Electrosynthesis of perchlorate using neodymium-doped PbO₂ electrode: application of experimental design methodology for optimization of the effective parameters

Meysam Cheraghveisi, Bozorgmehr Maddah and Mostafa Najafi

Department of Chemistry, Faculty of Science, University of Imam Hossein, Tehran, Iran
E-mail: bozorgmaddah@yahoo.com

Keywords: PbO₂, perchlorate, neodymium, lanthanide, design of experiment

Abstract
In recent decades, extensive research has been done on substrates (i.e., titanium and carbon) with lead dioxide coating to design a cheap anode in electrochemical systems instead of a platinized (Pt) electrode. Various factors can affect the structure and catalytic activity of lead dioxide coating. The most important of them are the type of substrate, how to prepare the substrate for the coating process and the types of lead dioxide additives. In this work, the effective factors in the preparation of the substrate were first investigated. Subsequently, the effect of neodymium as an additive on the catalytic activity of the electrode was studied. We prepared these electrodes and they were first evaluated by scanning electron microscopy (SEM), X-ray diffraction (XRD) spectrometer, voltammetry and electrochemical impedance spectrometer (EIS). The results showed that the potential of water oxidation on the modified PbO₂ electrodes by neodymium was 2 V. Here, we used an electrochemical method to prepare perchlorate. Since the anode potential for perchlorate oxidation is near that for water oxidation, conventional electrodes can’t be used in the perchlorate electrosynthesis. To achieve high production yield in the preparation of perchlorate from chlorate, various parameters including pH, time, and current density were optimized by the Box-Behnken design of the experiment method. The optimal values for this process were obtained at pH = 11, temperature 40 °C and current density of 0.5 mA cm⁻². The results at the optimal condition showed that the perchlorate production yield by modified PbO₂ electrodes was 80% in the 300 min. This value was only 60% for the unmodified PbO₂ electrode.

1. Introduction

Perchlorate (ClO₄⁻) is an inorganic chemical compound composed of chlorine attached to four oxygen atoms. It is commonly found as an anionic component in salts with ammonium (NH₄⁺), sodium (Na⁺), lithium (Li⁺), or potassium (K⁺) cations. Perchlorate salts have been used as a medicine for more than 50 years to treat thyroid disorders. In addition, ammonium perchlorate (NH₄ClO₄) is used as an oxidizer in rocket fuel and can be found in airbags, fireworks and fertilizers [1–3]. Lithium perchlorate is also used in oxygen candles in spacecraft, submarines, and other esoteric conditions. Most perchlorate salts are soluble in water and therefore naturally found in soil and food. It can be prepared by chemical and electrochemical methods. Perchlorates are produced electrochemically in three stages:

(1) Electrochemical production of sodium chloride (this salt is used due to its high water solubility compared to other chlorates);

(2) Electrochemical oxidation of sodium chloride to sodium perchlorate;
(3) Metathesis of sodium perchlorate to other metallic perchlorates.

These processes can be shown as follows:

\[
2\text{Cl}^- + 18\text{OH}^- \rightarrow 2\text{ClO}_3^- + 9\ \text{H}_2\text{O} + \frac{3}{2}\ \text{O}_2 + 18\ e^- \tag{1}
\]
\[
2\text{ClO}_3^- + \text{H}_2\text{O} \rightarrow 2\text{ClO}_2^- + 2\ \text{H}^+ + 2\ e^- \tag{2}
\]

The most common industrial method of producing perchlorate is electrochemical oxidation of aqueous solutions of chlorate, therefore the anode material is very important to form perchlorate with high current efficiency [4].

