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A novel approach towards multivariate optimization of graphite/PbO_2 anode synthesis conditions: Insight into its enhanced oxidation ability and physicochemical characteristics

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ABSTRACT

Electrochemical oxidation has drawn great interest for its potential application in degrading persistent organic pollutants (POPs) through electrogenerated hydroxyl radical at the surface of anode. This study aims at the preparation of an inexpensive graphite/PbO_2 anode. For enhancing oxidation performance, preparation process parameters viz. $Pb(NO_3)_2$ concentration, potential, and time of electrodeposition of a graphite/PbO_2 anode, electrodeposited from acidic electrolyte bath, were optimized targeting a POP, 2,4-dinitrophenol removal. The changes in morphological properties of the developed oxide films were analyzed using scanning electron microscopy (SEM) which manifested significant impacts of selected anode preparation process parameters. Furthermore, PbO_2 film prepared at optimum conditions were characterized using SEM, atomic force microscopy (AFM), energy dispersive X-ray spectroscope (ESD) elemental mapping, and X-ray diffraction (XRD) for thorough investigation of crystal structures, elemental distribution over surface, and phase of PbO_2. Angular structures in both SEM and AFM analysis and appearance of β-PbO_2 characteristic peaks in XRD analysis confirmed formation of electrocatalytically active phase of PbO_2. For further enhancing the oxidation ability, influencing experimental parameters viz. current intensity, pH, and NaCl concentration were optimized. After 2 h of electrolysis at optimum experimental conditions, COD and total organic carbon removal efficiency of 93.6 ± 0.63% and 71.7 ± 1.52% were obtained respectively.

1. Introduction

Nitrophenols, one of the most extensively used organic compounds in chemical industry have been discerned as persistent organic pollutant (POP) by the United States Environmental Protection Agency (USEPA) due to their inflicted toxicity, stability, and permanence in the environment. They are widely used for the manufacturing of pesticides, pigments, rubber chemicals, dyes, explosives, preservatives, plastics, and pharmaceuticals [1–4]. Among the six isomers of dinitrophenol, 1-hydroxy-2,4-dinitrobenzene or more commonly known as 2,4-dinitrophenol (2,4-DNP) is the most commercially employed isomer in dye, petrochemical, agriculture, and photochemical industry [5]. However, 2,4-DNP has been listed as “Priority Pollutant” by USEPA considering the adverse impact on human health and ecosystem and its recommended concentration in natural water bodies is less than 10 ng L^{-1} [6–8]. As identified as a POP, causing detrimental effect on the environment and human health through atmospheric mobility and accumulative tendency in fatty tissues of living organisms, removal of 2,4-DNP from contaminated water and wastewater is of pivotal significance [9,2]. Till date, various phenolic compounds have been reported as toxic posing threat to environment and human health [10–12]. Furthermore, it is hard to degrade by conventional wastewater treatment processes due to the presence of nitro groups which resist microbial degradation conferring stability to the pollutant [13]. Electrochemical/anodic oxidation has been identified as an excellent treatment technology for removing POPs from water among various advanced oxidation technologies solving one of the most pressing problems in environmental management today [14–16].

In electrochemical oxidation, hydroxyl radical, a strong oxidizing specie is generated in situ for conversion of organics into CO_2 and H_2O [17]. The major advantages of electrochemical oxidation process include mineralization of pollutant, no sludge generation, versatility, environmental compatibility, safety, energy efficiency, and amenability to automation [18,19]. Lead dioxide anodes are very popular in the field of electrochemical oxidation for degrading organic contaminants owing to its high oxygen evolution overpotential, conductive properties, chemically inert nature, and especially low cost in comparison with other high performance anode for example boron-doped diamond

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anode [20–25]. In electrochemical oxidation, contaminants are either eliminated by direct oxidation where they are oxidized by transfer of electrons to the anode surface or by indirect oxidation where generated electroactive species act as mediators for carrying out the degradation process. The most general mechanism of oxidizing organic contaminants through indirect oxidation using metal oxide electrodes has been proposed as follows: water is assumed to be discharged to form adsorbed hydroxyl radical on the anode surface which then mineralizes the target contaminant into CO_2 and H_2O as per Eq. (1) and (2) [26,27].

$$S[\,] + H_2O \rightarrow S[\bullet OH] + H^{+} + e^{-} \quad (1)$$

$$S[\bullet OH] + R \rightarrow S[\,] + RO + H^{+} + e^{-} \quad (2)$$

Where S[] represents sites for adsorption of generated hydroxyl radical, R represents organic contaminant, and RO represents oxidized organic contaminant.

Among the various techniques for deposition of PbO_2 on to substrate material including chemical deposition, sol-gel method, electrodeposition, oxidation of Pb in H_2SO_4 medium etc., electrodeposition is preferred for yielding better electrocatalytic activity owing to non-stoichiometry of developed coating [28,29]. A variety of substrate materials were employed in studies such as titanium [30–32], lead [33], aluminum [34], graphite felt [35], niobium [36], TiO_2 nanotube arrays [37], ceramic tube [38], Au [39], mild steel [40,41] etc., out of which titanium is the most widely studied base plate for deposition of PbO_2 owing to its inertness and excellent conductive properties. However, this chemically and dimensionally stable base material may undergo passivation in presence of oxygen through the formation of TiO_2 [42]. To overcome the drawbacks of passivation as well as the high cost associated with Ti substrate, the application of a low cost and conductive alternative, graphite plate is attempted in the present study as substrate for developing PbO_2 coating using electrodeposition technique.

