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Batch and continuous flow anodic oxidation of 2,4-dinitrophenol: Modeling, degradation pathway and toxicity

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ABSTRACT

Being a priority pollutant, complete degradation of 2,4-dinitrophenol (2,4-DNP) is recommended. This study attempts the electrochemical oxidation of 2,4-DNP using a novel PbO_2 electrode. Multiparameter optimization is studied to elucidate the interactive role of parameters on the degradation. The critical operational parameters and its range of operation were identified using uniparameter studies in a batch reactor as NaCl concentration (0.5–1.5 g L^{-1}), current density (0.96–1.91 mA cm^{-2}) and pH (4–8). The operational range was further optimized using response surface methodology as NaCl concentration of 0.08–1.4 g L^{-1} at pH of 4.5 to 8 and a current density of 1.2 to 1.79 mA cm^{-2}. Maximum COD removal efficiency was predicted as 94.2% at a pH of 6.59, NaCl concentration of 1.12 g L^{-1} and current density of 1.44 mA cm^{-2}, which upon experimentation was obtained as 93.9%. Complete degradation of the contaminant was obtained within 150 min in a continuous flow reactor at a flow rate of 500 mL h^{-1} with NaCl concentration of 0.5 g L^{-1} and current density of 1.44 mA cm^{-2}. Intermediates of the reaction were identified as benzoquinone, hydroquinone, catechol, 4-nitrocatechol and 2-nitrobenzoquinone using high performance liquid chromatography (HPLC) and mass spectroscopy (MS) analysis. Ion chromatography analysis showed nitrate removal to be one of the foremost steps in the degradation. Cytotoxicity of the intermediates was found to be lesser than that of 2,4-DNP. The results show feasibility for field application of the tested method for the degradation of 2,4-DNP.

1. Introduction

Nitrophenols are identified as priority pollution agents by the United States Environmental Protection Agency (USEPA) and their concentration in natural water is restricted to <10 ng L^{-1} [1,2]. They belong to the group of persistent organic pollutants (POPs), which are to be eliminated completely, according to the Stockholm convention of 2004 [3]. Owing to the persistent nature and bioaccumulation properties, they are included in the severely restricted group of hazardous chemicals. Among the nitrophenols, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol and 2-s-butyl-4,6-dinitrophenol are categorized as toxic organics by the USEPA [4]. The nitro group aids in the chemical stability of the compound and in-turn resists its biodegradation due to which nitrophenols accumulate in the fatty tissues and inflict toxicity [5,6]. Still, 2,4-DNP is extensively used in the production of pesticides, dyes, explosives, preservatives and plastics [7,8]. Considering its health effects, complete degradation of 2,4-DNP is a need of humanity, but the conventional treatment technologies are a failure in this regard [7]. Electrochemical oxidation is a promising technology, especially for the treatment of low concentration wastewater [9–11].

Even though a large number of studies had been conducted on phenols and nitrophenols [1,6,12–16], only limited researches were focused on 2,4-DNP degradation [6,9,13,11]. Cañizares et al. have studied the degradation of 2,4-DNP on boron doped diamond anode [9,13]. Liu et al. have studied the mechanism of electrochemical oxidation of 2,4-DNP on Bi doped PbO_2 electrode [11], while Quiroz et al. have studied the role of various electrode materials on the degradation [6]. The focus of all these studies has been on the identification of intermediate products and pathway of degradation. However, these studies have not discussed on the individual and interactive effect of the parameters affecting the degradation. Hence, in the present study the effect of the operating variables on the degradation was studied in batch and continuous flow reactors to understand its potential for application in field.

The traditional one variable at a time approach is time consuming and is unable to depict the interactive effect of the variables on the outcomes. Multiparameter optimization using response surface methodology has been used as a tool for studying the interactive role of the variables and optimizing the operating conditions with fewer numbers of experiments [17]. It is extensively used in analytical chemistry for optimizing the process parameters [18]. RSM has been successfully used in the optimization of contaminant degradation using advanced oxidation processes [19–22]. The application of RSM for studying the interactive effects of variables and optimizing the operating conditions of electrochemical degradation of 2,4-DNP has not been performed.

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Box–Benhkan design, which is a rotatable spherical design, is useful for this purpose. It is the best design for optimization within the design space with maximum efficiency (minimum number of experiments for 3 variables) and excellent predictability [23].

Continuous flow operation is better suited for field scale applications owing to its stability in effluent quality and larger throughput [24]. The performance in terms of pollutant degradation per unit reactor volume of plug flow reactor (PFR) is better than that of continuous stirred tank reactor (CSTR) as back mixing is avoided in a PFR [24,25]. The performance of a baffled reactor having PFR flow is reported to be more efficient than that without baffles [26]. Therefore a baffle reactor acting as a non-ideal PFR was used for the degradation of 2,4-DNP in continuous flow mode.

Toxicity profile of 2,4-DNP has been reported in details [27–29]. It induces general and reproductive/developmental toxicity in rats, but teratogenicity has not been reported [29]. It interrupts the uptake of inorganic phosphate into the mitochondria, thereby inhibiting tricarboxylic acid (TCA) cycle by preventing phosphorylation of adenosine diphosphate (ADP) to adenosine triphosphate (ATP). It is also shown to result in fatal hyperthermia [27,28]. However, the details of toxicity of 2,4-DNP and its degradation intermediates, at various stages of the degradation, have not been reported.

In the present study, the efficacy of the degradation of 2,4-DNP on a novel electrode i.e. PbO_2 coated on mild steel (MS-PbO_2) was examined. The operating ranges of the parameters were studied by uniparameter optimization and the effects of variables were studied using response surface methodology in a batch reactor. The parameters for continuous flow operation were also optimized. The optimum working conditions for the degradation of 2,4-DNP were studied using Box–Benhkan experimental design. A possible pathway of electrochemical degradation of 2,4-DNP was proposed and toxicity profile of the contaminant at different stages of degradation was studied.

