Electrochemical Degradation of PAHs in Produced Water Using Ti/Sb₂O₅-SnO₂-IrO₂ Anode

Asim YAQUB,^{a,*} Mohamed Hasnain ISA,^a Shamsul Rahman Mohamed KUTTY,^a and Huma AJAB^b

^a Civil Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar 31750 Tronoh, Perak, Malaysia

^b Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar 31750 Tronoh, Perak, Malaysia

* Corresponding author: environment_green@yahoo.com

ABSTRACT

In the study, ternary oxides coated Ti/SnO₂-Sb₂O₅-IrO₂ anode was used for degradation of 16 priority polycyclic aromatic hydrocarbons (PAHs) in a laboratory scale electrochemical batch reactor. To determine the optimum conditions for electrochemical degradation of PAHs from produced water, Box-Behnken design was used with three independent variables, viz., current density, pH and electrolysis time and response variable, viz., ΣPAHs removal %. Quadratic regression model was recommended as the best fit model. The results of Analysis of Variances (ANOVA) exhibited that the regression model adequately described the functional relationship between the independent variables and the response. This study affirmed that electrochemical degradation of PAHs followed first-order kinetics.

© The Electrochemical Society of Japan, All rights reserved.

Keywords : Electrochemical Degradation, PAHs, Produced Water, Optimization

1. Introduction

Produced water (PW) is the largest wastewater stream from oil and gas exploration. The oil and gas industry produces approximately 14 billion barrels of water annually.^{1,2} Volumes vary considerably throughout the lifetime of a field. Produce water is primarily relatively warm water from the oil reservoir. It contains dissolved and dispersed oils, high salt concentrations, heavy metals, high petroleum hydrocarbons and on occasions naturally occurring radioactive materials.³ Owing to its long contact with hydrocarbon-bearing formations, numerous aliphatic and aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and phenols are also found in produced water.

More than 160 PAHs have been characterized in nature, however only sixteen have been classified as priority pollutants by the USEPA due to their toxic properties.⁴ Feminization in male fish found on exposing them to very low levels of PAHs in produced water, which considerably diminishes fertility and delays the spawning period by quite a lot of weeks.⁵ Also cancer in fish and especially in benthic organisms has been related to pollution arising from offshore production installations.⁶

Electrochemical treatment effectively oxidized toxic organics in various types of wastewater.^{7–10} It is well known that the electrode material is the key factor in the development of electrochemical oxidation techniques and the effectiveness of electrochemical oxidation depends on the nature of the anodes.^{11–14} During oxidation of organic pollutants, electrodes require high oxygen evolution reaction to produce high concentration of OH[•] radicals.¹² Since their development in the 1960s by Beer for the chlorine production industry, dimensionally stable anodes (DSAs) have become the most important electrodes in electrochemical engineering.¹⁵ DSAs consist of a titanium substrate covered with conductive metallic oxides coating e.g. IrO₂, RuO₂, SnO₂, TiO₂ etc. used as electro-catalyst. The advantages of these metal oxide anodes include their high durability, good electro-catalytic activity against organic pollutants,

and low production cost. DSAs have been successfully applied as anode in a number of important electrolytic processes, such as oxygen and chlorine evolution or the electrochemical oxidation of bio-refractory organic pollutants in wastewaters.^{13,14}

Antimony doped SnO₂ oxide anodes are promising candidates for the electrochemical degradation of organic pollutants in wastewater because of their high over-potential for oxygen evolution, their ability to generate hydroxyl radicals and their lower cost compared to precious metal oxides; however, the commercial application of Ti/SnO₂-Sb₂O₅ is hampered by its short lifetime. IrO₂ is the most widely investigated electro-catalyst for O₂ evolution.¹⁵ In recent studies it was reported that the addition of iridium oxide (IrO₂) to the SnO₂-Sb₂O₅ coating greatly increases service life.^{16,17} This has been attributed to the incorporation of IrO₂ in the SnO₂-Sb₂O₅ coating by diffusion during electrode preparation. In Ti/SnO₂-Sb₂O₅-IrO₂ anode, SnO₂ acts as a dispersing agent, Sb₂O₅ as a doping agent and IrO₂ acts as a catalyst.¹⁸ Such ternary oxides anodes are among the best electrocatalysts being able to produce physisorbed hydroxyl radicals on their surface from water discharge. For example, Tian et al. found that DSA (OH[•]) reacted with nitrophenolic compounds leading to 85–90% removal over 3 h of electrolysis.¹⁹

