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Petrochemical wastewater treatment by electro-Fenton process using aluminum and iron electrodes: Statistical comparison

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ABSTRACT

Petrochemical manufacturing wastewaters often contain a high concentration of biodegradable compounds that possess either toxicity or activity inhibition to the biological unit. In this paper, a comparison between aluminum and iron plate electrodes on COD and color removal from Petrochemical wastewaters by electro-Fenton process was studied. The experiments were conducted to evaluate the effects of reaction time, current density, pH, H_2O_2/Fe^{2+} molar ratio, and H_2O_2 of petrochemical wastewater (PW) (ml/l) on the performance of the process. Response surface methodology (RSM) was employed to assess individual and interactive effects of the five main independent parameters on the COD and color removal. The results show that COD and color removal efficiencies of iron electrode (67.3% and 71.58%, respectively) were more than those of aluminum electrode (53.94% and 67.35%, respectively).

1. Introduction

The production stages of a petroleum industry, such as extraction and refining, are potentially responsible for generating large volumes of effluent to be discarded in the environment [1–3]. The waste generated in oil refineries contains many different chemical compositions, depending on the complexity of the refinery, the existing processes and the type of oil used [1,4].

The physical–chemical and bioremediation methods utilized for the degradation of these compounds have shown various operational problems, such as: partial degradation of the effluent, toxic intermediates production, energy consumption and secondary phases generation that impose extra cost in the process [5–7].

The traditional Fenton process, one of the advanced oxidation processes (AOPs), is widely used as a suitable treatment method for highly concentrated wastewaters due to its effectiveness in producing hydroxyl radicals [8,9]. Applicability of traditional Fenton process is limited by its acidic pH requirements, the formation of iron sludge and high cost of hydrogen peroxide [8,10]. Electrochemical advanced oxidation processes (EAOPs) based on Fenton's reaction chemistry are eco-friendly methods that have recently received much attention for wastewaters remediation [10]. The most popular EAOP is the electro Fenton (E-Fenton) process [11] which can proceed by the following chain reactions [11–13]:

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

Hydroxyl radicals are also generated at the surface of a high-oxygen overvoltage anode from water oxidation:

$$H_2O \rightarrow H^{+} + OH^{\bullet} + e^{-} \quad (2)$$

Also the produced ferric ion from Eq. (1) can be reduced to ferrous ion by electrochemical regeneration of Fe^{2+} ions on the cathode surface:

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

Since iron and aluminum electrodes have not been compared in detail for the treatment of petrochemical wastewaters, it is the purpose of this study is to compare the treatment of petrochemical wastewaters by electro-Fenton using aluminum and iron electrodes. The response surface methodology (RSM) is an excellent tool for optimization and statistical analysis [14]. It allows considerable reduction of experiments number and a rapid interpretation [11,15]. Furthermore, it is possible to study a large number of factors and to detect the possible interactions between them [15,16]. The RSM is a useful statistical method for the optimization of chemical reactions and/or industrial processes and widely used for experimental design [17]. In this paper, Optimizations of E-Fenton was carried out by the RSM which was used to develop a mathematical technique to describe the effects of main independent variables

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Table 1
Independent variables and their levels obtained from the statistical software.

Symbol	Factor	Coded levels of variables		
		−1	0	+1
X_1	Reaction time	10	50	90
X_2	Current density	25	52.5	80
X_3	pH	2	3.5	5
X_4	$\frac{H_2O_2}{PW}$	0.3	1.22	2.14
X_5	$\frac{H_2O_2}{Fe^{2+}}$	0.5	2.75	5

(such as reaction time, current density, pH, H_2O_2/Fe^{2+} molar ratio and H_2O_2 of PW (ml/l)), to maximize COD and color removal.

2. Experimental

2.1. Materials and methods

2.1.1. Wastewater sampling and characterization

The study was conducted into an industrial wastewater obtained from Shazand Petrochemical Company (Arak, Iran). Sample is taken from the equalization basin (EQU). EQU is a place where materials are separated based on the density in API separator. 40 l of sample from the EQU is taken and saved in a plastic container. It immediately transported to Arak University Chemical Engineering Research Laboratory and stored in a refrigerator at 4 °C before further analysis. The applied petrochemical wastewater had COD 1400–1700 mg/l, color 100 color unit, BOD/COD 0.4–0.6 and pH 6–6.7.

2.1.2. Electro-Fenton experiments

The experiments were conducted at room temperature (25 ± 2 °C) and atmospheric pressure in an open cylindrical glass cell with 400 ml capacity. pH of sample was adjusted with H_2SO_4 or NaOH and measured by pH meter (METTLER-TOLEDO 320). Before measurements, the pH meter was calibrated with the standard buffers at room temperature.