It has been shown that the possible mechanism for the formation of perchlorate from chlorate involves the oxidation of a water molecule in a single electron transfer step to obtain the adsorbed hydroxyl radical as the rate-determining step of reaction [1, 5]:

\[
\text{H}_2\text{O} \rightarrow (\text{OH})^{\text{ad}} + \text{H}^+ + e^- \tag{3}
\]
\[
\text{ClO}_3^- + (\text{OH})^{\text{ad}} \rightarrow \text{ClO}_2^- + \text{H}^+ + e^- \tag{4}
\]
\[
2(\text{OH})^{\text{ad}} \rightarrow \text{O}_{\text{ad}} + \text{H}_2\text{O} \tag{5}
\]
\[
\text{2O}_{\text{ad}} \rightarrow \text{O}_2 \tag{6}
\]

Various mechanisms have been proposed for the formation of perchlorate from chlorate, which includes the conversion of chlorate ions to the chlorate radical (\text{ClO}_3^-), the formation of reactive oxygen species, followed by the formation of perchlorate, and the controlled reaction of chlorate with adsorbed oxygen in the anode [1, 6]. Various anodes are used in the electrolysis step including smooth platinum, graphite, magnetite, metal oxide coated with titanium electrodes and \text{PbO}_2 electrodes [3]. It should be noted that the standard potential for the anodic reaction in perchlorate synthesis is about 1.19 V which is close to water oxidation potential (1.228 V).

Note that only oxygen and perchlorate are formed in the anode under electrolysis conditions. To minimize oxygen production (water oxidation), the cell must operate at high potential, so it needs a platinum anode or \text{PbO}_2 electrode with broad working potential. Sodium dichromate is usually added to the electrolyte in anode platinum cells to prevent perchlorate reduction at the cathode. Sodium fluoride is added to lead dioxide anode cells to improve current efficiency [1]. According to the literature, lead dioxide anode in graphite substrate [7], platinum [5], lead dioxide [8] and Pt/Ti [9] electrodes have been used for direct oxidation of chlorate to perchlorate. As well, the kinetics, and mechanism of the reaction on these electrodes have been studied.

Since \text{PbO}_2 is one of the best candidates for oxidation chlorate to perchlorate, we selected it as the anode electrode in this study. Different metals are doped into the \text{PbO}_2 matrix to improve reaction performance (minimum oxygen production). As well as, metal ions can improve the electrochemical activity and stability of \text{PbO}_2 electrodes.

Rare earth elements have remarkable catalytic properties due to unoccupied 4f orbitals and a robust spin–orbit bond which makes it considerable in various fields such as water and gas treatment [10–15]. Neodymium-doped \text{PbO}_2 electrodes show higher overvoltages than \text{PbO}_2 because the formation rate of M-OH to OH$^\cdot$ is higher due to the special nature of its external electron structure ([Xe] 4f$^4$6s$^2$). Also, the surface area of the Nd $-$ \text{PbO}_2 electrode donor is higher than the \text{PbO}_2 electrode, and higher reactive oxygen species (ROS) are produced on its surface, which makes chlorate oxidation more efficient [16, 17].

Design of Experiment (DOE) is a statistical and mathematical tool for conducting systematic experiments and efficient data analysis [18–20]. In the 1980s, Taguchi introduced the design of robust parameters and popularized the use of DOE in various industries. In the DOE method, the levels of influential factors are changed simultaneously, and the effect of individual factors is determined by their response to effective factors [21]. In this work, the optimization of the \text{PbO}_2 electrode composition for chlorate oxidation has been performed through experimental design. The effect of neodymium as a modifier was investigated in anode performance. The main effective factors can include the mass ratio of the modifier to the primary electrode material, the particle size of the modifier, temperature and applied potential. The desired response can be conductivity, current intensity, overvoltage for oxygen evolution, produced H$^+$, and so on. The significant effect of variables on the response was determined by analysis of variance according to the estimated laboratory error by repeating the experiments at the same level of factors. Given that simultaneous interaction between experimental variables in the fabrication of \text{PbO}_2 $-$based electrodes are time-consuming and costly, the DOE has been done with the response surface methodology (RSM) to obtain more information about such interactions. Finally, the electrochemical oxidation mechanism of chlorate to perchlorate was discussed based on the pH and concentration of produced H$^+$. 
2. Experimental

2.1. Materials
The pure reagents with analytical grade were purchased from Merck Company (Darmstadt, Germany). Sodium chlorate, nitric acid, sodium hydroxide, hydrofluoric acid, hydrochloric acid, lead (II) nitrate, copper nitrate, sodium fluoride and neodymium nitrate were also prepared from Merck Company.