Optimization plays a key role in environmental engineering applications since the best system performance mainly corresponds to an optimum point or optimum range of operating parameter values. Majority of wastewater treatment processes are multi-variable and optimization through the classical method of one variable at a time is inflexible, unreliable and time-consuming. Thus, response surface methodology (RSM), as an efficient design and widely used technique, can be adapted for parameters optimization of various wastewater treatment processes.^{20–25}

The main objectives of this research were to study the degradation kinetics and optimization of operational parameters for electrochemical degradation of PAHs on Ti/Sb₂O₅-SnO₂-IrO₂ anode using Box-Behnken design.

Figure 1. (Color online) Schematic set-up of the electrochemical reactor.

2. Materials and Methods

2.1 Chemicals and apparatus

Tin (IV) chloride (SnCl_4) extra pure, antimony (III) chloride SbCl_3 (99.0%), iridium (III) chloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$), ethylene glycol and acetic acid (glacial) anhydrous were purchased from Merck Chemicals. Dichloromethane DCM (HPLC grade) was used as solvent for the extraction of PAHs from water samples. The DCM was concentrated under vacuum using rotary evaporator (Rotavapor® R-205/Vacuum Controller V-800/Heating Bath B-490 manufacture by BÜCHI Switzerland).

2.2 Electrochemical cell

Real PW samples locally collected from an offshore oil exploration site were used for all electrochemical experiments. A laboratory scale electrochemical batch reactor was used for electrochemical oxidation experiments for degradation of PAHs in PW. All experiments were performed under galvanostatic conditions (under controlled current). Dimensions of electrodes used in this study were $8 \text{ cm} \times 10 \text{ cm} \times 0.2 \text{ cm}$. Volume of PW used in electrochemical cell was 100 ml. The electrochemical cell consisted of an anode ($\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5\text{-IrO}_2$) and a cathode (Ti plate) connected to DC power supply. The electrode inter-distance was 2 cm in all experiments. Schematic set-up of the electrochemical cell is shown in Fig. 1.

2.3 Anode coating

Titanium plates for anodes were coated by thermal decomposition method.^{16–18} Firstly the titanium plate was pre-treated before coating. Three coating materials (CM) SnCl_4 , SbCl_3 and $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ were dissolved in acetic acid (AA) and ethylene-glycol (EG) in ratios of (CM:AA:EG) (2 ml:2 ml:10 ml), (2 g:2 ml:10 ml) and (0.1 g:2 ml:10 ml) respectively at 60°C for 1 hr. Proportion of 80:10:10 was taken from SnCl_4 , SbCl_3 and $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ solutions respectively to make final precursor solution. It was applied (about 20 times) on a degreased and etched Ti plate. After each application the solvent was removed by drying at 200°C for 10 min to evaporate the solvent and after 10 applications the plate was dried at 500°C for 10 min and finally heated at 600°C for 1 h to remove all the organic contents.

2.4 Analytical techniques

Priority PAHs were extracted by Liquid-Liquid Extraction GC-MS Method.²⁶ For 100 ml sample of PW, 12.5 ml, 5 ml, 5 ml

Table 1. GC-MS set up and quantification of PAH in PW.