In each run, 250 ml of wastewater was placed in an electrolytic cell and desired amounts of iron (Fe^{2+}) and hydrogen peroxide (H_2O_2) were added before the electrical current was turned on. Then, electrodes were placed in the reactor and solutions were mixed at 350 rpm. The current density (CD) was adjusted by a digital DC power supply (fabricated by Kala Gostaran-e-Farda supplier, 30 V and 3 A) operated at galvanostatic mode and the experiment was started. Both electrodes (anode and cathode) were in square shape and made from plates with dimensions of 2 cm × 0.5 cm. The effective electrode area was 1 cm^2 and the spacing between electrodes was 3 cm.

At the end of the run, the samples were allowed to stand for 30 min (for solids sedimentation) and the supernatant was then taken for wastewater quality measurements. The electrodes were washed thoroughly with water to remove any solid residues on the surfaces. Color and COD were respectively measured at 475 nm and 605 nm wavelength using a UV–Vis spectrophotometer (HACH, US).

2.1.3. Experimental design

In this study, the optimization of experimental conditions for petrochemical wastewater mineralization and decolorization by electro-Fenton process was conducted using the central composite design (CCD) technique under RSM. The software Design Expert 8.0.7.1 Trial was used for the experimental design, data analysis, quadratic model extraction, and graph plotting.

The independent variables of reaction time (X1), current density (X2), pH (X3), H_2O_2 ml/l of PW (X4) and H_2O_2/Fe^{2+} molar ratio (X5). They were coded with low and high levels in the CCD as shown in Table 1. COD and color removal efficiencies (Y1 and Y2, respectively) were considered as the dependent factors (response). The response was expressed as removal (%) which could be calculated by using the following equation.

$$\text{Removal}\,(\%) = \frac{C_i - C_0}{C_i} \times 100 \quad (4)$$

where C_i and C_0 are initial and final COD or color concentrations.

Table 2 shows the matrix design obtained with the Design Expert software for both experimental systems (iron and the aluminum electrodes). Accordingly, 47 experiments were conducted with 32 factorial points, 10 axial points and 1 central point.

3. Results and discussion

3.1. Regression models and statistical testing

In this paper, correlations between the responses and the independent variables were obtained by the following second-order model with a least-squares method [18]:

$$Y = \beta_0 + \sum_{j=1}^{k}\beta_j x_j + \sum_{i<j}\beta_{ij}x_i x_j + \sum_{j=1}^{k}\beta_{jj}x_j^2 + \epsilon \quad (5)$$

where Y is the response, β_0 is a constant coefficient, β_j, β_{ij} and β_{jj} are the coefficients for the linear, quadratic and interaction effects, respectively. x_i and x_j are the coded levels for the independent variables. k is the number of independent variables and ε is the random error.

Reduced models for describing the COD and color removal using aluminum (Eqs. (6) and (7)) and iron (Eqs. (8) and (9)) electrodes after excluding the insignificant coefficients can be presented:

EF-Al process:

$$\begin{aligned}\text{COD removal}\ (\%) = {} & 46.62 + 6.61\text{A} + 4.27\text{B} - 2.78\text{C} + 3.98\text{D} \\ & + 3.01\text{E} - 1.14\text{AC} + 1.48\text{AE} + 1.18\text{BC} \\ & + 1.11\text{BD} + 2.32\text{BE} + 1.32\text{DE} - 2.78A^2 \\ & - 5.65B^2 - 3.64C^2 - 4.17D^2 - 4.33E^2 \end{aligned} \quad (6)$$

$$\begin{aligned}\text{Color removal}\ (\%) = {} & 51.56 + 7.08\text{A} + 4.93\text{B} - 3.23\text{C} + 4.06\text{D} \\ & + 3.73\text{E} - 1.35\text{AC} + 1.06\text{AD} + 2.14\text{AE} \\ & + 1.22\text{BC} + 0.74\text{BD} + 2.66\text{BE} - 0.69\text{CD} \\ & + 1.68\text{DE} - 7.06A^2 - 8.46B^2 - 6.11C^2 \end{aligned} \quad (7)$$

EF-Fe process:

$$\begin{aligned}\text{COD removal}\,(\%) = {} & 63.28 + 7.1\text{A} + 4.35\text{B} - 3.5\text{C} + 3.56\text{D} \\ & + 2.34\text{E} + 0.63\text{AB} + 1.32\text{AD} + 2.65\text{AE} \\ & + 0.88\text{BE} - 0.62\text{CD} - 0.79\text{CE} + 0.82\text{DE} \\ & - 4.56A^2 - 8.72B^2 - 6.81C^2 - 7.19D^2 \\ & - 7.47E^2 \end{aligned} \quad (8)$$

$$\begin{aligned}\text{Color removal}\ (\%) = {} & 64.51 + 8.29\text{A} + 4.32\text{B} - 5.13\text{C} + 3.74\text{D} \\ & + 5.39\text{E} + 1.99\text{AD} + 2.49\text{AE} - 0.07\text{BC} \\ & + 1.78\text{BD} + 0.61\text{BE} - 1.1\text{CE} + 0.69\text{DE} \\ & - 4.39A^2 - 6.59B^2 - 7.12C^2 - 7.2D^2 \\ & - 6.27E^2 \end{aligned} \quad (9)$$