2.2. Instruments
The crystalline structure of the synthesized materials was studied with the x-ray diffraction (XRD) instrument (X’PertPRO; PANa-lytical). An SEM (ZEISS Supra 40) with a Field Emission Gun emitter (10 kV) equipped with Energy Dispersion Spectrum (EDS) was utilized for characterization of the morphology of the synthesized nanomaterials.

2.3. Preparation of PbO₂ electrode
A titanium rod with dimensions of 1 × 3 cm was used to prepare the PbO₂ electrode. After washing the rod with water, it was placed in a boiling sodium hydroxide (10%) solution for 30 min to remove impurities. The titanium rod was then immersed in a mixture of nitric acid and fluoric acid for 20 s and finally immersed in boiling hydrochloric acid for 30 min to form a convex-concave structure. The prepared titanium rod was used as the anode, and stainless steel was used as the cathode connected to the positive and negative poles of the DC power, respectively, to prepare the PbO₂ electrode. 1.5 cm of two electrodes were immersed into the electrolyte solution containing 20 ml of deposition solution (lead nitrate (0.5 M), sodium fluoride (0.04 M), nitric acid (0.1 M), antimony trichloride (0.05 M), nickel nitrate (0.15 M) and copper nitrate (0.2 M)). The PbO₂ was electrodeposited on a titanium rod with a current density of 10 mA cm⁻² for 1 h. Modification of the PbO₂ electrode by neodymium was performed using the same method in the presence of neodymium nitrate (0.01 M) salt [17, 22, 25]. Also, the current densities and the electrodeposition time for the modification were 10 mA cm⁻² and 100 min, respectively. Analysis and characterization of the prepared electrodes were performed using the SEM and XRD.

2.4. Perchlorate preparation
To prepare perchlorate, modified PbO₂ electrodes with neodymium and stainless steel were used as anode and cathode, respectively. For this purpose, the very close anode and cathode electrodes were immersed in a solution of sodium chlorate at a concentration of 250 g l⁻¹ and pH = 11 and the electrolysis was performed at a current density of 0.5 mA cm⁻² for 60 min at 40 °C. After electrolysis, the solution contained chloride and perchlorate ions. To separate these two from each other, potassium chloride saturated solution was added to the obtained solution of electrolysis. Potassium perchlorate salt precipitated rapidly in the bottom of the beaker.

2.5. Box-Benken experimental design
To optimization the production of perchlorate, the chemometrics technique was used to design the experiments using the box-Benken design method. In this method, the impact of effective factors on the process was first estimated, and then the reaction conditions were optimized to maximize the desired response. Three factors (A: pH, B: current and C: time) were examined. Subsequently, the range of each factor was determined and the conditions of each experiment were designed using the mentioned input data and Design-Expert software. The parameters affecting the reaction are shown in the following table 1.

