



Electro-oxidation of nitrophenol by ruthenium oxide coated titanium electrode: Parametric, kinetic and mechanistic study

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HIGHLIGHTS

- Electrochemical oxidative degradation of *p*-nitrophenol by Ti/RuO₂ electrode.
- Study of effect of parameters such as initial pH, current density, NaCl concentration and initial concentration.
- Identification of intermediates and mineralization products by GC/MS.
- Proposal of degradation mechanism.
- Kinetic modeling by heterogeneous kinetics.

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ABSTRACT

Present study investigates mechanism of electrochemical (EC) oxidative degradation of *p*-nitrophenol (PNP) by ruthenium oxide coated titanium (Ti/RuO₂) electrode. First, the process proficiency was determined in terms of chemical oxygen demand (COD), total organic carbon (TOC), current efficiency (CE) and specific energy consumption (SEC) under different experiment conditions of initial pH (pH₀), current density (*j*), electrolyte concentration (*m*) and initial PNP concentration (C₀). Maximum COD and TOC removal efficiencies of 98.9% and 81.9%, respectively, were obtained at *j* = 168.9 A/m², pH₀ = 5.5, C₀ = 100 mg/L and *m* = 300 mg/L with SEC of 535.7 kW h/kg COD. PNP degradation mechanism has also been proposed on the basis of identification of intermediates by gas chromatograph coupled with mass spectrometry (GC/MS). Various intermediates such as quinone, benzoquinone, organic acids and small mineralization products were obtained during the EC treatment of PNP. PNP was found to be oxidized by both direct (hydroxyl radical generated via water electrolysis on anode surface) and indirect (via mediators, hypochlorous acid and active chlorine generated during chlorine oxidation in solution) EC oxidation. Kinetics of EC oxidation was represented by pseudo-first order kinetic model.

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1. Introduction

Phenol is used as a model pollutant which is representative of many industrial wastes such as pharmaceutical, petrochemical industries, oil refineries, pesticide and textile industries, chemical and plastic plants, coal tar distillation plants and industries involved in the production of polymeric resins [1]. Nitro aromatic compounds are used in industries and agriculture as explosives, pesticides, pharmaceuticals, polymers, synthesis of dyes and other high volume chemicals [2–4]. *p*-Nitrophenol (PNP) is one such toxic phenolic compound which is present in many industrial

wastewaters. It exhibits high toxicity and/or mutagenic activities in several living organisms [5].

Many physico-chemical methods can be used for treatment of wastewaters [6]. Electrochemical (EC) treatment is a highly efficient treatment process which is being utilized for treatment of various types of wastewaters [7–11]. In EC oxidation process, oxidation of organics contained in wastewater occurs directly at electrode [12] and even smaller colloidal particles get oxidized and low or no amount of sludge is produced. Thus, wastewater can be treated efficiently at neutral conditions using various electrodes [13,14]. Coated electrodes have high efficiency towards organic compound oxidation. Several studies related on degradation of various phenolic compounds including PNP have been reported in the literature [15–17].

Comparative assessment of the literature on use of ruthenium oxide coated titanium (Ti/RuO₂) electrode for electrochemical

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oxidation of various types of compounds is given in Table S1 (Supporting Information). It may be seen in the table that most of the previous studies are on oxidation of dyes. Few studies are on electrochemical oxidation of other types of compounds such as phenol, 2,6-dichloro phenol (DCP), *p*-hydroxybenzaldehyde (PHB), etc. Degradation of PNP has not been reported earlier.

Several types of dimensionally stable anode (DSA) such as instant boron doped diamond, titanium coated with metal oxides (e.g. RuO₂, PbO₂, TiO₂ and SnO₂), etc. have been researched in the literature for the treatment of wastewaters [18,19]. Transition metals such as ruthenium, tantalum, iridium, tin, antimony, etc. can be used for fabrication of DSA type of electrodes [20,21]. Compared to other metal oxides, RuO₂ is highly stable and has high mechanical and chemical resistance even under strong acid conditions. Moreover, it can produce powerful oxidants such as chlorine, ozone, and free radicals, which are responsible for the oxidation of organic pollutants [5,22]. In fact, the Ti/RuO₂ has very high electrocatalytic activity for chlorine evolution and is widely used in the chlor-alkali process. This is due to the fact that the surface redox reactions taking place because of the transition metal ion act as active sites for the absorption of chlorine atoms [23]. It is well understood that the chlorine not only helps in the complete mineralization of toxic-organic compounds [24–27] and but also helps in treatment of actual industrial wastewaters by other electrodes [28–31]. Considering the fact that only a few papers are reported in the literature on the electro-oxidation of phenols by using ruthenium-based DSAs, and that Ti/RuO₂ is highly active in chlorine evolution along with other powerful oxidants such as ozone, and free radicals, it was decided to study oxidative degradation of *p*-nitrophenol (PNP) by ruthenium oxide coated titanium (Ti/RuO₂) electrode. In addition, in the present work, the mechanism of PNP degradation during the electrochemical oxidation using Ti/RuO₂ has been reported, which was not reported in the literature previously.

