still better than those at pH = 2.8, a greater improvement in the removal was observed when current density was increased at the higher pH level.

In Figure 4, when the initial H_2O_2 dosage was equal to 422 mol/m^3, increasing the current density from 164 A/m^2 to 246 A/m^2 had a positive effect on the removal of COD at pH = 2.8. On the other hand, increasing the current density at pH = 2.2 had a negative effect on the percent COD removal.

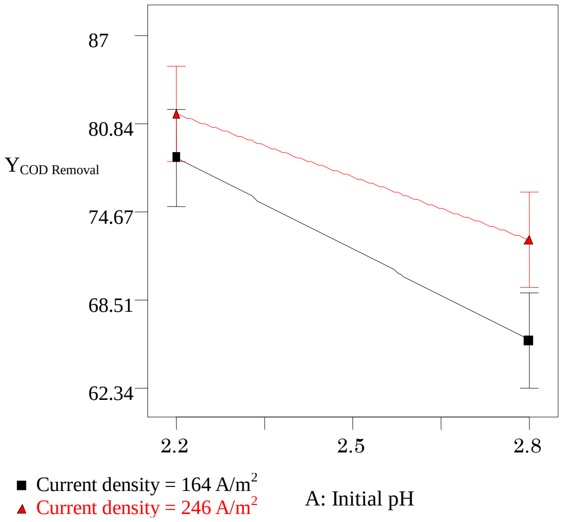

Figure 3. AC interaction plot at initial H_2O_2 dosage = 332 mol/m^3

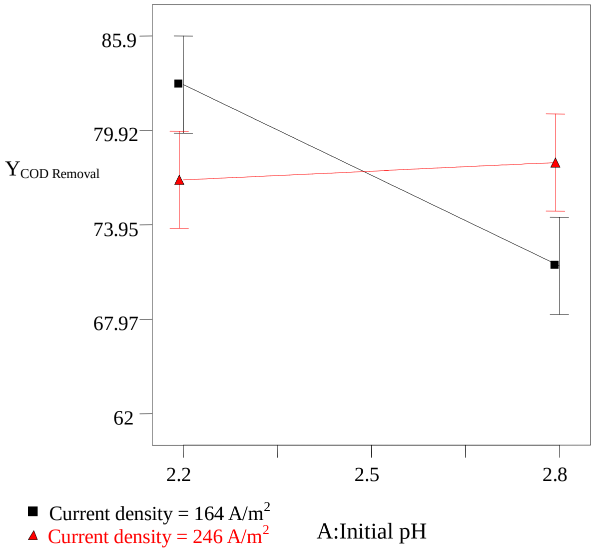

Figure 4. AC interaction plot at initial H_2O_2 dosage = 422 mol/m^3

The smaller magnitude of increase in the percent COD removal observed in Figure 3 and the decrease in the percent COD removal observed in Figure 4 when current density was increased at pH = 2.2 may be attributed to the occurrence of parasitic reactions where hydroxyl radicals are consumed by Fe(II) and H_2O_2. At pH = 2.2, more hydroxyl radicals were expected to form and when this was coupled with a higher current density value, which consequently elevated the amount of Fe(II) in the solution, the incidence of Fe(II) reacting with hydroxyl radicals also increased. This reduced the amount of hydroxyl radicals that were supposed to degrade the intermediates of the dye. Moreover, percent COD removal was further reduced when the amount of initial H_2O_2 dosage was increased due to the reaction of H_2O_2 with the hydroxyl radicals in the solution.

CONCLUSIONS

Results of the study showed that electrochemical peroxidation (ECP) process is effective in degrading a 5,000 g/m^3 RB19 synthetic dye wastewater, removing color with up to 99.98% reduction in absorbance and up to 82.83% COD removal at a treatment time of 60 minutes. It has been found that interaction AC (initial pH – current density) significantly affects the percent removal of COD. At initial pH = 2.8, removal of COD greatly increased when the current density was increased. At pH = 2.2, and current density = 246 A/m^2, increasing the initial H_2O_2 dosage from 332 mol/m^3 to 422 mol/m^3 caused a reduction in the percent COD removal due to the competing reactions that consumed the hydroxyl radicals.

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