3. Result and discussion

3.1. Characterization
XRD patterns of all PbO₂ electrode presented a characteristic signal with tetragonal geometry at 2θ = 25.36°, 32.0°, 36.2°, 49.1°, 52.1°, 58.9°, 62.5° and 66.9° assigned to the (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (3 1 0),

Table 1. Factors evaluated for the optimization of the perchlorate production yield and experimental values of assayed variables.

| Factors  | Low level | High level | Block |
|----------|-----------|------------|-------|
| (A) pH   | 4         | 11         | 0     |
| (B) Time | 20        | 60         | 0     |
| (C) Current | 0.3      | 0.5        | 0     |
and (202) plane of $\beta$-PbO$_2$, with a good arrangement of JCPDS file (card number # 75–2420) (figure 1). The intensity of peaks in the $\beta$-PbO$_2$ XRD reflects that the formed lead dioxide nanoparticles are crystalline and broad diffraction peaks indicate small size crystallite. We calculated the average particle size of $\beta$-PbO$_2$ from remarkably intensive diffraction peaks at 2$\theta$ values of 25.36, 32, 36.2 and 49.1, deg corresponding to (110), (101), (200) and (211) planes from Debye–Scherer formula. According to table 2, the estimated $\beta$-PbO$_2$ size is 31.8 nm. Unlike PbO$_2$, the peak intensities were attenuated in the XRD pattern of the neodymium-doped lead dioxide electrode. However, diffraction peaks were not detected in the neodymium-doped lead dioxide electrode. These results confirmed that Nd deposition has lesser crystallinity than $\beta$-PbO$_2$. Some of the investigators were also reported the similar observation [17, 24–26].

In order to characterization and identification of the surface morphology and constituent elements of the synthesized composite, different techniques such as SEM and EDS were employed. Figure 2 shows the SEM...
images of the electrode surface coated with lead dioxide and neodymium-doped lead dioxide. As shown in figure 2(a), the morphology of the electrode with pure PbO$_2$ is dense and shows a typical pyramid shape. The surface morphology of PbO$_2$ doped with neodymium does not change much but it causes more compaction and smaller of the lead dioxide layer (figure 2(b)). This image shows the homogeneous dispersion of neodymium on the PbO$_2$ surfaces that leads to the increase of the number of reaction sites and consequently high catalytic activity.

In addition to XRD and SEM characterization, the existence of relevant elements was confirmed by EDX. Figure 3(a) shows the EDX spectrum of pure PbO$_2$ electrodes in which the existence of constituents including Pb (67.64%) and O (15.67%) can be seen. According to figure 3(b), the EDX spectrum of neodymium-doped lead dioxide contains Pb (68.01%), O (15.06%), and Nd (3.99%) elements that indicate the successfully doping of neodymium into the PbO$_2$ structure.

Oxygen formation is a side reaction in the electrochemical degradation of POPs, which leads to reduce the current efficiency of treatment process. Recorded polarization curves used to study the anodic oxygen evolution
reaction at the prepared electrodes showed an increase in energy consumption which is required to degrade organic pollutants [27]. The performance of the pure lead dioxide and neodymium-doped lead dioxide electrodes regarding the oxygen evolution was assessed by means of linear sweep voltammetry (LSV). These curves were recorded in 8.0 g l\(^{-1}\) Na\(_2\)SO\(_4\) solution at a scan rate of 2 mV s\(^{-1}\) (see figure 4(a)). The results show that the overpotential for oxygen evolution on neodymium-doped PbO\(_2\) electrode is higher than pure lead dioxide electrode. The oxygen evolution reaction (OER) occurs when the current intensity suddenly increases in the linear polarization curve. An additional amount of oxygen evolution potential (OEP) is needed to reduce the side-reaction of oxygen evolution [28]. The OEPs obtained for PbO\(_2\) and neodymium-doped PbO\(_2\) electrodes were 1.72 and 2 V, respectively, indicating significant improvement in neodymium-doped PbO\(_2\) electrocatalytic performance after incorporation of neodymium in the PbO\(_2\) matrix [29, 30]. This confirms that the electrodeposition technique is more suitable method than other methods for preparation of electrodes. In addition, since neodymium-doped PbO\(_2\) electrode has a high overvoltage for oxygen evolution, it favors the generation of reactive oxygen species and produces effectively more powerful oxidizer species, such as H\(_2\)O\(_2\), O\(_3\) and HO\(_2\).

