Int. J. Electrochem. Sci., 12 **(2017)** 11920 – 11928, doi: 10.20964/2017.12.08

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Preparation of Nanostructured β-PbO_2 Films for the Electrochemical Oxidation of Acid Blue and Basic Brown Dyes

Song Ye[*], *Aihuan Wu and Tingting Yang*

School of Environmental and Municipal Engineering, Qingdao University of Technology, Qingdao City, Shandong Province, 266033, P.R. China
[*]E-mail: songyetech@126.com

Received: 28 July 2017 / *Accepted:* 20 September 2017 / *Published:* 12 November 2017

In this study, PbO_2 electrodes incorporating a three-dimensional β-PbO_2 nanostructure coating were prepared by galvanostatic deposition using an aqueous lead(II) and methanesulfonic acid (CH_3SO_3H) bath. Simulated wastewater containing the Acid Blue (AB) and Basic Brown (BB) dyes was electrocatalytically degraded using the PbO_2 as the anode in an electrochemical cell containing various conducting electrolytes. Thoroughness for dye degradation was determined to mainly depend on the concentration and type of the conducting electrolyte used. The electrocatalytic activity was observed to reach a maximum value when using NaCl as electrolyte at a concentration of 2 g/L, indicating indirect oxidation of the test dyes, where chloride oxidation contributes to the electro-generation of hypochlorite ions.

Keywords: Nanostructured β-PbO_2; Electrochemical oxidation; Dyes; Acid blue; Basic brown

1. INTRODUCTION

The evolution of the synthetic dye industry has led to increased discharge of coloured wastewaters that contain toxic and non-biodegradable organic pollutants. To ensure thorough decolourization and degradation of dyestuff together with removal of the corresponding metabolites in the spent dyeing baths, it is necessary to develop effective oxidation strategies. However, the physico-chemical treatments of dye wastewater (i.e., adsorption, filtration, coagulation and precipitation) are limited by the formation of sludge or the necessary regular regeneration of adsorbent materials [1-3]. Although advanced oxidation processes (such as an ozone or UV treatment combined with hydrogen peroxide), photocatalytic oxidation, or chemical oxidation with different chemicals (such as hypochlorite, hydrogen peroxide, ozone, Fenton's reagent) can be used for efficient decolourization, all these methods suffer from high cost and numerous operating problems [4-8].

The electrochemical oxidation of refractory effluents has recently been the subject of substantial interest; it is versatile, energy efficient, amenable to automation, and environmentally compatible due to the clean property of the major reagent, the electron [9]. For the direct electro-oxidation, the oxidization of the pollutants occurs after they are adsorbed onto the surface of the anode, with no participation by any other agents. In theory, direct electro-oxidation occurs at low potentials before the evolution of oxygen. On the other hand, the rate of this reaction depends on the electrocatalytic activity of the anode and is normally associated with slow kinetics. Moreover, a polymer layer can form on the electrode surface during the electrolysis process (at a low potential before the evolution of oxygen), leading to the poisoning of the anode.

The electrolysis of discharged water carried out at high anodic potentials has been proposed to bring about an increase in the oxidation rate and prevent deactivation, with consideration given to the involvement of the intermediates formed by oxygen evolution. Nevertheless, due to the concomitant secondary reaction (oxygen evolution during oxidation), a decrease in the current efficiency was observed in the potential region mentioned above [10-13]. Previous studies have determined that the electro-oxidation efficiency can be significantly affected by the choice of electrode material; some anodes show particularly significant enhancement of the selective and partial pollutant oxidization (conversion), whereas others facilitate the thorough combustion to CO_2 [14-18].

Due to their high stability, easy preparation, and low cost, PbO_2 coatings have been widely used for the electrodes in electrochemical cells [19]. PbO_2 electrodes have been conventionally prepared by anodic deposition in the presence of strongly oxidizing, toxic and acidic media (e.g., HNO_3 and $HClO_4$) [20]. In contrast, a few reports show that it is possible to use much more eco-friendly electrolytes. For example, methanesulfonic acid (CH_3SO_3H), with its low toxicity, desirable chemical stability and biodegradability [21], can be used to deposit thick PbO_2 coatings that show improved mechanical features [22] and an exceptionally high optical reflectance [23].