The purpose of this study was to investigate PNP degradation by the EC oxidation using Ti/RuO₂ electrode. Effect of various operating conditions such as PNP concentration (*C*₀), applied current density (*j*), initial pH (pH₀), and addition of electrolyte concentration (*m*) have been studied in terms of chemical oxygen demand (COD), total organic carbon (TOC), current efficiency (CE) and specific energy consumption (SEC). Intermediates and mineralized products have been found using gas chromatograph coupled with mass spectrometry (GC/MS) and mechanism of PNP degradation has been proposed.

2. Materials and methods

2.1. Materials

All chemicals used were of analytical grade. PNP provided by Hi Media Laboratories Pvt. Ltd., Mumbai, India, was used for preparation of synthetic wastewater. All solutions were prepared with distilled water at room temperature. Ti/RuO₂ electrodes were purchased from Titanium Tantalum Ltd. Company, Chennai, India.

2.2. Electrochemical treatment

EC oxidative degradation of PNP was done in a circular cross-section lab-scale glass batch reactor having 1 L volume. Experiments were performed under current controlled electrolysis conditions and monitored by a D.C. power supply under potentiostat/galvanostat modes using a regulated D.C. power supply. Ti/RuO₂ electrodes having equal 1.5 mm thickness and 9 × 10 cm dimension with effective electrode surface area of 90 cm² were used as anode and cathode with 1 cm electrode gap. Electrode bottom

was kept 5 cm above the bottom of the EC reactor so as to provide easy stirring of the solution at 400 rpm with a magnetic stirrer. Voltage during the experiment was varied in the range of 1–15 V. All the experiment during the study was done under the control condition of temperature at 30 ± 2 °C. Actual experimental setup is shown in Fig. S1 (Supporting Information).

In each EC experiment, 0.9 L of PNP solution was fed into the EC reactor and the initial pH of the solution was adjusted to the desired level by adding the 0.1 N sodium hydroxide or HCl solution. Sodium chloride was used for adjusting the initial conductivity of the solution. To optimize the EC oxidation experimental conditions, the experiments were performed over a range of experimental parameter such as *j* = 56.3–225.2 A/m², pH = 3.5–7.5, *C*₀ = 50–300 mg/L, and *m* = 150–400 mg/L. At the end of the experiment, sample was centrifuged, filtered and analyzed for residual COD and TOC.

Current efficiency (CE) which is defined as the ratio of the charge used for oxidation of compound to the total charge passed during electrolysis was calculated using the following relationship:

$$CE = \frac{(COD_i - COD_f) F V_R}{8 I \Delta t} 100 \quad (1)$$

where, COD_i and COD_f are the initial and final COD (g/L), *F* is the Faraday's constant (96,485 C/mol), *I* is the current intensity (A), *V*_R is the reactor volume (L), and 8 is the oxygen equivalent mass (32 g O₂ per mol/4 e⁻).

SEC defined as the energy consumed in kW h for removal of per kg of COD removed was calculated using the following equation:

$$SEC = \frac{U I \Delta t}{(COD_i - COD_f) V_R} \quad (2)$$

where, *I* is the current intensity (A), *U* is voltage (V), Δt is the electrolysis time, COD_i and COD_f are the initial and final chemical oxygen demand (g/L). Considering electro-oxidation as the surface process, the degradation kinetics can be represented in term of heterogeneous rate constant (*k*_h) by the following equation:

$$r = - \left(\frac{V}{A_e} \right) \frac{d[COD]}{dt} = k_h [COD] \quad (3)$$

Also inside the batch electro-oxidation reactor, the COD removal rate is proportional to the concentration of the organic pollutant and the amount of oxidants formed [29]. Therefore, kinetics for COD removal can be represented by the pseudo first-order kinetic model as:

$$- \frac{d[COD]}{dt} = k [COD] \quad (4)$$

where, *k* the pseudo first-order reaction rate constant (min⁻¹) and is related to *k*_h by the following equation:

$$k_h = k \left(\frac{V}{A_e} \right) \quad (5)$$

Values of *k* and *k*_h can be determined from ln(COD/COD₀) versus time plots.

2.3. Instruments and analytic measurement

COD was determined using COD analyzer (HACH/ DR 5000). The digestion of the sample was done in COD reactor AL 38 SC, Analytic, (Serial No. 0908/2210) of 400 W. The digestion period was 2 h at 150 °C. TOC contents were calculated using TOC-VCPH, TOC Analyser, Shimadzu and ASI-V Shimadzu (Serial No. 521048). For GC–MS analysis, all samples were put in refrigerator or immediately analyzed to avoid further reaction. 5 mL sample containing PNP and intermediates was extracted two times with 10 mL of dichloromethane (DCM) then dehydrated with sodium sulfate

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