The electrochemical impedance spectrometer (EIS) method was used to evaluate the charge transfer impedance [31–33] of prepared electrodes in a 8.0 g l\(^{-1}\) Na\(_2\)SO\(_4\) solution in the frequency range of 10\(^{-1}\)–10\(^{5}\) Hz. The arc diameter of the Nyquist diagram (figure 4) is directly related to the charge-transfer impedances. The smaller arc diameter indicates a lower charge transfer resistance (Rct) and a fast charge transfer process. The arc diameter of the neodymium-doped PbO\(_2\) electrode was lower than the PbO\(_2\) electrode, which indicates that the introduction of neodymium significantly reduces the charge-transfer impedance and improves the conductivity of the PbO\(_2\) electrode [34, 35].

### 3.2. Evaluation of reaction parameters

The Box-Behnken design was used to investigate the effect of different parameters on the reaction yield. In this method, the different levels of each parameter were determined and the design of the conditions for each parameter was performed with the help of software before performing the experiments. Subsequently, modeling was performed, and the effect of different parameters was determined using statistical methods of Analysis of Variance (ANOVA) and p-value test (table 2). Also, the ability of the prediction model was investigated by analyzing the correlation coefficient between the model results and the predicted ones. According to the results obtained from the experimental design, our data follow a quadratic model. Before the final analysis of the model, outlier data should be removed from the model. Finding the outlier data is based on calculating the residuals of the predicted values by the model and the real value for each model. No outlier data was detected in these experiments.

According to the ANOVA analysis results to design the prediction model, the p-value for the model is less than 0.05, which indicates that the model can reasonably predict the reaction efficiency from the sample conditions. Also, a p-value greater than 0.05 shows the inconsistency between the model and the experimental
Table 3. ANOVA analysis of the investigated model for the optimization of the perchlorate production.

| Factor      | Sum of squares | Degree of freedom | Mean of squares | F-Value | p-value | Prob > F |
|-------------|----------------|-------------------|-----------------|---------|---------|----------|
| Model       | 220.74         | 9                 | 24.53           | 43.14   | 0.0003  |          |
| A - pH      | 43.56          | 1                 | 43.56           | 76.61   | 0.0003  |          |
| B - I       | 59.46          | 1                 | 59.46           | 104.58  | 0.0002  |          |
| C - t       | 0.7086         | 1                 | 0.7086          | 1.25    | 0.3150  |          |
| AB          | 20.90          | 1                 | 20.90           | 36.76   | 0.0018  |          |
| AC          | 22.68          | 1                 | 22.68           | 39.88   | 0.0015  |          |
| BC          | 1.42           | 1                 | 1.42            | 2.49    | 0.1752  |          |
| A²          | 18.43          | 1                 | 18.43           | 32.41   | 0.0023  |          |
| B²          | 9.92           | 1                 | 9.92            | 17.44   | 0.0087  |          |
| C²          | 38.24          | 1                 | 38.24           | 67.26   | 0.0004  |          |
| Residual    | 2.84           | 5                 | 0.5686          |         |         |          |
| Lack of Fit | 1.23           | 3                 | 0.4089          | 0.5061  | 0.7165  |          |
| Pure Error  | 1.62           | 2                 | 0.8080          |         |         |          |