Component	Conditions				
GC-MS	Agilent Model GC-MS 5975C				
Column	DB 5MS column (30 m length, 0.25 mm diameter, 0.25 μm thickness)				
Column temperature	60 to 175°C at $6^\circ\text{C}/\text{min}$, then increased at $3^\circ\text{C}/\text{min}$ until 240°C and finally held at 300°C for 7 min				
Injector and transfer line temperatures	280 and 300°C				
Data acquisition mode	Selected ion monitoring (SIM) mode				
Carrier gas	Helium				
PAHs	No. of benzene rings	Molecular weight	Retention time (min)	Concen. of PAHs ($\mu\text{g}/\text{l}$)	
Naphthalene	2	128.17	7.57	58.06	
Acenaphthylene	3	152.20	11.19	13.66	
Acenaphthene	3	154.20	11.61	6.42	
Fluorene	3	166.22	12.84	14.43	
Phenanthrene	3	178.23	15.12	2.29	
Anthracene	3	178.23	15.13	15.44	
Fluoranthene	4	202.26	17.96	12.77	
Pyrene	4	202.26	18.48	12.44	
Benz(a)anthracene	4	228.28	21.38	6.87	
Chrysene	4	228.28	21.46	2.82	
Benzo(b)fluoranthene	5	252.31	23.77	4.59	
Benzo(k)fluoranthene	5	252.31	23.83	2.24	
Benzo(a)pyrene	5	252.31	24.45	3.61	
Indeno(1,2,3-cd)pyrene	6	276.33	27.28	2.28	
Dibenz (a,h) anthracene	6	278.34	27.40	1.75	
Benzo (g,h,i) perylene	6	276.33	28.05	1.19	
				ΣPAHs	160.86

volumes of Dichloromethane (DCM) was used as solvent for serial extraction of PAHs. For GC-MS analysis, the final volume of PAHs extracted sample through rotary evaporator was 1 ml. GC-MS was used for the detection of each PAH (conditions for GC-MS SIM mode and PAHs characteristics are shown in Table 1). Each PAH was separately quantified using a five-point calibration of mixed standard solutions. Intermediates were determined by GS-MS scan mode. Characteristics of PW (Table 2) were determined by standard methods for the examination of water and wastewater.²⁷

2.5 Experimental design

A three-level factorial design was established with the help of the Design Expert 6.0.7 software. Box-Behnken design (BBD) was selected to determine the suitable combination of three independent variables X_1 : current density (mA/cm^2), X_2 : initial pH, and X_3 : electrolysis time (h) for optimization of PAHs degradation. BBD yielded an experimental plan that consisted of 17 experiments as shown in Table 3.

Mathematical relationship of response (Y : PAHs removal %) and independent variables (X_1 : current density, X_2 : pH, and X_3 : electrolysis time) was represented by the second order polynomial regression model shown below (Eq. 1).

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

Table 2. Characteristics of produced water [27].

Chemical parameters of produced water (mg/l)	
BOD	590
COD	1347
TOC	1022
Phenol	13.8
NH3-N	8.5
Chlorides	>10,000
Sulfates	156
Physical parameters of produced water	
pH	7.8
Conductivity	30,000 mS/cm
Turbidity	72 NTU
TDS	16105 (mg/l)
TSS	250 (mg/l)

where Y is the predicted response; β_0 is constant; $\beta_1, \beta_2, \beta_3$ are linear coefficients; $\beta_{11}, \beta_{22}, \beta_{33}$ are quadratic coefficients; $\beta_{12}, \beta_{13}, \beta_{23}$ are cross product coefficients; X_1, X_2 , and X_3 are the levels of independent variables.²⁸ The significance of each coefficient in the equation was determined by F-test and P-values.

3. Results and Discussion

3.1 Modeling and optimization of PAHs degradation

The effects of three independent variables: current density (X_1), pH (X_2) and electrolysis time (X_3) on electrochemical PAHs degradation were determined according to the completely randomized experimental design shown in Table 3. Experimental data were fitted into a second order regression model. Relationship between PAHs removal efficiency and the variables is expressed by the following second-order polynomial equation.

$$Y_{(\Sigma \text{PAHs Removal } \%)} = +87.56 + 9.27X_1 + 1.77X_2 + 5.69X_3 - 5.23X_1^2 + 2.27X_3^2 + 2.77X_1X_3 \quad (2)$$

The model terms in Eq. (2) are after the elimination of insignificant variables. In this case significant model terms are $X_1, X_2, X_3, X_1^2, X_3^2, X_1X_2$ and X_1X_3 . It shows that efficiency of Ti/SnO₂-Sb₂O₅-IrO₂ significantly depends on current density, pH, time and combination of current density with electrolysis time. Based on statistical analysis the model terms were highly significant with very low probability value (0.034 to <0.0001).