2. Materials and methods

2.1. Chemicals

Lead monoxide (Ranbaxy Pvt. Ltd., India), sodium dodecyl sulphate and NaOH (Merck specialties Pvt. Ltd. India) were used in electrodeposition of lead dioxide on mild steel [30]. Sodium chloride (Merck India) was used as the supporting electrolyte. Sulphuric acid (1:3 dilution) and NaOH (1 N) (Merck India) were used to adjust the pH of the 2,4-DNP (Loba Chemie) solution prepared using double distilled water. Potassium dichromate, sulphuric acid, mercuric sulphate and silver sulphate (Merck India) were used for COD determination. All these chemicals were of analytical reagent grade and highest purity available. Thiazolyl Blue Tetrazolium Bromide (TC191 — 500 mg) was obtained from HiMedia. Dulbecco's Modified Eagle Medium (DMEM) with 10% fetal bovine serum (FBS) and antibiotic antimycotic solution 100× liquid (with 10,000 U penicillin, 10 mg streptomycin and 25 μg amphotericin B per mL in 0.9% normal saline; product code: A002A) was used as the growth medium in the toxicity analysis and was obtained from HiMedia.

2.2. Instrumental

A high precision electrical balance (0.0001 g), of Mettler Toledo (model AG 135), India was used for weighing. Magnetic stirrer was obtained from Remi, India and pH meter was manufactured by Toshniwal Inst. Mfg. Pvt. Ltd., India. DC power supply with a voltage range of 0 to 15 V and with a current range of 0 to 5 A was used as the power source. Spectroquant TR 320 of Merck was used for COD analysis using closed reflux colorimetric method (Method 5220 D) and the absorbance was measured at 420 nm using genesis 20 spectrophotometer of Thermo Spectronic USA (model no: 4001/14) [31]. Peristaltic pump (PP 20 EX) of Miclins, India was used for maintaining constant flow in the continuous flow reactor.

Intermediate products (15 min, 30 min, 45 min and 60 min oxidized samples) were identified by HPLC analysis using Agilent 1200 series HPLC system with Zorbax C18 reverse phase column (4.6 × 250 mm) and methanol:water (50:50 v/v) with 54 μL trifluoro acetic acid as eluent at a flow rate of 0.5 mL min^{-1}. The detection wavelength was set at 254 nm. Mass spectra of the HPLC purified samples were obtained using Xevo G2 QTof mass spectrometer in ESI^+ mode. Ion chromatography (IC) analysis was fulfilled using 761 compact ion-chromatogram (Metrohm, Canada) with a Metrosep A Supp 5 analytical column (4 mm × 250 mm) at a flow rate of 0.70 mL min^{-1} using an eluent of 3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$.

2.3. Reactor

The batch experiments were conducted in an undivided cylindrical reactor of 600 mL volume, mounted on a magnetic stirrer. Electrodes of size 3 cm × 10 cm with an immersed area of around 41.8 cm^2 and an interelectrode gap of about 1.5 cm were connected to a DC power supply. Lead dioxide electrodeposited on mild steel was used as the anode and graphite plate was used as the cathode [19]. Leaching of lead was not observed for the electrode [30]. Experiments were carried out with 400 mL of 50 mg L^{-1} 2,4-DNP solution with a NaCl dose of 1.5 g L^{-1} and current density of 1.44 mA cm^{-2} at ambient temperature (30 ± 2 °C) and natural pH of the contaminant (5.2 ± 0.3), unless otherwise specified. All the solutions were prepared in double distilled water.

Continuous flow experiments were carried out under galvanostatic conditions in a horizontal flow baffle reactor with 5 anodes and cathodes acting as the baffles. A schematic diagram of the reactor is presented in Fig. 1. The total volume of the reactor was 1.5 L. Electrodes of size 10 cm × 8 cm × 0.8 cm were used for the degradation and the immersed area of one electrode was 104 cm^2. The depth of flow in the reactor was maintained at 5 cm. Samples were collected in 30 min interval and COD analysis was carried out in duplicate and the results are reported as average of the two. Proper QA/QC was followed and the sample replicates produced consistent results. The blank samples were below detectable limit for the analytes.

2.4. Analytical

The performance of an electrochemical reactor is determined by its current efficiency and energy consumption. Current efficiency gives the utilization rate of the charge applied for oxidation and is calculated as given in Eq. (1). The energy consumption of the reactor is the measure of the power required for the degradation of 1 kg COD, which is calculated using Eq. (2) [24].

$$\text{Current Efficiency} = \left(\frac{COD_0 - COD_t}{8I\Delta t}\right) FV \times 100 \quad (1)$$

where, COD_0 and COD_t are the initial and final COD (g O_2 L^{-1}) respectively, I is the current (A), F is the Faraday's constant (96,487 C mol^{-1}), Δt is the time (s), V is the volume of wastewater treated (L) and 8 represents the equivalent weight of oxygen.

$$\text{Energy Consumption} = \frac{E_{cell} I \Delta t}{\Delta COD \times V} \quad (2)$$

where, E_{cell} is the average cell voltage (V), I is the current applied (A), Δt is the electrolysis time in hours and ΔCOD is the reduction in COD (g L^{-1}) during the time Δt and V is the volume of wastewater treated (L).

2.5. Toxicity analysis

The cytotoxicity of 2,4-DNP and its degraded products on human keratinocyte cell (HaCaT cell) was studied. HaCaT cells of density