data. In this design, the P-value for the model is 0.0003 (lower than 0.05); therefore, our model was significant. P-value in linear terms for two factors A and B were less than 0.05, so, the effect of these factors on the reaction efficiency was significant. But for factor C, the P-value was greater than 0.05, which indicates that the impact of this factor on the reaction efficiency was low. The P-value for all interaction factors except interaction between B and C factors was also significant. For the interaction between the B and C factors, the P-value is greater than 0.05, indicating that this interaction’s effect is not significant on the reaction yield. Among the quadratic terms that express the nonlinear behavior of the parameters, the quadratic factors, including I, time and pH are important and significant. F-value obtained from ANOVA are used to determine the importance of each parameter. The results (table 3) for F-value showed that factor B with an F-value of 104.58 has a substantial effect on the reaction, followed by factors A and C, respectively have the greatest importance on the reaction efficiency. Also, the lack of fit (LOF) index means the inconsistency of model data with the experimental ones should be significant in the model. Its P-value was 0.7165 and was greater than 0.05 which indicates consideration of the model. According to the following equation, the sensitivity coefficients for effective factors and type of influence on response were investigated. According to the obtained equation, the pH and I factors have the inverse effect on reaction efficiency, while the t factor directly affects the reaction. Also, the interaction between the factors (pH and I; I and t) directly affects the reaction efficiency, while the interaction between the pH and t factors has the inverse effect on the reaction efficiency.

\[
R = +37.71805 - 3.32071 \text{pH} - 164.73395 I + 0.764824 t + 6.53063 \text{pH} \times t \\
- 0.034014 \text{pH} \times I + 0.297619 I \times t + 0.182378 \text{pH}^2 + 163.88919 I^2 \\
- 0.008046 t^2
\] (7)

3.3. Optimization of the production yield of perchlorate using Box-Behnken design method

The residual diagrams are used to check the adequacy of the model. In this diagram as shown in figure S1 (available online at stacks.iop.org/MRX/9/025801/mmedia), the distribution of scattered points around the red line without any special behavior shows the degree of normalcy indicating the model’s adequacy. The investigation between pH and I at a constant value of the t showed that the pH factor directly affects the reaction efficiency and the reaction rate. The response tends to redline and enhancement with increasing pH value. Also, factor I in the middle values has the maximum response level. The plot of response changes against each factor in the optimal condition is shown in figure S2.

The study of pH factor showed that the response level has an upward trend with increasing pH value while the two other factors are at their optimal level. The higher pH of the media, the higher the reaction efficiency. Also, the study of factor I showed that behavior was similar to the pH factor’s behavior (figure 5). But for factor t, the situation is different. The factor t showed an arc behavior when the two other factors are in their optimal condition. Initially, the response increases with increasing this factor, but the response value decreases after the maximum point.

In the next step and using the developed model, the optimal point of the factors was predicted to maximize the reaction efficiency. The optimal points of the factors are proportional to the maximum value of the response as shown in table 4.
Time plays an important role in the synthesis of perchlorate under the optimal pH and current density on the neodymium-doped lead dioxide electrode. Hence, the efficiency variation of the synthesized perchlorate as a function of the time was studied (figure 6). In the beginning, the synthesis percentage was enhanced by applying a longer contact time of up to 300 min (80% on neodymium-doped PbO$_2$ and 60% on the PbO$_2$ surfaces). But beyond this time, it remained almost unchanged.

Table 4. The optimal points of the factors proportional to the maximum value of the response.

| Coded factor | Factor name | The optimal amount | Low level | High level | The standard deviation |
|--------------|-------------|--------------------|-----------|------------|------------------------|
| A            | pH          | 10.97              | 4.00      | 11.00      | 0.0000                 |
| B            | I           | 0.4986             | 0.3000    | 0.5000     | 0.0000                 |
| C            | t           | 40.60              | 20.00     | 60.00      | 0.0000                 |
4. Conclusion

Electrochemical synthesis of perchlorate on the surface of the neodymium-modified PbO$_2$ electrode as the anode was done by using sodium chlorate oxidation. The electrodes with the neodymium modifier exhibited excellent performance in the electrosynthesis of perchlorate because on their surface, the water oxidation occurred at a potential higher than 2. Neodymium also reduced the resistance of the PbO$_2$ electrode and increased the conductivity, thus it improved the efficiency of the modified electrode. The examination result of the Box-Behnken method showed that the maximum efficiency of the perchlorate synthesis was obtained at a pH of 11 and the current density of 0.5 mA cm$^{-2}$, respectively. The highest percentage of perchlorate synthesis on the neodymium-modified PbO$_2$ surface was obtained 80% in the 300 min. As a result, this prepared electrode could be used in industrial and operational work.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Bozorgmehr Maddah https://orcid.org/0000-0002-8074-5250