ANOVA results for the study are presented in Table 4. Values of “Prob > F” less than 0.05 indicate model terms are significant. It was noted that the model terms of independent variables were significant at 99% confidence level. The Model F-value of 151.31 implies the model is significant. There is only a 0.01% chance that a “Model F-Value” this large could occur due to noise. F-value 1.17 implies the Lack of Fit is not significant as P value was greater than 0.05. There is a 42.66% chance that a “Lack of Fit F-value” this large could occur due to noise. In this case Lack of Fit is good “Prob > F” for Lack of Fit should be greater than 0.10. For response, coefficient of determination R^2 value was 0.995 which was in reasonable agreement with the adjusted R^2 of 0.988. It showed high significant regression at 95% confidence level.

Figure 2 shows the 3D surface plots to facilitate the interpretation of effects X_1, X_2 and X_3 on response Y (Σ PAHs removal %). Figure 2a shows the surface plot drawn at actual factor $X_3 = 2.5$ h. Surface plot was found straight and smooth with response of 80.5% at X_1 values of 4.46 and 4.47 mA/cm² and X_2 value of 3.1 and 8.98 respectively. Contour lines show non-linear trend at maximum

Table 3. Experimental design and response for electrochemical removal of PAHs.

Std. order	Independent variable			Response (Σ PAHs removal %)	
	X_1	X_2	X_3	Actual value	Predicted value
	Current density (mA/cm ²)	pH	Time (hour)		
1	3.33	3	2.5	74.80	74.52
2	10.00	3	2.5	86.26	87.52
3	3.33	9	2.5	73.77	72.51
4	10.00	9	2.5	96.33	96.61
5	3.33	6	1.0	67.11	68.58
6	10.00	6	1.0	90.18	90.12
7	3.33	6	4.0	82.90	82.96
8	10.00	6	4.0	98.12	98.52
9	6.67	3	1.0	84.40	83.19
10	6.67	9	1.0	87.10	86.88
11	6.67	3	4.0	94.52	94.74
12	6.67	9	4.0	96.91	98.11
13	6.67	6	2.5	87.54	87.55
14	6.67	6	2.5	88.88	87.55
15	6.67	6	2.5	87.54	87.55
16	6.67	6	2.5	87.22	87.55
17	6.67	6	2.5	86.60	87.55

Table 4. ANOVA for response surface quadratic model Ti/SnO₂-Sb₂O₅-IrO₂.

Source	Sum of squares	DF	Mean square	F value	Prob > F
Model	1013.62	9	112.62	151.31	<0.0001
X_1	606.22	1	606.21	814.45	<0.0001
X_2	24.96	1	24.95	33.53	0.0007
X_3	210.02	1	210.02	282.16	<0.0001
X_1^2	107.13	1	107.13	143.93	<0.0001
X_2^2	0.33	1	0.33	0.44	0.5293
X_3^2	35.36	1	35.36	47.52	0.0002
$X_1 X_2$	30.80	1	30.80	41.38	0.0004
$X_1 X_3$	5.11	1	5.11	6.86	0.0344
$X_2 X_3$	0.024	1	0.02	0.032	0.8625
Residual	5.21	7	0.74		
Lack of fit	2.43	3	0.81	1.17	0.4266
Pure error	2.78	4	0.69		

values of X_1 and all X_2 values. In Fig. 2b $X_2 = 6$ is actual factor between X_1 and X_3 . Surface plot and contour lines show curved structure which indicated that higher response can be predicted if one of X_1 or X_3 has higher values. Similarly in the case of Fig. 2c $X_1 = 0.67$ mA/cm² taken as actual factor where surface plot was found to be linear between X_2 and X_3 values 3 to 9 and 1 to 2.5 hr respectively. Inclination in surface plot was found for a combination of the 2 independent variables, at X_2 above 6 and the X_3 between the ranges of 3.25–4 hr with prediction of high response %.

