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Research article

Mineralization of pyrrole, a recalcitrant heterocyclic compound, by electrochemical method: Multi-response optimization and degradation mechanism

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ABSTRACT

In this study, the electrochemical (EC) oxidation of a recalcitrant heterocyclic compound namely pyrrole has been reported using platinum coated titanium (Pt/Ti) electrodes. Response surface methodology (RSM) comprising of full factorial central composite design (CCD) with four factors and five levels has been used to examine the effects of different operating parameters such as current density (j), aqueous solution pH, conductivity (k) and treatment time (t) in an EC batch reactor. Pyrrole mineralization in aqueous solution was examined with multiple responses such as chemical oxygen demand (COD) (response, Y_1) and specific energy consumption (SEC) in kWh/kg of COD removed (response, Y_2). During multiple response optimization, the desirability function approach was employed to concurrently maximize Y_1 and minimize Y_2. At the optimum condition, 82.9% COD removal and 7.7 kWh/kg of COD removed were observed. Degradation mechanism of pyrrole in wastewater was elucidated at the optimum condition of treatment by using UV-visible spectroscopy, Fourier transformed infra-red spectroscopy (FTIR), cyclic voltammetry (CV), ion chromatography (IC), higher performance liquid chromatography (HPLC) and gas chromatography-mass spectroscopy (GC-MS). The degradation pathway of pyrrole was proposed on the basis of the various analysis.

1. Introduction

The discharge of organic pollutants and hazardous chemicals from the various manufacturing industries is a cause of global environment concern. Heterocyclic aromatic compounds are difficult to mineralize in wastewater because of rigid chemical structure and high solubility in water (Subbaramaiah et al., 2013a; Singh et al., 2015; Li et al., 2016a). Pyrrole is a typical heterogeneous compound which is most frequently used as an intermediate and solvent in the synthesis of various pharmaceutics, insecticides, pesticides, cosmetics, agrochemicals and disinfectants (Zaid et al., 1994; Brett, 2011; Subbaramaiah et al., 2013b; Hiwarkar et al., 2014; Xiao et al., 2015; Garg et al., 2015). These industries utilize and manufacture pyrrole and discharge the highly concentrated effluent into the environment and aquatic bodies, and create a severe health hazard since pyrrole is toxic, carcinogenic and teratogenic (Mudliar et al., 2008; Martin et al., 2009; Padoley et al., 2011; Hiwarkar et al., 2015).

A large number of treatment methods such as chemical coagulation, adsorption, biological methods, ozonation, supercritical oxidation, ion-exchange, Fenton oxidation and photo-catalytic oxidation could be employed for the treatment of heterogeneous aromatic compounds such as pyrrole in wastewater (Chaudhary et al., 2006; Sun et al., 2008; Mondal et al., 2013; Li et al., 2016a,b,c; Singh et al., 2016a,b,c; Zhu et al., 2016). Most of these treatment methods have limitations in terms of low mineralization efficiency and high operation cost (Mudliar et al., 2008; Martin et al., 2009; Padoley et al., 2011; Hiwarkar et al., 2015; Chaudhary et al., 2006; Sun et al., 2008; Li et al., 2011; Singh et al., 2016b; Zhu et al., 2016). Due to these considerations, it is essential that the developed treatment technologies are able to oxidize the heterocyclic compounds from wastewater. Electrochemical oxidation (EO_x) process has no such limitation in which a clean oxidizing agent, electron is used as an oxidant. EO_x is being focused as a

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developing treatment technology with high oxidation ability, environmental friendly nature and mild reaction conditions (Hamza et al., 2009; Singh et al., 2013, 2014; Kumar et al., 2015; Sahu and Chaudhari, 2015; Sarkka et al., 2015; Singh et al., 2016a,b,c). EO_x has been used as a favorable treatment technology to treat highly polluted wastewater and has attained a significant consideration in wastewater treatment (Xing et al., 2012; Souza et al., 2014).

A review of the literature shows that EO_x method has not been tested in the open literature for the mineralization of pyrrole in aqueous solution. Considering the same, in the present study, it was aimed to study the suitability of EO_x of pyrrole degradation using Pt/Ti anode. Response surface methodology (RSM) with full factorial central composite design (CCD) was employed to design the experimental runs for evaluating the effect and interaction of different operating parameters including current density (j), solution pH, conductivity (k) and treatment time (t). Multi-response optimization with maximization of chemical oxygen demand (COD) removal (response Y1), and minimization of the specific energy consumed (kWh/kg of COD removed) (response Y2) using desirability function has been carried out. Various analysis techniques such as UV-visible spectroscopy, Fourier transformed infrared spectroscopy (FTIR), cyclic voltammetry (CV), ion chromatography (IC), high performance liquid chromatography (HPLC) and gas chromatography-mass spectroscopy (GC-MS) were used for proposing pyrrole degradation pathway during EO_x.