References

[1] Seiler M A, Jensen D, Neist U, Deister U K and Schmitz F 2017 Determination of trace perchlorate in water: a simplified method for the identification of potential interferences Environmental Sciences Europe 29 1–9
[2] Mitra K and Catalano I G 2019 Chlorate as a potential oxidant on Mars: rates and products of dissolved Fe (II) oxidation Journal of Geophysical Research: Planets 124 2893–916
[3] Hosseini S G and Safshekan S 2017 Synthesis, characterization and application of BiVO$_4$ photoanode for photoelectrochemical oxidation of chlorate Chin. J. Catal. 38 710–6
[4] Wang M, Chen B, Huang S, Yang H, Hu B, Zhang C, Wang X and Xu Y 2018 Extraction of molybdenum and nickel from Ni-Mo ore by acid leaching combined with chlorate oxidation and phosphate complexation Miner. Eng. 124 63–7
[5] Janssen L and Van Der Heyden P 1995 Mechanism of anodic oxidation of chlorate to perchlorate on platinum electrodes J. Appl. Electrochem. 25 126–36
[6] Sugino K and Aoyagi S 1956 Studies on the mechanism of the electrolytic formation of perchlorate J. Electrochem. Soc. 103 166
[7] Udupa H, Sampath S, Narasimham K, Nagalingam M, Thagarajan N, Subramanian G, Subbiah P, Palanisamy R, Peter S I and Pushpavanam S 1974 Lead dioxide anodes in the large scale production of potassium chlorate from potassium chloride Journal of Applied Chemistry and Biotechnology 24 43–7
[8] Munichandraiah N and Sathyaranayana S 1987 Kinetics and mechanism of anodic oxidation of chlorate ion to perchlorate ion on lead dioxide electrodes J. Appl. Electrochem. 17 33–48
Liu Y and Liu H 2008 Comparative studies on the electrocatalytic properties of modified PbO2 electrodes: electrode characterization, operational parameters optimization and degradation pathways Chem. Eng. J. 350 960–70

Gao W, Wen D, Ho J and Ou Y 2019 Incorporation of rare earth elements with transition metal–based materials for electrocatalysis: a review for recent progress Materials Today Chemistry 12 266–81

Zhang Y, Ni Z and Yao J 2020 Enhancement of the activity of electrochemical oxidation of BPS by Nd-doped PbO2 electrodes: performance and mechanism Water 12 1317

Qiao Q, Singh S, Lo S-L, Li Y, Jin J and Wang L 2018 Electrochemical oxidation of acid orange 7 dye with Ce, Nd, and Co-modified PbO2 electrodes: preparation, characterization, optimization, and mineralization J. Taiwan Inst. Chem. Eng. 84 110–22

Fisher R A 1947 The Design of Experiments 4th edn (Edinburgh: Oliver and Boyd)

Curris M J, Alexander S, Cirino G, Docherty J R, George C H, Giembycz M A, Hoyer D, Insel P A, Izzo A A and Ji Y 2018 Experimental design and analysis and their reporting II: Updated and simplified guidance for authors and peer reviewers British Journal of Pharmacology 175 887–93

Shields C A, Rutj E L, Leung I Y, Ralph F M, Wehner M, Kawzneuk B, Lora J M, McClen G, Osborne T and Payne A E 2018 Atmospheric river tracking method intercomparison project (ARTIMP): project goals and experimental design Geoscientific Model Development 11 2455–74

Nair V N, Abraham B, MacKay I, Box G, Kacker R N, Lorenzen T J, Lucas J M, Myers R H, Vining G G and Nelder J A 1992 Taguchi’s parameter design: a panel discussion Technometrics 34 127–61