The physicochemical properties of electrodeposited PbO_2 film may vary with the electrodeposition process parameters and thereby may affect the electrocatalytic activity of developed anode material. Significant influences of potentiostatic or galvanostatic conditions, precursor electrolyte solution chemistry, and time of electrodeposition on physicochemical properties of lead dioxide anodes have been reported in various studies through physical, chemical, and electrochemical characterization techniques [43–47]. Nevertheless, study on the effect of electrodeposition conditions on degradation/mineralization efficiencies of contaminants have not been conducted yet which is a better comprehensive approach for recognizing the enhancement of electrocatalytic activity, more precisely oxidation ability. In the current study, the effects of various electrodeposition conditions on degradation efficiency of a selected synthetic pollutant, 2,4-DNP as well as on physicochemical properties of the developed PbO_2 oxide film are elaborated.

The major deficiency of univariate effect analysis lies in its inability in delineating the interactive effects of parameters and consequently predicts the optima of a designed experimental system [48]. Application of multivariate approach to overcome the drawbacks can be proved as very efficient in this regard [49]. In this context, the use of response surface methodology (RSM) associated with properly designed experiments seems to be eminently effective for optimization of electrodeposition conditions and assessment of combined effects of parameters [50–52]. Although the application of multivariate analysis for optimizing experimental parameters such as NaCl concentration, current density, and pH of an electrochemical oxidation system for enhanced treatment of 2,4-DNP has been reported in literature [1], use of the same for assessing optimum electrodeposition conditions may also be proved as efficacious in encouraging the industrial applicability of electrodeposited anode materials. This study presents a well-organized and simple optimization technique of electrodeposition conditions for obtaining best possible degradation efficiency of POP.

To meet this objective, the study is aimed at the synthesis of a low cost, stable PbO_2 electrode and its detailed evaluation for the effects of various electrodeposition and experimental process parameters on degradation efficiency of a POP, 2,4-DNP. The developed graphite/PbO_2 anodes were examined for changes in morphological properties with variation in electrodeposition conditions using scanning electron microscopy (SEM). Furthermore, the surface properties of PbO_2 coating developed at optimum electrodeposition conditions obtained from RSM coupled with Box-Behnken design study were analyzed using SEM, atomic force microscopy (AFM), X-ray diffraction (XRD), and energy dispersive X-ray spectroscope analysis (EDS).

2. Materials and methods

2.1. Reagents

All the reagents employed in electrode preparation and experimental analyses were of analytical reagent grade. Lead nitrate ($Pb(NO_3)_2$, ≥98.5%), sodium dodecyl sulfate, ($C_{12}H_{25}OSO_2ONa$, ≥90%), nitric acid (HNO_3, 69%), sodium chloride (NaCl, ≥99%), hydrochloric acid (HCl, 35%), sodium hydroxide (NaOH, ≥97%), and sulfuric acid (H_2SO_4, 98%) were obtained from Merck, India. 2,4-dinitrophenol (≥99%) was obtained from Loba Chemie, India. Deionized water was used for preparing all reagents and synthetic stock solution containing 2,4-dinitrophenol (2,4-DNP).

2.2. Selection of experimental design and influencing process variables

Conventional one variable at a time (OVAT) study for determining the effects of variables on response/outcome of a system consists of substantially large number of experiments. Furthermore, OVAT or univariate approach is not effective in depicting synergistic influences of variables on the response of a system [53]. Being able to achieve optimum response with lower number of designed experiments, multivariate optimization techniques profess great interest among the researchers. The interactive effects of the adopted parameters on the outcome can also be evaluated from properly designed sets of experiments. This can be achieved through RSM overcoming the drawbacks of OVAT [54]. Therefore, RSM associated with Box-Behnken experimental design was adopted in this study aiming at examining multivariate effects of process parameters which is also an extensively used process optimization technique in analytical chemistry [48,55].

Various factors including the physicochemical properties of electrode [56], substrate properties [57], electrolyte solution chemistry [46], galvanostatic or potentiostatic conditions [47], time of electrodeposition [45], and temperature during electrodeposition [46] were observed to exert effect on electrocatalytic properties and thus on oxidation ability of the electrode material. In this study, the key influencing factors and their ranges affecting pollutant degradation efficiency of the developed anode materials were selected based on literature and a preliminary OVAT study (Section S1 and S2, supplementary material (SM)). Concentration of $Pb(NO_3)_2$, which is the major constituent for developing PbO_2 coating, potential, and time of electrodeposition were selected for examining the effect of electrodeposition conditions on pollutant removal efficiency (Section S1 in SM). The ranges of $Pb(NO_3)_2$ concentration, potential, and time of electrodeposition were varied from 0.1 to 0.3 mol L^{-1}, 1.7 V to 2.5 V, and 1 to 5 h respectively. For investigating the impacts of experimental parameters on degradation efficiency, current intensity (0.02–0.06 A), pH of the solution (3–7), and NaCl concentration (0.5–1.5 g L^{-1}) were selected as significant influencing variables based on the univariate study (Section S2 and Fig. S1 in SM).

2.3. Development of graphite/PbO_2 anodes

Graphite plates (12 cm × 3 cm × 0.5 cm), used as substrates were