In the present study, PbO_2 electrodes were prepared using CH_3SO_3H as the electrolyte, and used to demonstrate potential for the OH-mediated oxidative destruction of organic pollutants in aqueous medium. The open and porous structure with large surface area of β-PbO_2 coatings is determined to promote the adsorption of organic materials and the formation of OH adsorbents, thus facilitating the decontamination process. Through both direct and indirect electrochemical oxidation, the electrocatalytic degradation of AB and BB dyes, as present in simulated wastewater, was investigated.

2. EXPERIMENTS

2.1. Chemicals

Lead(II) methanesulfonate ($Pb(CH_3SO_3)_2$) and CH_3SO_3H of reagent grade was provided by Aldrich and Fisher. Basic Brown (BB) 4 (Bismarck brown R) (FW = 461.40) (CI 21010) and Acid

Blue (AB) (FW = 695.69) (CI 26400) were supplied by Sigma. Ultra-pure water was used for the preparation of all test solutions.

2.2. Electrodeposition

β-PbO_2 coatings were prepared by electrodeposition. $Pb(CH_3SO_3)_2$ was used as a precursor for the β-PbO_2 synthesis. The deposition baths were composed of a mixture of CH_3SO_3H (0.2 M) and $Pb(CH_3SO_3)_2$ (1 M). Galvanostatic deposition was carried out in a small glass cell filled with electrolyte (80 cm^3). Note that this cell was undivided, cylindrical and isothermal. For both the anode and cathode, a 4.0 × 6.0 cm carbon/polyvinyl-ester composite (thickness, 6 mm) from Entegris GmbH was placed into the cell in the parallel plate configuration, where the gap between the electrodes was measured to be 2.0 cm. The electrode back and sides were covered with an insulation treatment. Before electrodeposition, all the electrodes were mechanically roughened, with grades 800 and 1200 SiC paper. To ensure the reproducibility of the stirring conditions, the solution in the cell was magnetically stirred using a PTFE-coated bar at 300 rpm. Following the electrodeposition, the thickness of the as-prepared β-PbO_2 coating was measured and determined to have a mean thickness of 45 μm.

2.3. Electrochemical advanced oxidation processes

Bulk electrolysis was carried out in a small glass cell that contained 275 cm^3 of 0.25 mM AB/BB and 2 g/L NaCl. Note that this cell was open and undivided. The reaction temperature and pH were 22.5 °C, and 3.0, respectively. To promote the mass transfer, the cell was vigorously stirred using a magnetic follower. The anodic oxidation was performed with a Ni plate (6 cm^2) and an exposed PbO_2-coated electrode (6 cm^2) used as the cathode and anode, respectively. For characterization of the Electro-Fenton (EF) process, electrolysis was performed using a carbon-felt cathode (geometric surface area, 6 cm^2 or 60 cm^2) in the presence of Fe^{2+} (0.2 Mm or 1.0 Mm) at 60 mA. Hydrogen peroxide was produced by the two-electron reduction of pure O_2 that was dissolved into the solution via a microporous glass port. In evaluating the efficiency of the electrochemical process, the remaining dye concentration and COD (oxygen equivalent of the organic matter content of the test specimen) are considered the primary factors, which were assessed by a liquid chromatograph (Shimazu LC-6A) and Reactor Digestion strategy, respectively.

3. RESULTS AND DISCUSSION

First, we compared the performance of the proposed β-PbO_2 coating for electrochemical removal with a normal Fe electrode. In a NaCl electrolyte environment, the β-PbO_2 coating was determined to remove more than 80% of AB and BB within 60 min. On the other hand, only approximately 40% of AB and 45% of BB was oxidised using a Fe electrode. Therefore, our proposed β-PbO_2 coating shows a much higher performance for dye degradation compared with that of the commercial electrode. We then investigated the use of a more realistic electrolyte for the electrocatalytic degradation by preparing a solution of 2 g/L salt (NaCl), base (NaOH) and acid (H_2SO_4) at 25 °C with an initial dye concentration of 100 mg/L (corresponding to a COD concentration of 200 mg/L), and carrying out the electrolysis with an applied current density of 30 mA/cm^2 for 0.5 h at a pH of 2. The influence of different conducting electrolytes on the AB and BB dye degradation rates (represented by the concentration of the remaining dye and residual COD) was studied, as shown in Fig. 1A and 1B. Under acid solution conditions, the dye degradation showed an undesirable electrocatalytic rate. Both dyes showed a remaining dye concentration and residual COD of less than half of the initial concentration. For the AB and BB dyes, the dye percentage and corresponding COD removal was determined to be 41.5% and 34.7% and 48.9% and 41.2%, respectively, in this solution condition. These results indicate a poor performance for the practical application of the proposed β-PbO2 coating in industrial wastewater treatment.