2. Materials and methods

2.1. Chemicals and materials

All analytical grade chemicals were used in this study. Pyrrole (S.D. Fine Chemicals, India), Pt/Ti anodes (Titanium Tantalum Ltd. Company, Chennai, India), sulphuric acid (H_2SO_4), sodium hydroxide (NaOH), and sodium hydroxide (NaCl) (Ranken Pvt. Limited, India) were bought from many companies.

2.2. Electrochemical experiments

Electrochemical (EC) experiments were performed in a 1.0 L volume of lab scale glass batch reactor. Pt/Ti electrode plates having equal 9 × 10 cm dimensions and 1.5 mm thickness with 90 cm^2 effective electrode surface area were used as an anode and cathode pair, and both were fixed 1.0 cm electrode gap during each experimental run. The electrodes bottom were kept 5.0 cm above the EC reactor bottom for easy homogenous mixing of the solution by magnetic starrier at 450 rpm. Each experimental run was performed under the controlled electrolysis condition of constant current modes of D.C. power supply. Voltage was varied in the range of 1–15 V during all experimental runs. All EC experiments were performed under the controlled conditions of temperature of 30 ± 5 °C during the study of pyrrole degradation optimization.

2.3. Experimental design and statistical analysis

In the present study, a statistical technique, RSM was used for optimizing responses (dependent output variables) and analyze the effects of independent variables (Singh et al., 2013). To attain the maximum COD removal along with minimum energy consumption at the optimum condition, RSM requires lesser number of experiments as compared to the classical approach. RSM with five level full factorial CCD was used for studying the effect of four factors X_i (X_1 (pH_o: 2.8–8.8); X_2 (j (Am^{-2}): 83.33–416.7); X_3 (K ($mScm^{-1}$): 2.91–6.7 and X_4 (t (min): 30–150). The statistical calculation of the five levels designated as −2, −1, 0, +1, and +2 for the four operating variables X_i (X_1 (pH_o); X_2 (j); X_3 (K); and X_4 (t)) which were coded as x_i using following relationship:

$$x_i = \frac{X_i - X_o}{\delta X} \quad (1)$$

where, X_i is the value of X_o at the center point and δX shows the step change. Table S1 (supporting information) shows the levels for the four variables whereas Table 1 represents the 30 different experimental runs. Design–expert trial-version software 6.0.8 was used for determining the regression analysis of the experimental results. Second-order polynomial equation as given below was further used to represent the experimental data:

$$Y = c_o + \sum_{i=1}^{4} c_i x_i + \sum_{i=1}^{4} c_{ii} x_i + \sum_{i=j}^{3} \sum_{i=j+1}^{4} c_{ij} X_{ij} \quad (2)$$

where, c_o, c_i, c_{ii}, c_{ij} and X_i are constant coefficients and independent variables, respectively, while Y is the response. The value of coefficient of correlation (R^2) was used for determining the quality of model. The values of regression and mean square of residual error was used for the analysis of variance (ANOVA) to estimate the statistical significance of the model. In multi-response optimization, the desirability function approach can be used for optimization of multiple responses simultaneously (Derringer and Suich, 1980; Singh et al., 2016a). One-sided desirability, d_i, is expressed by the following expression:

$$d_i = \begin{cases} 0 & \text{if } Y_i \le Y_{i-\min} \\ \left[\frac{Y_i - Y_{i-\min}}{Y_{i-\max} - Y_{i-\min}}\right]^r & \text{if } Y_{i-\min} < Y_i < Y_{i-\max} \\ 1 & \text{if } Y_i \ge Y_{i-\max} \end{cases} \quad (3)$$

where, $Y_{i\text{-min}}$ and $Y_{i\text{-max}}$ are the minimum and maximum values of response i, respectively. Y_i is the response value, and is represented by the positive constant value (Mondal et al., 2013). Desirability function have three case for r, if r = 1, d_i linearly increases; for r > 1 and r < 1, d_i is concave and convex, respectively. The geometric mean of all the individual desirability functions is used for determining the overall desirability D given by following equation:

$$D = (d_1 d_2 d_3 \ldots . d_k)^{(1/k)} \quad (4)$$

where, k represents the numbers of responses.

2.4. Analysis of wastewater

In each experimental run, 0.9 L of pyrrole containing aqueous solution was taken in a reactor. Sodium hydroxide (0.1 N) or HCl (0.1 N) aliquots were used for adjusting the solution pH from the initial to desired value. Sodium chloride was used for adjusting the initial conductivity of the solution. At the end of each EC experiment, samples after centrifugation were used for the analysis of final pH and residual COD. COD of the solution was measured by using the double beam UV–visible spectrophotometer (HACH, DR 5000, USA) and a digestion unit (DRB 200, HACH, USA).

The efficiency of COD removal was determining using following expression:

$$\text{COD}\ (\%) = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (5)$$

where, COD_i and COD_f is the initial and final COD. After each experiment, the electrode plate was cleaned manually with 15%