To check that selected model provides adequate approximation of real system or not, Fig. 3a shows normal probability plot of the studentized residuals. It is the difference between actual and

Figure 2. (Color online) Effect of electrolysis time (a) pH (b) and current density (c) on Ti/SnO₂-Sb₂O₅-IrO₂ efficiency.

predicted response for PAH removal. It is clear from figure that residual follow a straight line and falls within ± 2.13 . Figure 3b shows normal distribution plot between actual and predicted response. All the data points in the plot lies close to straight line which indicates that data is fairly distributed.

Optimum condition was found by using numerical model considering all the parameters in range and for maximum PAH removal. The optimized condition obtained at current density of 8.77 mA/cm², pH 8.51 and electrolysis time 2.5 hour shows maximum removal of 92.72%. On same optimized conditions experimental value of PAHs removal was 90.56%.

Figure 3. (Color online) Normal plot of residuals (a) scattered diagram of predicted response vs actual response (b) for PAHs at Ti/SnO₂-Sb₂O₅-IrO₂.

3.2 Degradation kinetics of PAHs in PW

In electrochemical process individual contribution of each of direct/indirect oxidation is imperative for total removal of pollutants. Both the processes are considered for development of a kinetic model for the PAHs degradation in a batch electrochemical reactor by Ti/SnO₂-Sb₂O₅-IrO₂. A first-order model (Eq. 3)²⁷ was attempted to determine the rate constant k for the experimental-kinetic data of each PAHs degradation. Plots of $\ln(C/C_0)$ versus time (Fig. 4) shows linear relationship confirming that the degradation of all PAHs followed first-order kinetic behaviour.

$$\ln\left(\frac{[\text{PAH}]_t}{[\text{PAH}]_0}\right) = -kt \quad (3)$$

The kinetic rate constants k for each PAHs were calculated from the magnitude of the slopes of the straight lines and are shown in Table 5. Rate constant was positively affected by increase in current density in all experiments. The rate constant k values increased with current density. Acenaphthylene and fluorene showed higher k

Figure 4. (Color online) Plots of $\ln(C/C_0)$ vs. time for the degradation of PAHs at 3.33, 6.67 and 10 mA/cm².

values at 3.33, 6.67 and 10 mA/cm² respectively among 3 benzene ring PAHs. Similarly in case of 4 benzene rings PAHs, fluoranthene had higher k values at 10 mA/cm². In case of 5 and 6 benzene ring PAHs decrease in k values was observed because of their low solubility and molecular structure.

Table 5. Value of rate constant k at different current densities and electrolysis time.

Current density (mA/cm ²)	Rate constant k		
	3.33	6.67	10
PAHs			
Naphthalene	0.018	0.033	0.053
Acenaphthylene	0.070	0.074	0.085
Acenaphthene	0.045	0.058	0.046
Fluorene	0.063	0.08	0.084
Phenanthrene	0.040	0.044	0
Anthracene	0.067	0.085	0.107
Fluoranthene	0.057	0.073	0.118
Pyrene	0.056	0.075	0.090
Benz(a)anthracene	0.047	0.062	0.084
Chrysene	0.031	0.042	0.051
Benzo(b)fluoranthene	0.047	0.051	0.067
Benzo(k)fluoranthene	0.037	0.050	0.049
Benzo(a)pyrene	0.041	0.046	0.071
Indeno(1,2,3-cd) pyrene	0.034	0.068	0.056
Dibenz (a,h) anthracene	0.035	0.057	0.035
Benzo (g,h,i) perylene	0.020	0.012	0.029