A similar investigation was carried out for the BB dye under the same operating conditions, except that the solution pH was 2 and the electrolysis time was 20 min. The data show a trend similar to that observed for the AB dye, with a sharp decrease in the dye concentration and COD with increasing current density followed by a gradual decrease in both towards zero [1, 3, 24]. The COD residual and the concentration of the remaining dye was significantly decreased, suggesting that AB and BB have higher electrocatalytic degradation rates in NaOH than in H_2SO_4. AB and BB degradation showed an electrocatalytic efficiency and COD removal of 76.4% and 79.6% and 74.2% and 77.1%, respectively. The dyes were nearly completely removed, and the COD was also considerably depleted, confirming the suitable conductivity and effectiveness of the NaCl as an electrolyte. Using this electrolyte, both AB and BB dyes showed a maximum degradation efficiency of 97.6%, with a maximal COD removal efficiency of 94.3% and 95.8%, respectively. Compared with other candidate electrolytes, the electrochemical degradation of AB and BB dyes on the PbO_2 electrode showed the maximum conductivity when using NaCl as the electrolyte. Additionally, the highest value determined for the electrocatalytic activity of the lead dioxide electrode was obtained using the same NaCl electrolyte. Thus, NaCl was used as the conducting electrolyte for all the subsequent measurements.

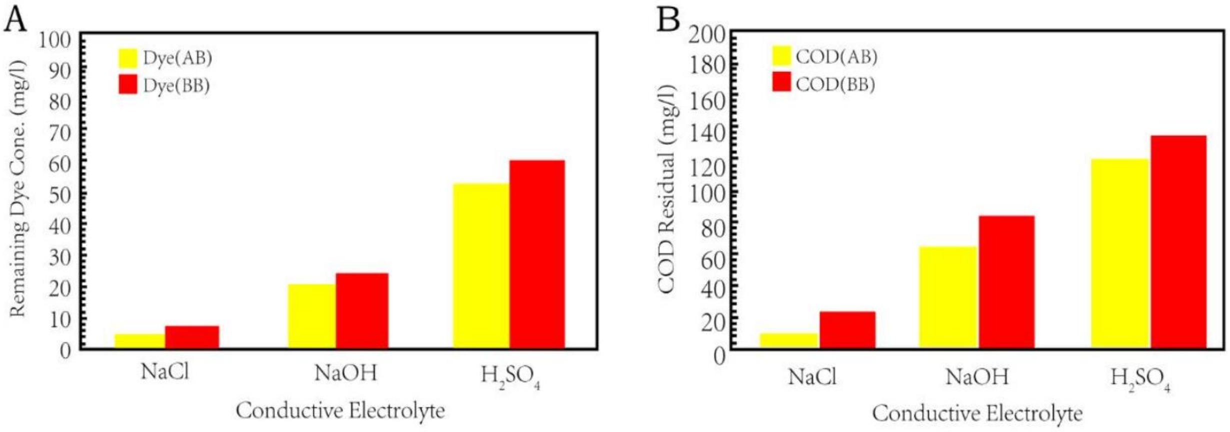

Figure 1. (A) Influence of conducting electrolyte on the removal rate of AB and BB dyes. (B) Influence of conducting electrolyte on the removal of COD.

To study the electrocatalytic degradation of AB dye in NaCl solution, the current density was varied in a range of 0 to 45 mA/cm^2 (initial dye concentration, 100 mg/L; corresponding initial COD, 200 mg/L). Prior to this degradation process, electrolysis was carried out at 25 °C (pH, 3) for 0.5 h. As the current density was increased, an increase was observed not only for COD removal but also dye degradation (Fig. 3). For an applied current density of 2 mA/cm^2, the COD and dye concentration were significantly decreased. However, as the current density was further increased to 30 mA/cm^2, both factors began to show a gradual decrease until a thorough COD removal and dye degradation.

The influence of solution pH on the electrocatalytic oxidation of AB and BB dyes was investigated on lead dioxide electrodes over a pH range of 1-12. The observed dependence of the remaining dye concentration and COD residual on pH is shown in Fig. 3. Both dyes were electrochemically treated in the presence of NaCl (2 g/L) at 25 °C with an initial dye concentration of 100 mg/L.