Abramov V, Abramov O, Gekhman A, Kuznetsov V and Price G 2006 Ultrasonic intensification of ozone and electrochemical destruction of 1, 3-dinitrobenzene and 2, 4-dinitrotoluene Ultrason. Sonochem. 13 303–7

Ansari A and Nematoohlai D 2020 Convergent paired electrocatalytic degradation of p-dinitrobenzene by Ti/SnO2-Sb/β-PbO2 anode: A new insight into the electrochemical degradation mechanism Appl. Catalysis B 361 118226

Liu Y and Liu H 2008 Comparative studies on the electrocatalytic properties of modified PbO2 anodes Electrochim. Acta 53 5077–83

Cao J, Zhao H, Cao F, Zhang J and Cao C 2009 Electrocatatytic degradation of 4-chlorophenol on F-doped PbO2 anodes Electrochim. Acta 54 2595–602

Zhao J, Zhu C, Lu J, Hu C, Peng S and Chen T 2014 Electro-catalytic degradation of bisphenol A with modified Co3O4/β-PbO2/Ti electrode Electrochim. Acta 118 169–75

Zhang L, Xu L, He J and Zhang J 2014 Preparation of Ti/SnO2-Sb electrodes modified by carbon nanotube for anodic oxidation of dye wastewater and combination with nanofiltration Electrochim. Acta 117 192–201

Xu M, Mao Y, Song W, Ouyang X, Hu Y, Wei Y, Zhu C, Fang W, Shao B and Lu R 2018 Preparation and characterization of Fe–Ce co-doped Ti/TiO2 NTs/β-PbO2 nanocomposite electrodes for efficient electrocatalytic degradation of organic pollutants J. Electroanal. Chem. 823 193–202

Wang S, He P, Jia L, He M, Zhang T, Dong F, Liu M, Liu H, Zhang Y and Li C 2019 Nanocoral-like composite of nickel selenide nanoparticles anchored on two-dimensional multi-layered graphitic carbon nitride: a highly efficient electrocatalyst for oxygen evolution reaction Appl. Catalysis B 243 463–9

Wang Y, Chen M, Wang C, Meng X, Zhang W, Chen Z and Crittenden J 2019 Electrochemical degradation of methylisothiazolinone by using Ti/SnO2–Sb2O3/α–β-PbO2 electrode: kinetics, energy efficiency, oxidation mechanism and degradation pathway Chem. Eng. J. 374 626–36

Adib K, Sohoulie E, Ghalkhiani M, Naderi H R, Rezvani Z and Rahimi-Nasrabadi M 2021 Sononchemical synthesis of Ag2WO4/RGO-based nanocomposite as a potential material for supercapacitors electrodes Ceram. Int. 47 14075–86

Sohouli E, Khosrovshahi E M, Radi P, Naghian E, Rahimi-Nasrabadi M and Ahmadi F 2020 Electrochemical sensor based on modified methylcellulose by graphene oxide and Fe3O4 nanoparticles: application in the analysis of uric acid content in urine J. Electroanal. Chem. 877 114503

Sanatkar T H, Khosrshidi A, Yaghoubi R, Sohoulie E and Shakeri J 2020 Stöber synthesis of salen-formaldehyde resin polymer-and carbon spheres with high nitrogen content and application of the corresponding Mn-containing carbon spheres as efficient electrocatalysts for the oxygen reduction reaction RSC Adv. 10 27575–84

Vasilescu C, Drob S, Necas E and Rosca J M 2012 Surface analysis and corrosion resistance of a new titanium base alloy in simulated body fluids Corros. Sci. 65 431–40

Zhu Y, Jin K, Li H, Qian H, Wang H and Zhao L 2018 A novel anode with anticorrosive coating for efficient degradation of toluene Chem. Eng. J. 334 206–15