3.3 Reactivity of OH[•] radicals and PAHs

Organic compounds in aqueous solutions can be oxidized on an anode by direct electron transfer and indirect oxygen atom transfer.²⁹ During electrolysis of aqueous solution oxidation of water molecules on the electrode surface gives rise to formation of hydroxyl radicals (OH[•]) (Eq. 4). The OH[•] radicals readily react with PAHs adsorbed on metallic oxides surface (MO_x) of anode (Eq. 5) commencing the direct electron transfer from adsorbed PAH to the electrode. During the indirect oxygen atom transfer, oxygen radicals, especially OH[•] radicals help in the oxidation of PAHs. Hydroxylation strips off outer hydrogen atom and replaces it with a hydroxyl group and converted to possible intermediate. GC-MS detected possible intermediates that contains hydroxyl group they are listed in Table 6 and their chromatogram is shown in Fig. 5. Further hydroxylation and abstraction of H⁺ ions resulted in formation of quinones (benzoquinone and hydroquinone). Continuous hydroxylation could result in formation of carboxylic acid, and acetic acid and carbon dioxide and water.

Produced water contains high concentrations of salts which contribute as electrolyte during electrochemical treatment. Cl[−] ions are directly oxidized on the anode surface to produce molecular chlorine (Eq. 6) which reacts with OH[•] ions to generate ClO[−] ion (Eq. 7) and also react with water molecules to form hypochlorous acid (Eq. 9). Because of interaction of Cl[−] ions some chlorinated phenolic compounds listed in Table 6 were also detected.

4. Conclusion

In this study, an effective electrochemical oxidation process is put forward for degradation of PAHs to reasonable extent using Ti/

Table 6. Analytical data of GC-MS chromatogram for intermediates formed during electrochemical oxidation.

Identified intermediate compounds	Retention time	Peak area (%)	Qualitative (%)
Dimethoxy-9-(2-penylethenyl)-9H-fluoren-9ol	8.88	0.98	38
Methyl 2,3-dihydro-1,4-benzodioxin-6-ylacetate	11.06	1.39	40
2,6-Dichlorophenol	11.69	0.41	10
Benzoic acid, 2,3-bis[(trimethylsilyl)oxy]-, trimethylsilyl ester	13.02	2.08	23
Carbamic acid, N-(2,3-dimethylphenyl)-, oxiranylmethyl ester	14.71	1.29	27
Benzene-1-3-dicarboxylic acid-5-hydroxymethyl-diethyl ester	15.35	0.45	9
Carboxylic acid	16.22	0.92	10
1,2-Dihydro-2-methylpiperazine	17.59	1.10	25
Benzeneacetic acid	18.83	0.52	32
Benzene, 1,2-dichloro-3-nitro-	19.09	0.40	9
7-Chloro-4-methoxy-3-methylquinoline	23.37	1.93	38

Figure 5. (Color online) GC-MS chromatogram of intermediates formed during electrochemical oxidation using Ti/SnO₂-Sb₂O₅-IrO₂.

Sb₂O₅-SnO₂-IrO₂ anode. Sn and Sb, relatively cost effective materials for coating of anode, can be tested for industrial scale. Ti/Sb₂O₅-SnO₂-IrO₂ anode worked on low current densities and short contact time which can be helpful in reducing energy consumption cost. Ti/Sb₂O₅-SnO₂-IrO₂ anode also eliminates refractory byproducts and other pollutants. It can be used as an effective pre-treatment process with other conventional biological and physical and chemical treatments.