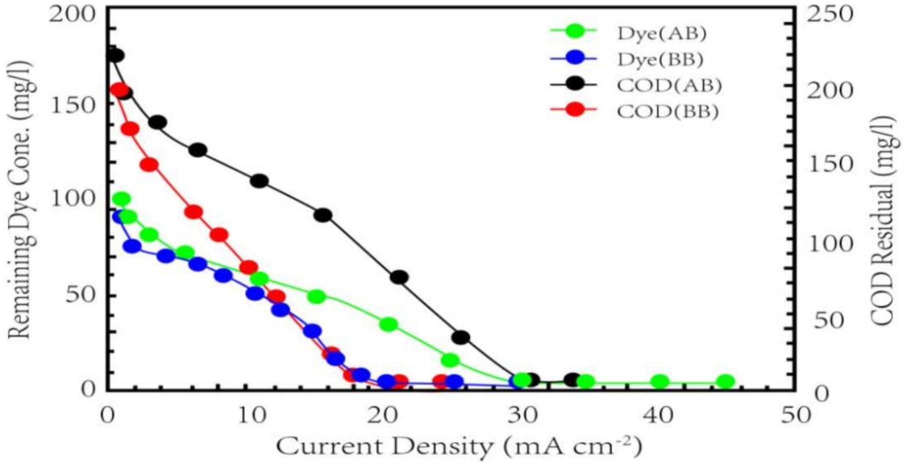

Figure 2. Influence of current density on dye and COD removal in2 g/L NaCl.

For the AB and BB dyes, the applied current density was 30 mA/cm^2 and 20 mA/cm^2, respectively. The electrolysis was carried out for 0.5 h and 20 min for the AB and BB dyes, respectively. As the pH is decreased, the two dyes show an increase in the electrocatalytic degradation rate, as shown in Fig. 3A. The electrocatalytic activity reaches a maximum in acidic conditions. The BB dye showed thorough oxidation and the corresponding COD showed total removal when the pH was 2; similar results were obtained for the AB dye in less acidic conditions (pH 3). This was followed by a gradual depletion of both dye concentrations and the corresponding COD with increasing time. The data show that the BB dye is totally removed after 20 min of electrolysis in NaCl, while the complete degradation of the AB dye is observed to require a longer time for the electrolysis [25, 26].

The influence of the electrolysis time on the electrocatalytic degradation of AB dye was studied at 25 °C with an initial dye concentration of 100 mg/L in 2 g/L NaCl at pH 3, with an applied current density of 30 mA/cm^2. These experimental conditions are comparable to those used in the study of the BB dye, except for the applied current density and pH, which was 20 mA/cm^2 and 2, respectively. Compared with the AB dye, the BB dye shows a sharper depletion after the initial 5 min, as indicated by the decay in dye concentration and COS removal shown in Fig. 3B.

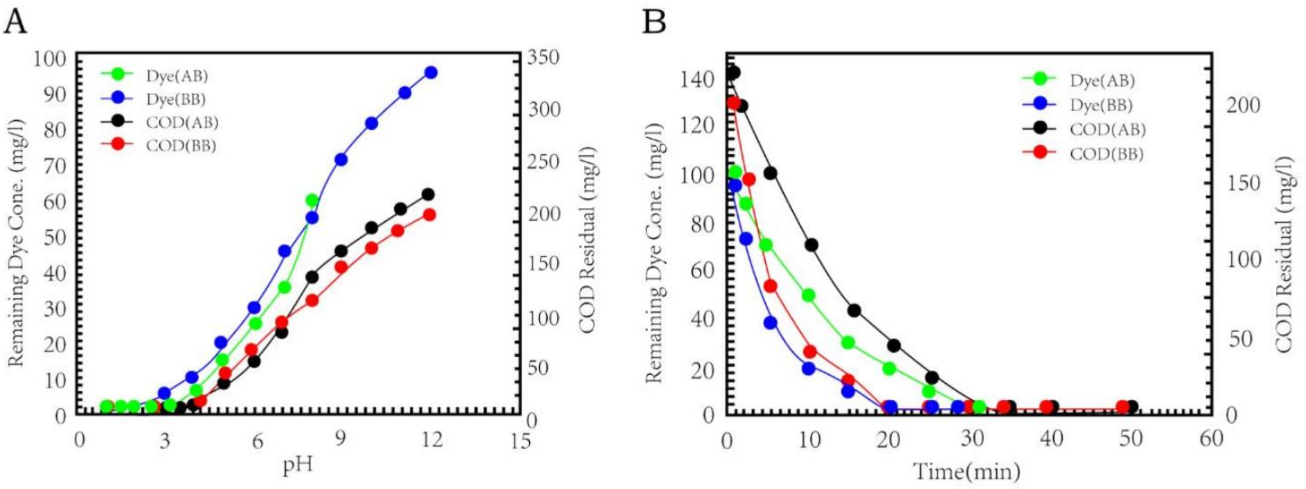

Figure 3. (A) Influence of solution pH value on the removal rate and COD depletion of AB and BB dyes in 2 g/L NaCl. (B) Concentration of remaining dye and COD residual as a function of electrolysis time in 2 g/L NaCl.

The influence of the temperature on the AB dye and COD removal was studied at pH 3, with an initial dye concentration of 100 g/L in the presence of NaCl (2 g/L), an applied current density of 30 mA/cm^2 and an electrolysis time of 0.5 h. For the BB dye, the same operating conditions were used except for a pH of 2, applied current density of 20 mA/cm^2 and an electrolysis time of 20 min. It is worth noting that the conditions described above have enabled the thorough electrocatalytic degradation of dyes, as demonstrated by the results discussed above. At 25 °C (low), a low dye degradation and COD removal was observed, as shown in Fig. 4A (representing the remaining dye concentration and COD residual as a function of the solution temperature).

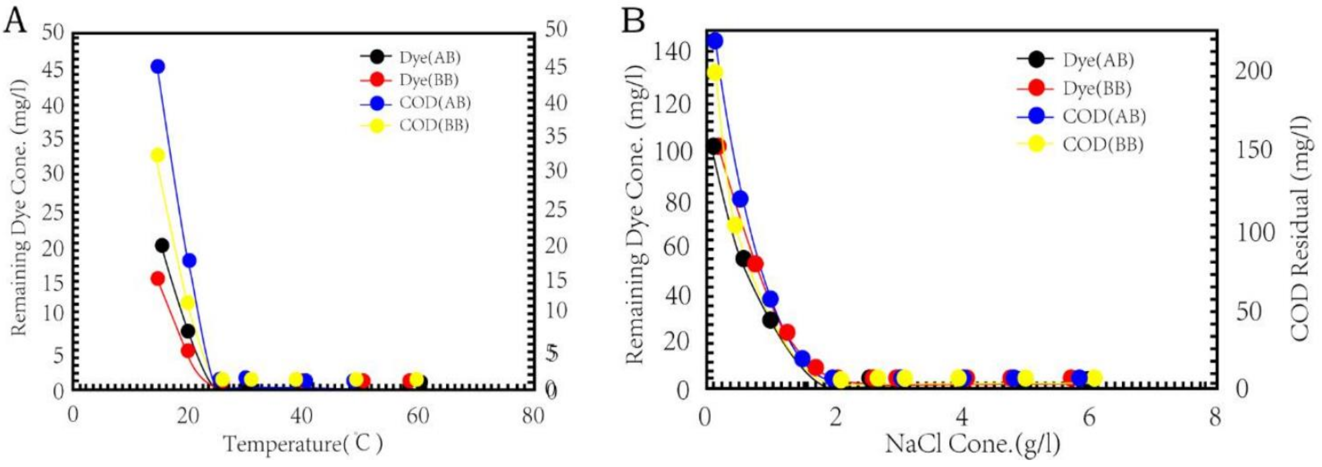

Figure 4. (A) Remaining dye concentration and COD residual as a function of the solution temperature in 2 g/L NaCl. (B) Influence of NaCl concentration on dye and COD removal.

The rate of the dye degradation and COD removal was determined to be significantly enhanced with increasing solution temperature up to 25 °C at which temperature complete dye degradation and total COD removal were obtained; increasing the temperature above 25 °C showed no further enhancement [27, 28]. The influence of the NaCl concentration on the degradation rate and the corresponding COD removal for the AB and BB dyes was measured under comparable conditions to those detailed above, with a varying NaCl concentration in the range of 0 to 6 g/L at a temperature of 25 °C, as shown in Fig. 4B. It can be seen that as the concentration of the electrolyte was increased to 2 g/L, the degradation rates and corresponding COD removal of the AB and BB dyes were also increased. Further increase in the NaCl concentration showed no additional benefit. Therefore, both dyes show thorough dye degradation and COD removal for a NaCl concentration of 2 g/L.