References

1. R. R. Reynolds, *Produced Water and Associated Issues, a manual for independent operator*, Petroleum Technology Transfer Council (2003).
2. J. A. Veil, M. G. Puder, D. Elcock, and R. J. Redweik, Jr., *A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane*, US DOE January (2004).
3. D. W. Woodall, R. P. Gambrell, and N. N. Rabalais, *Mar. Pollut. Bull.*, **42**, 1118 (2001).
4. E. N. Pakpahan, M. H. Isa, S. R. M. Kutty, S. Chantara, and W. Wiriya, *Environ. Technol.*, **34**, 407 (2013).
5. S. Meier, E. T. Andersen, L. Hasselberg, O. S. Kjesbu, J. Klugsoyr, and A. Svardal, *Hormonal effects of C4-C7 Alkylphenols on cod (Gadus morhua)*, Report to the Norwegian Oil Industry Association, Norwegian Institute of Marine Science, 68 (2002). Available on: <http://www.imr.no/>.
6. D. P. Anderson, *Biological indicators of stress in fish*, American Fishery Society Symposium 8, Maryland, p. 1 (1990).
7. E. J. Klekowski, J. E. Corredor, J. M. Morrel, and C. A. Del Castillo, *Mar. Pollut. Bull.*, **28**, 166 (1994).
8. A. G. Vlyssides, P. K. Karlis, N. Rori, and A. A. Zorpas, *J. Hazard. Mater.*, **95**, 215 (2002).
9. Y. J. Feng and X. Y. Li, *Water Res.*, **37**, 2399 (2003).
10. A. Yaqub and H. Ajab, *Rev. Chem. Eng.*, **29**, 123 (2013).
11. A. Yaqub, H. Ajab, M. H. Isa, H. Jusoh, M. Junaid, and R. Farooq, *J. New Mat. Electrochem. Systems*, **15**(4), 289 (2012).
12. A. Remes, M. Ilos, and F. Manea, *Chem. Bull. "POLITEHNICA" Univ. (Timisoara)*, **55**(69)2, 152 (2010).
13. G. H. Chen, X. M. Chen, and P. L. Yue, *J. Phys. Chem. B*, **106**, 4364 (2002).
14. S. Kim, S. K. Choi, B. Y. Yoon, S. K. Lim, and H. Park, *Appl. Catal., B*, **97**, 135 (2010).
15. H. B. Beer, "Electrode and coating therefor." U.S. Patent 3,632,498, issued January 4, 1972.
16. X. Chen, G. Chen, and P. L. Yue, *J. Phys. Chem. B*, **105**, 4623 (2001).
17. A. Yaqub, M. H. Isa, S. R. M. Kutty, and H. Ajab, *J. New Mater. Electrochem. Syst.*, **17**, 39 (2014).
18. R. Chaiyont, C. Badoe, C. Ponce de León, J. L. Nava, F. J. Recio, I. Sires, and F. C. Walsh, *Chem. Eng. Technol.*, **36**, 123 (2013).
19. N. Matyasovszky, M. Tian, and A. Chen, *J. Phys. Chem. A*, **113**, 9348 (2009).
20. M. Tian, L. Bakovic, and A. Chen, *Electrochim. Acta*, **52**, 6517 (2007).
21. A. A. L. Zinatizadeh, A. R. Mohamed, A. Z. Abdullah, M. D. Mashitah, and M. H. Isa, *Biochem. Eng. J.*, **35**, 226 (2007).
22. L. Mohajeri, H. A. Aziz, M. H. Isa, and M. A. Zahed, *Bioresour. Technol.*, **101**, 893 (2010).
23. S. Mohajeri, H. A. Aziz, M. H. Isa, M. A. Zahed, M. J. K. Bashir, and M. N. Adlan, *Water Sci. Technol.*, **61**, 1257 (2010).
24. M. A. Zahed, H. A. Aziz, M. H. Isa, L. Mohajeri, and S. Mohajeri, *Bioresour. Technol.*, **101**, 9455 (2010).
25. M. A. Zahed, H. A. Aziz, L. Mohajeri, S. Mohajeri, S. R. M. Kutty, and M. H. Isa, *J. Hazard. Mater.*, **184**, 350 (2010).
26. A. D. Eaton and M. A. H. Franson, *Standard methods for the examination of water & wastewater*. 21st edition, American Public Health Association (2005).
27. A. Yaqub, M. H. Isa, S. R. M. Kutty, and H. Ajab, *Appl. Mech. Mater.*, **567**, 80 (2014).
28. A. Yaqub, M. H. Isa, and H. Ajab, *J. Environ. Eng.*, (ASCE) (2014) Accepted.
29. X. Y. Li, Y. H. Cui, Y. J. Feng, Z. M. Xie, and J. D. Gu, *Water Res.*, **39**, 1972 (2005).