The influence of varying initial dye concentrations, in a range of 10 to 200 mg/L, on the dye degradation and COD removal rate is shown in Fig. 5A. Complete dye and COD removal was observed up to an initial dye load of 100 mg/L. As the dye concentration is further increased, both dyes show a decrease in the electrocatalytic degradation rate. As the initial dye dose is increased, a decrease in the degradation rate is observed for the two dyes. However, as shown in Figs. 5B and 5C, as the dye load reaches a relatively high level, both dyes show desirable dye and corresponding COD removal. In particular, the two dyes show a removal efficiency of 200 mg/L (initial concentration, 74.6%). The COD removal efficiency of the AB and BB dyes was determined to be 70.9% and 74.7%, respectively. Therefore, the treatment efficiency can be optimized by adjustment of the operating factors, considering the important role of these factors in electrochemical degradation of organic pollutants.

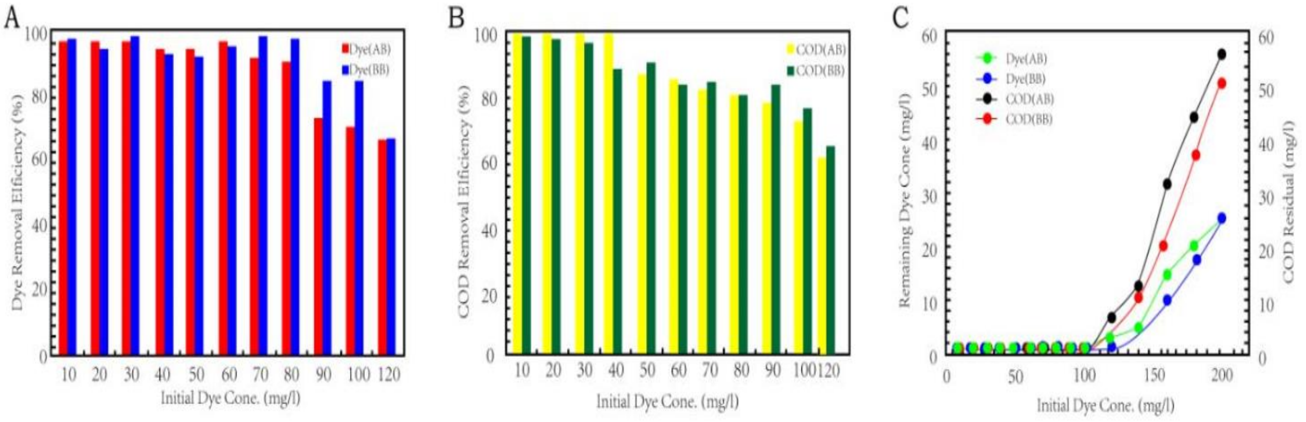

Figure 5. (A) Influence of initial dye load on dye removal and COD depletion in 2 g/L NaCl. (B) Dye removal efficiency obtained in 2 g/L NaCl as a function of initial dye concentration. (C) COD removal efficiency in 2 g/l NaCl as a function of initial dye concentration.

4. CONCLUSIONS

In the present study, an eco-friendly electrochemical oxidation technique was demonstrated for the sustainable decontamination of wastewater. Lead dioxide, β-PbO_2, anodes were prepared using a relatively clean and safe method of fabrication based on CH_3SO_3H. An experimental procedure was developed for the direct electrochemical oxidization of pollutant organic compounds and realized through oxidization of the water molecule near the surface of the electrode, followed by the generation of hydroxyl radicals. Two different dyes were observed to be degraded by both direct as well as indirect oxidation, with maximum electrocatalytic activity reached using a NaCl electrolyte at a concentration of 2 g/L.

ACKNOWLEDGEMENT

This work was supported by grants from Natural Science Foundation of China“Based on hazard identification and response model of early warning technology research in the water system”.

References

1. C. Ramírez, A. Saldaña, B. Hernández, R. Acero, R. Guerra, S. Garcia-Segura, E. Brillas and J.M. Peralta-Hernández, *Journal of Industrial and Engineering Chemistry*, 19 (2013) 571.
2. F. Sopaj, M. Rodrigo, N. Oturan, F. Podvorica, J. Pinson and M. Oturan, *Chemical Engineering Journal*, 262 (2015) 286.
3. E. Brillas and C. Martínez-Huitle, *Applied Catalysis B: Environmental*, 166 (2015) 603.
4. S. Wang, D. Li, C. Sun, S. Yang, Y. Guan and H. He, *Applied Catalysis B: Environmental*, 144 (2014) 885.
5. A. Ajmal, I. Majeed, R. Malik, H. Idriss and M. Nadeem, *Rsc Advances*, 4 (2014) 37003.
6. Y. He, L. Zhang, M. Fan, X. Wang, M. Walbridge, Q. Nong, Y. Wu and L. Zhao, *Solar Energy Materials and Solar Cells*, 137 (2015) 175.
7. Q. Rahman, M. Ahmad, S. Misra and M. Lohani, *Materials Letters*, 91 (2013) 170.
8. R. Sankar, P. Manikandan, V. Malarvizhi, T. Fathima, K.S. Shivashangari and V. Ravikumar, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 121 (2014) 746.
9. K. Rajeshwar, J.G. Ibanez and G.M. Swain, *Journal of applied electrochemistry*, 24 (1994) 1077.
10. S. Shukla, N.H. Loc, P.P. Boix, T.M. Koh, R.R. Prabhakar, H.K. Mulmudi, J. Zhang, S. Chen, C.F. Ng and C.H.A. Huan, *ACS nano*, 8 (2014) 10597.
11. J.R. Swierk, D.D. Méndez-Hernández, N.S. McCool, P. Liddell, Y. Terazono, I. Pahk, J.J. Tomlin, N.V. Oster, T.A. Moore and A.L. Moore, *Proceedings of the National Academy of Sciences*, 112 (2015) 1681.
12. A.L. Giraldo, E.D. Erazo-Erazo, O.A. Flórez-Acosta, E.A. Serna-Galvis and R.A. Torres-Palma, *Chemical Engineering Journal*, 279 (2015) 103.
13. S. Garcia-Segura, J. Keller, E. Brillas and J. Radjenovic, *Journal of Hazardous Materials*, 283 (2015) 551.
14. M.M. Momeni, Y. Ghayeb and Z. Ghonchegi, *Ceramics International*, 41 (2015) 8735.
15. S. Zodi, B. Merzouk, O. Potier, F. Lapicque and J.-P. Leclerc, *Separation and Purification Technology*, 108 (2013) 215.
16. Y. Shen, Q. Xu, R. Wei, J. Ma and Y. Wang, *Ultrasonics Sonochemistry*, 38 (2017) 681.
17. N. Muhd Julkapli, S. Bagheri and S. Bee Abd Hamid, *The Scientific World Journal*, 2014 (2014)
18. Z. Yu, I.R. Perera, T. Daeneke, S. Makuta, Y. Tachibana, J.J. Jasieniak, A. Mishra, P. Bäuerle, L. Spiccia and U. Bach, *NPG Asia Materials*, 8 (2016) e305.
19. J.P. Carr and N.A. Hampson, *Chemical Reviews*, 72 (1972) 679.
20. R.S. N'Dri, M. Coulibaly, A.N.G. Yao, D. Bamba and E.G. Zoro, *Int J Electrochem Sci*, 11 (2016) 5342.

21. M. Gernon, *Green Chemistry*, 1 (1999) 127.
22. A.B. Velichenko, R. Amadelli, E.V. Gruzdeva, T.V. Luk'yanenko and F.I. Danilov, *Journal of Power Sources*, 191 (2009) 103.
23. C. Low, D. Pletcher and F. Walsh, *Electrochemistry Communications*, 11 (2009) 1301.
24. J. Kaur and S. Singhal, *Ceramics international*, 40 (2014) 7417.
25. G. Reddy, T.M. Reddy, P. Narayana, P. Gopal and K. Reddaiah, *Indian J. Adv. Chem. Sci*, 4 (2016) 250.
26. S. Chellammal, P. Kalaiselvi, P. Ganapathy and G. Subramanian, *Arabian Journal of Chemistry*, 9 (2016) S1690.
27. T.N. Ramesh, D.V. Kirana, A. Ashwini and T. Manasa, *Journal of Saudi Chemical Society*, 21 (2017) 165.
28. S. Kourdali, A. Badis and A. Boucherit, *Ecotoxicol. Environ. Saf.*, 110 (2014) 110.